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1933

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TECHNOLOGY OF CELLULOSE ETHERS

A THEORETICAL AND PRACTICAL TREATISE ON THE ORIGIN, HISTORY, CHEMISTRY, MANUFACTURE, TECHNICAL APPLICATION AND ANALYSIS OF THE ETHERIFIED CELLULOSES AND CARBOHYDRATE CARBOXYLATE ETHERS (ESTERIFIED CELLULOSE ETHERS, ETHERIFIED ORGANIC CELLULOSE ESTERS)

Including

ALKYLCELLULOSES, ARYLCELLULOSES, ARALKYLCELLULOSES, AS METHYLCELLULOSE, ETHYLCELLULOSE, BENZYLCELLULOSE, WITH CELLULOSE FORMATE, CELLULOSE ACETATE, THEIR SOLVENTS AND PLASTIFIERS, AS APPLIED TO TECHNOLOGY, PHARMACY, MEDICINE, MICROSCOPY, PHOTOGRAPHY, DENTISTRY AND THE PEACEFUL ARTS

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LIST OF ABBREVIATIONS TO LITERATURE

Prepared by Clara Harmon Lewis

A. and N. J.	Army and Naval Journal
Aarau, Archiv der Med.	Archiv. der Medizin, Chirurgie, und Pharmazie
Aarau, Mitth.	Mittheilungen des Aargauischen Naturforschenden Gesellschaft
Abbeville, Bull. Soc. Linn.	Compte Rendu et Bulletin de la Société Linneenne du Nord de la France
Abbeville, Mem. Soc. Emul.	Memoires de la Société d'Emulation d'Abbeville
Abeille, J.	L'Abeille, Journal d'Entomologie
Abeille mem.	L'Abeille: memoires d'Entomologie
Abeille Soc.	(Publications de la Soc. Entomologie de France.) LaAbeille. Journal de Entomologie
Acad.	Memoires de l'Academie des Sciences
Acad. Caes. Leop. Nova Acta	Nova Acta physico-medica Academiae Caes. Leopoldino-Carolinae Naturae Curiosorum
Acad. Natur. Curios. Nova Acta	Nova Acta Academiae Caesareae Leopoldino-Carolinae Germanicae Naturae Curiosorum
Acireale Accad. Atti	Atti e Rendiconti dell' Accademia di Scienze, Lettere e Arti dei Zelanti e PP. dello Studio di Acireale
Acireale, Soc. Ital. Micro. Boll.	Bollettino della Societa Italiana dei Microscopisti
Acquoy, Tijdschrift	Tijdschrift voor Wis-, Natuur-, en Wertuigkunde
Acta Math.	Acta Mathematica
Actes Soc. Helvetique	Actes de la Société Helvetique des Sciences Naturelles
Adansonia	Adansonis: Recueil d'observations botaniques
Adelaide Phil. Soc. Trans.	Transactions and Proceedings and Report of the Philosophical Society of Adeliade, South Australia
Aeronaut. J.	The Aeronautical Journal
Aeronaut. Soc. Reports	Annual Reports of the Aeronautical Society of Great Britain
Aeronaute	L'Aeronaute: bulletin mensuel international de la Navigation Aerienne
Afhandl. Fysik.	Afhandlingar i Fysik, Kemi, och Mineralogi
African Assoc. Proc.	Proceedings of the African Association for promoting the Discovery of the Interior Parts of Africa
Agen. Soc. Agric. Recueil.	Recueil des Travaux de la Société d'Agriculture, Sciences, et Arts d'Agen
Agram., Program Gymnas.	Program des k. k. Akademischen Gymnasiums zu Agram
Agric. Gaz.	The Agricultural Gazette
Agric. Gaz. N. S. Wales	Agricultural Gazette of New South Wales, The
Agric. J. India	Agricultural Journal of India
Agric. Ledg.	Agricultural Ledger
Agric. Soc. J.	The Journal of the Royal Agricultural Society of England
Agric. Stud. Gaz.	Agricultural Students' Gazette. A Quarterly Journal edited by Students at the College, Cirencester
Agron. Ztg.	Agronomische Zeitung
Aix, Acad. Mem.	Recueil de Memoires de la Société des Amis des Sciences, des Lettres, de l'Agricultur, et des Arts a Aix

Albany Inst. Proc.	Proceedings of the Albany Institute
Albany Inst. Trans.	Transactions of the Albany Institute
Alger. Bull. Soc. Climat.	Bulletin de la Societe de Climatologie Algerienne
Alk.	Alkohol
Allelod. Soc. Trans.	The transaction of the Allelodidactic Society
Allg. Berg. Ztg.	Allgemeine berg- und hüttenmännische Zeitung
Allg. Bot. Zts.	Allgemeine Botanische Zeitscrift für Systematik, Floristik, Pflanzengeographie, etc.
Allg. Deut. Naturhist. Ztg.	Allgemeine Deutsche naturhistorische Zeitung
Allg. Deut. Ornith. Ges.	See J. Ornith
Allg. Fischerei Ztg.	Allgemeine Fischerei Zeitung
Allg. Forst-Jagd-Zts.	Allgemeine Forst- und Jagd-Zeitung
Allg. Gerber-Ztg.	Allgemeine Gerber-Zeitung
Allg. Schweiz. Ges. Gesam. Naturwiss.	See Zürich, Schweiz. Ges. N. Denkschr.
Allg. Syn. Suikerfab.	Algemeen Syndicat van Suikerfabrikanten in Nederl.-Indie. With Arch-Suikerind, etc.
Allg. Zts. Bierbr. Malzfabr.	Allgemeine Zeitschrift für Bierbrauerei und Maz.l fabrikation
Allier, Bull. Soc. Emul.	Bulletin de las Société d'Émulation du département de l'Allier: Sciences, Arts, et Belles-Lettres
Alpina	Alpina, eine Schrift der genauen Kenntniss der Alpen gewidmet; von Carl Ulisses von Salis und J. R. Steinmueller
Altenburg Mitth.	Mittleilungen aus dem Osterlande; herausgegeben von der Naturforschenden Gesellschaft zu Altenburg
Amat. Mechan. Soc. J.	The (Quarterly) Journal of the Amateur Mechanical Society
Amer. Acad. Mem.	Memoirs of the American Academy of Arts and Sciences
Amer. Acad. Proc.	Proceedings of the American Academy of Arts and Sciencess
Amer. Agric.	American Agriculturist
Amer. Ann. Phot.	American Annual of Photography
Amer. Apoth. Ztg.	Deutsch-Amerikanische Apotheker Zeitung
Amer. Artisan	American Artisan
Amer. Assoc. Proc.	Proceedings of the American Association for the Advancement of Science
Amer. Brewers Rev.	American Brewers Review
Amer. Builder	The American Builder
Amer. Chem. J.	American Chemical Journal
Amer. Chemist	American Chemist
Amer. Drug.	American Druggist and Pharmaceutical Record
Amer. Electrochem. Soc.	American Electrochemical Society
Amer. Engin. & Railroad J.	American Engineer (Car Builder), and Railroad Journal
Amer. Ethnol. Soc. Trans.	Transactions of the American Ethnological Society
Amer. Entom. Soc. Trans.	Transactions of the American Entomological Society and Proceedings of the Entomological Section of the Academy of Natural Sciences
Amer. Fertilizer	American Fertilizer, The
Amer. Food J.	American Food Journal
Amer. Gas Light J.	American Gas Light Journal, The
Amer. Geogr. Soc. Bull.	Bulletin of the American Geographical and Statistical Society
Amer. Geogr. Soc. J.	Journal American Geographical Society, New York
Amer. Geogr. Soc. Proc.	Proceedings of the American Geographical and Statistical Society of New York

Amer. Geol. and Nat. Assoc. Reports	Reports of the Meetings of the Association of American Geologists and Naturalists at Philadelphia
Amer. J. Conchol.	American Journal of Conchology
Amer. J. Dent. Sci.	American Journal of Dental Science
Am. J. Math.	American Journal of Mathematics
Amer. J. Med. Sci.	American Journal of the Medical Sciences.
Amer. J. Otol.	The American Journal of Otology
Amer. J. Pharm.	American Journal of Pharmacy
Amer. J. Physiol.	The American Journal of Physiology
Amer. J. Physiol., Boston	American Journal of Physiology, Boston
Amer. J. Psychol.	The American Journal of Psychology
Amer. J. Pub. Health	American Journal of Public Health
Amer. J. Sci.	The American Journal of Science
Amer. Mach.	American Machinst
Amer. Math. Soc.	See N. Y. Amer. Math. Soc.
Amer. Med.	American Medicine
Amer. Med. Assoc. Trans.	Transactions of the American Medical Association
Amer. Med. Phil. Reg.	The American Medical and Philosophical Register; or Annals of Medicine, Natural History, Agriculture, and the Arts
Amer. Med. Recorder	American Medical Recorder
Amer. Meteorol. J.	American Meteorological Journal
Amer. Micro. J.	The American Quarterly Microscopical Journal. With which is also published the Transaction of the New York Microscopical Society
Amer. Micro. Soc. Proc.	Proceedings of the American Microscopical Society
Amer. Micro. Soc. Trans.	Transactions of the American Microscopical Society
Amer. Mineral. J.	The American Mineralogical Journal
Amer. Min. Gaz.	The American Mining Gazette and Geological Magazine
Amer. Monthly Micro. J.	American Monthly Microscopical Journal
Amer. Mus. Bull.	Bulletin of the American Museum of Natural Histor
Amer. Mus. Mem.	Memoirs of the American Museum of Natural Historyy
Amer. Natur.	American Naturalist
Amer. Ophthalm. Soc. Trans.	Transactions of the American Ophthalmological Society
American Perfumer	American Perfumer and Essential Oil Review, The
Amer. Phil. Soc. Proc.	Proceedings of the American Philosophical Society held at Philadelphia
Amer. Phil. Soc. Trans.	Transactions of the American Philosophical Society, held at Philadelphia, for promoting useful knowledge
Amer. Phot.	American Photography
Amer. Poly. J.	The American Polytechnic Journal
Amer. Quart. J. Agric.	American Quarterly Journal of Agriculture and Science
Amer. Reports State Entom.	See Ill., Mass., Mo., N. Y.
Amer. Soc. Agr. Sci. Proc.	Proceedings of the Society for the Promotion of Agricultural Science
Amer. Soc. Civ. Engin. Trans.	Transactions of the American Society of Civil Engineers
Amer. Soc. Micro. Proc.	Proceedings of the American Society of Microscopists
Amer. Sugar. Ind.	American Sugar Industry and Beet Sugar Gazette, The
Amer. Vet. Rev., N. Y.	American Veterinary Review, N. Y.
Amherst. Agric. Sta. Report	Annual Report of the State Agricultural Experiment Stations, at Amherst, Mass.
Amici, Giorn. Loscano	Giornale Loscano di Scienze medichi, fisiche e naturali
Amiens Acad. Sci. Mem.	Memoirs de l'Academie des Sciences, des Lettres et des Arts d'Amiens

Ammon, Monatschr. Med.	Monatschrift für Medecin, Augenheilkunde, und Chirurgie
Ammon, Zts. Opthalm.	Zeitschrift für die Ophthalmologie
Amsterdam	Werken van het Genootschap ter Bevordering der Natuur-, Geneesen Heelkunde. See Maandbl. Nat.
Amsterdam, Akad. Jaarb.	Jaarboek van de koningklijke Akademie van Wetenschappen gevestigd te Amsterdam
Amsterdam, Akad. Proc.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings of the Section of Sciences
Amsterdam, Akad. Verh.	Verhandelingen der koninklijke Akademie van Wetenschapp.
Amsterdam, Akad. Versl. Mededeel.	Verslagen en Mededeelingen der Koninklijke Akademie van Wetenschappen. Afdeeling Naturkunde
Amsterdam, Akad. Wet. Proc.	Processen-Verbaal van de gewone Vergaderingen der Koninklijke Akademie van Wetenschappen. Afdeeling Natuurkunde.
Amsterdam, Archief Wisk. Genoots.	Archief uitgegeven door het Wiskundig Genootschap
Amsterdam Bijdr. Dierk.	Bijdragen tot de Dierkunde uitgegeven door the (Koninckliijk Zoologisch) Genootschap Natura Artis Magistra, te Amsterdam
Amsterdam, Bull. Congr. Bot.	Bulletin du Congres International de Botanique et d'Horticulture reuni a Amsterdam
Amsterdam Congr. Bot. Actes	Actes du Congres International de Botanistes, d'Horticulteurs.....tenu a Amsterdam, en 1877
Amsterdam Genootsch. "Natura Artis Magistra"	See Amsterdam Bijdr. Dierk
Amsterdam Genootsch. Nat.-, Genees- en Heelkunde	See Maandbl. Nat.
Amsterdam, Het Inst.	Het Instituut
Amsterdam, Mengelwerk	Mengelwerk von uitgeleezene en andere Wisen Natuurkundige Verhandelingen
Amsterdam, Nieuw. Verh.	Nieuwe Verhandelingen der eerste Klasse van het Koninklijk Nederlandsche Instituut van Wetenschapen, en Schoone Kunsten te Amsterdam
Amsterdam, Nieuw. Wis. Voorstel.	Verzameling van nieuwe wiskundige Voorstellen door de Leden van het Wiskundig Genootschap, onder de zinspreuk: *Een onvermoeide arbeid komt alles te boven,* elkander tot onderlinge oefening opgegeven
Amsterdam Nederl. Aardr. Genootsch. Tijdschr.	Tijdschrift van het (Kon.) Nederlandsch. Aardrijkskundig Genootschap, gevestigd te Amsterdam
Amsterdam, Onderz. Phys. Lab.	Onderzoekingen gedaan in het Physiologisch Laboratorium van de Doorluchtige en Klinische Scholen te Amsterdam
Amsterdam, Tijdschr. Natuurk. Wetens.	Tijdschrift voor Natuurkundige Wetenschappen en Kunsten
Amsterdam, Tijdschr. Wis. Natuurk. Wetens.	Tijdschrift voor de Wis- en Natuurkundige Wetenschappen, Letterkunde, en Schoone Kunsten te Amsterdam
Amsterdam, Verh.	Verhandelingen der Eerste Klasse van het Koninklijk Nederlandsche Instituut van Wetenschappen, Letterkunde, en Schoone Kunsten te Amsterdam
Amsterdam, Verh. Genoots. Geneesk.	Verhandelingen van het Genootschap ter Bevordering der Geneesen Heilkunde, en Schoone Kunsten te Amsterdam
Amsterdam, Verzam. Ber. Navig.	Verzameling van Berichten over eenige onderwerpen des Navigatie

Amsterdam Zool. Genootsch. "Natura Artis Magistra"	See Nederl. Tijdschr. Dierk.
Anales agron.	Anales Agronomicos
Anales fis. quim.	Anales de la sociedad espanola de fisica y quimica
Anales inst. med. nacional	Anales del instituto medico nacional
Anales Mineria Mex.	Anales de la Mineria Mexicana, Revista de Minas
Analyst	The Analyst, including the Proceedings of the Society of Public Analysts
Anat.	Anatomie
Anat. Anz.	Anatomischer Anzeiger. Centralblatt für die Gesamte Wissenschaftliche Anatomie. (Amtliches Organ der Anatomischen Gesellschaft)
Anat. Ges.	See Anat. Anz.
Anat. Hefte	Anatomische Hefte. Referate und Beitrage (Beiträge und Referate) zur Anatomie und Entwickelungsgeschichte.
Anat. Soc. Proc.	See J. Anat. Physiol.
Anat. Studien	Anatomische Studien
Angers Acad. Sci. Mem.	Memoires de l'Academie des Sciences et Belles-Lettres d'Angers
Angers, Ann. Soc. Linn	Annales de la Société Linneenne du departement de Maine et Loire
Angers, Mem. Soc. Agric.	Mémoires de la Société d'Agriculture, Sciences, et Arts
Angers, Soc. Sci. Bull.	Bulletin de la Société d'Études Scientifiques d'Angers
Ann.	Liebig's Annalen der Chemie
Ann. Bot.	Annals of Botany
Ann. Chim.	Annales de Chimie
Ann. Chim. anal.	Annales de Chimie analytique applique á l'Industrie, a l'Agriculture, á la Pharmacie et á la Biologie
Ann. chim. farm.	Annali di Chimica e de farmacologia
Ann. Chim. Phys.	Annales de Chimie et de Physique
Ann. Chimica	Annali di Chimica (Medico-Farmaceutica e di Farmacologia)
Ann. Conduct. Ponts et Chauss.	Annales des Conducteurs des Ponts et Chaussees et des Gardes-Mines
Ann. Conserv. Arts Met.	Annales du Conservatoire des Arts et Metiers
Ann. Dermatol.	Annales de Dermatologie et de Syphiligraphie
Ann. Ecole norm.	Annales scientifiques de l'Ecole Normale superieure (L. Pasteur)
Ann. Falsif.	Annales des Falsifications
Ann. Farm. Chim.	Annali di Farmacoterapia e Chimica (Biologica)
Ann. Fis. Chim.	Annali di Fisica, Chimica, etc.
Ann. Génie Civil	Annales du Génie Civil
Ann. Gén. Sci. Phys.	Annales générales des Sciences Physiques
Ann. Geogr.	Annales de Geographie
Ann. Hydrogr.	Annales Hydrographiques
Ann. Hydrogr. Mar. Met.	Annalen der Hydrographie und Maritimen Meteorologie. Organ des Hydrographischen Bureaus (Amtes) und der Deutschen Seewarte
Ann. hyg. pub.	Annales d'hygiene publique
Ann. Ind.	Annales industrielles, par Fredureau, etc.
Ann. Inst. Pastuer	Annales de l'Institut Pasteur
Ann. Landw.	Annalen der Landwirthschaft in den K. Staaten
Ann. Landw. Wochenbl.	Annalen der Landwirtschaft, Wochenblatt
Ann. Mag. Natur. Hist.	The Annals and Magazine of Natural History, including Zoology, Botany and Geology

Ann. Matemat.	Annali di Matematica pura ed applicata
Ann. Math.	Annals of Mathematics
Ann. Med.	Annali di Medicina
Ann. Med. Psychol.	Annales medico-psychologiques; Journal de l' anatomie, Physiologie, etc., du systeme nerveux
Ann Med. Surg.	Annals of Medicine and Surgery, or Records of the occurring Improvements and Discoveries in Medicine, Surgery, and their immediately connected Arts and Sciences
Ann. Microgr.	Annales de Micrographie specialement consacrees a la Bacteriologie, aux Protophytes et aux Protozoaires
Ann. Mines	Annales des Mines. . .redigees et publiees sous l'Autorisation du Ministre des Travaux Publics
Ann. Museo Ind. Ital.	Annali del R. Museo Industriale Italiano
Ann. Natur. Hist.	Annals of Natural History
Ann. Oculist	Annales d'Oculistique et de Gynecologie
Ann. Pharm.	Annals of Pharmacy
Ann. Pharm. Louvain	Annales de Pharmacie, Louvain
Ann. Phil.	Annals of Philosophy
Ann. Phys.	Annalen der Physik
Ann. Phys. Chem.	Annalen der Physik und Chemie
Ann. Ponts et Chauss.	Annales des Ponts et Chaussees
Ann. R. Staz. Chim.	Annali della R. Stazione Chimico Agraria Sperimentale di Roma
Ann. Rep., U. S. Dept. Agric.	Annual Report of the United States Department of Agriculture
Ann. sci. agron.	Annales de la science agronomique francaise et étrangére
Ann. Sci. Bot. Nat.	Annales des Sciences Naturelles, Botanique
Ann. Sci. Lomb. Veneto	Annali delle Scienze del Regno Lombardo-Veneto
Ann. Sci. Nat.	Annales des Sciences Naturelles. Botanique. Zoologie et Paleontologie, comprenant l'Anatomie, la Physiologie, la Classification et l'Histoirie Naturelle des Animaux
Ann. Sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy
Ann. Scott. Natur. Hist.	The Annals of Scottish Hatural History
Ann. Surg.	Annals of Surgery
Ann. Storia Natur.	Annali di Storia Naturale
Ann. Telegr.	Annales Telegraphiques
Annab.-Buchh. Ver. Naturk. Ber.	Bericht uber den Annaberg-Buchholzer Verein für Naturkunde
Annab.-Buchh. Ver. Naturk. Jahr.	Jahresbericht des Annaberg-Buchholzer Vereins für Naturkunde
Annaes Sci. Natur.	Annaes de Sciencias Naturaes
Anneè Biol.	L'Anneè Biologique. Comptes Rendus annuers des Travuax de Biologie Generale
Annot. Zool. Jap.	Annotationes Zoologicae Japonenses, Auspiciis Societatis Zoologicae Tokyonensis seriatim editae
Annuaire Ancienne Normandie	Annuaire des cinq. Departements de l'Ancienne Normandie, par l'Association Normandie
Annuaire Inst. Provinces	Annuaire de l'Institut des Provinces, des Societes Savantes, et des Congres Scientifiques
Annuaire met. France	Annuaire Meteorologique de la France
Annuaire Mines Russie	Annuaire du Journal des Mines de Russie
Anthropol. (Paris)	Materiaux pour l'Histoire de l'Homme. Revue d'Anthropologie. Revue d'Ethnographie reunis.
Anthropol. Congr	See Congr. Int. Anthrop. C. R.
Anthropol. Inst. J.	The Journal of the Anthropological Institute of Great Britain and Ireland

Anthropol. Rev.	The Anthropological Review
Anthropol. Soc. Mem.	Memoirs read before the Anthropological Society of London
Antwerpen, Verh. Genoots. Occ. qui non.	Verhandelingen van het Genootschap: "Occidit qui non servat"
Anvers, Ann. Soc. Med.	Annales de la Societe de Medecine d'Anvers
Anvers, Congr. Sci. Geogr.	Compte-Rendu du Congres des Sciences Geographiques, Cosmographiques et Commerciales
Anvers, J. Pharm.	Journal de Pharmacie, publ. par la Soc. de Pharmacie d'Anvers
Apoth. Ztg.	Apotheker Zeitung, Berlin
Apothecary	Apothecary, Boston
Appreturzeitung	Appreturzeitung
Apt, Ann. Soc. Sci.	Annales de la Societe litteraire, scientifique et artistique d'Art (Vaucluse)
Aquila	Aquila. A Magyar Ornithologiai Kozpont Folyoirata. Periodical of Ornithology
Arb. Kais. Gesundhts.	Arbeiten aus dem kaiserlichen Gesundheitsamte, Berlin
Arb. pharm. Inst., D. Univ. Berlin	Arbeiten aus dem pharmazeutischen Institut der Universitat Berlin
Arcachon Soc. Sci. Stat. Zool. Trav.	Société Scientifique et Station Zoologique d'Arcachon
Arcetri Oss. Pubbl.	See Firenze R. Ist. Pubbl. (Arcetri Oss)
Archief Suikerind.	Archief Suikerindustrie in Nederlandsch-Indie
Archief Wisk. Genoots.	Archief uitgegeven door het Wiskundig Genootschap
Archit. and Eng.	Architect and Engineer
Archiv. Agriculturchem.	See Hermbstadt
Archiv. Anat. Micro.	Archives d'Anatomie Microscopique
Archiv. Anat. Physiol.	Archiv. fur Anatomie, Physiologie und wissenschaftliche Medicin
Archiv. Anthropol.	Archiv. fur Anthropologie...Organ der deutschen Gesellschaft fur Anthropologie, Ethnologie und Urgeschichte
Archiv. Anthropol. Etnol.	Archivio per l'Anthropologia e la Etnologia
Archiv. Augenheilk.	Archiv. für Augenheilkunde
Archiv. Augen-. Ohrenheilk.	Archiv. fur Augen- und Ohrenheilkunde
Archiv. belges méd. mil.	Archives belges de médicine militaire
Archiv. Biol.	Archives de Biologie
Archiv. Bot. Nord. France	Archives Botaniques du Nord de la France
Archiv. Chem. Mikros.	Archiv. Chemie und Mikroskopie
Archiv. Cosmol.	Archives cosmologiques. Revue des Sciences Naturelles, avec leurs applications a la Medecine, a l'Agriculture, aux Arts, et a l'Industrie
Archiv. Dent.	Archives of Dentistry: A record of Dental knowledge; medical, surgical, microscopical, chemical, and mechanical
Archiv. Elect.	Archives de l'Electricite
Archiv. Entwickl. Organ.	Archiv. fur Entwicklungsmechanik der Organismen
Archiv exper. Path. Pharm.	Archiv. fur experimentelle Pathologie und Pharmakologie
Archiv. Farmacol. sper. Roma	Archivio di Farmacolagia sperimentale e Scienze affin' Roma
Archiv. fisiol.	Archivio di fisiologia
Archiv. gen. Med.	Archives generales de Medecine
Archiv. ges. Physiol.	Archiv. fur die gesammte Physiologie des Menschen und der Thiere (Pfluger)
Archiv. Heilk.	Archiv der Heilkunde

Archiv. Hyg.	Archiv. für Hygiene
Archiv. Internal Med.	Archives of Internal Medicine
Archiv. intl. pharmacodyn.	Archives internationales de pharmacodynamie et de thereapie
Archiv. Ital. Biol.	Archives Italiennes de Biologie. Revues, Résumés Reproductions des Travaux Scientifiques Italiens
Archiv. Kinderheilk.	Archiv. fur Kinderheilkunde
Archiv. Math. Naturvid.	Archiv. for Mathematik og Naturvidenskab
Archiv. Math. Phys.	Archiv. der Mathematik und Physik
Archiv. Med.	Archives of Medicine
Archiv. Med. comparee.	See Rayer
Archiv. med. exp.	Archives de medicine experimentale et d'anatomie pathologique
Archiv. Med. Navale	Archives de Medecine Navale (et Coloniale)
Archiv. Med. Pharm. Militair.	Archives de Medecine et de Pharmacie Militaires
Archiv. Mikro. Anat.	Archiv. für Mikroskopische Anatomie (und Entwickelungsgeschichte)
Archiv. Miss. Sci.	Archives des Missions Scientifiques et Litteraires
Archiv. Naturgesch.	Archiv. für Naturgeschichte
Archiv. Naturk. (Dorpat)	Archiv. für die Naturkunde Liv-, Ehst- und Kurlands. Herausgegeben von der Dorpater Naturforscher-Gesellschaft
Archiv. Neerland.	Archives Neerlandaises des Sciences Exactes et Naturelles publiees par la Societe Hollandaise des Sciences a Harlem
Archiv. Ohrenheilk.	Archiv. für Ohrenheilkunde
Archiv. Ophthalm.	Albrecht von Graefe's Archiv für Ophthalmologie
Archiv. Ophthalm. Otol.	Archives of Opthalmology and Otology
Archiv. Otol.	Archives of Otology
Archiv. Parasit.	Archives de Parasitologie
Archiv. path. Anat.	Archiv fur pathologische Anatomie und Physiologie und für klinische Medizin (Virchow's)
Archiv. Pharm.	Archiv. der Pharmacie; Archiv des Apothekervereins im nördlichen Deutschland.
Archiv. Pharm. og Chemi	Archiv. de Pharmaci og Chemi, Copenhagen
Archiv. Physiol.	Archives de Physiologie Normale et Pathologique
Archiv. Psychiatr.	Archiv. fur Psychiatrie und Nervenkrankheiten
Archiv. Sci.	Archives of Science and Transactions of the Orleans County Society of Natural Sciences
Archiv. sci. med.	Archivio per les scienze mediche
Archiv. Sci. Phys. Nat.	Bibliotheque Universelle. Archives des Sciences Physiques et Naturelles
Archiv. Sci. Pract. Med.	Archives of Scientific and Practical Medicine
Archiv. Slaves Biol.	Archives Slaves de Biologie
Archiv. Verdauungskrankh.	Archiv. fur Verdauungs-krankheiten
Archiv. Wiss. Heilk.	Archiv. des Vereins für gemeinschaftliche Arbeiten zur Forderung der wissenschaftlichen Heilkunde
Archiv. Wiss. Prakt. Thierheilk.	Archiv. für wissenschaftliche und praktische Thierheilkunde
Archiv. Zool. Anat. Fis.	Archivio per la Zoologia, l'Anatomia, e la Fisiologia
Archiv. Zool. Exper.	Archives de Zoologie Experimentale et Generale
Arcueil, Mem. Phys.	Memoires de Physique et de Chimie de la Societe d'Arcueil
Argent. Inst. Geogr. Bol.	Boletin del Instituto Geografico Argentino
Argent. P.	Argentine Patent
Argent. Soc. Ci. An.	Anales de la Sociedad Cientifica Argentina

Arkiv. Kemi, Minerol Geol.	Arkiv for Kemi, Mineralogi och Geologi
Arkiv. Math. Astron. Fysik	Arkiv for Mathematik Astronomi och Fysik
Armagh Nat. Hist. & Phil. Soc.	See Irish Natlist.
Arms and Expl	Arms and Explosives
Arnhem, Natuurk	Natuurkunde. Tijdschrift, inhoudende Phijsica, Chemie, Pharmacie, Natuurlijke Historie en Litteratuur, uitgegeven van wege het Genootschap: *Tot nut en vergenoegen*, te Arnhem
Arras, Mem. Acad.	Memoires de l'Academie d'Arras
Arras, Mem. Soc. Roy.	Memoires de la Societe Royale d'Arras
Art. J.	The Art Journal
Artiz.	The Artizan (London)
Artus, Jahr. ökon. Chemie	Jahrbuch fur okonomische Chemie, etc.
Artus, Vierteljahresschrift	Vierteljahresschrift fur technische Chemie, Landwirthschaftliche Gewerbe, Fabrickwesen und Gewerbetreibende überhaupt.
Ashmol. Soc. Proc.	Abstracts of the Proceedings of the Ashmolean Society
Asiat. Researches	Asiatic Researches; or Transactions of the (Bengal) Society
Asiot. Soc. J.	Journal of the Royal Asiatic Society
Assoc. Franc. Compt. rend	Association Francaise pour l'avancement des Sciences. Comptes Rendus
Assoc. Med. J.	See Med. Assoc. Journ.
Assur. Mag.	The Assurance Magazine (and Journal of the Institute of Actuaries)
Astron. Nachr.	Astronomische Nachrichten
Astron. Soc. Mem.	Memoirs of the Astronomical Society of London
Astron. Soc. Month. Not.	Monthly Notices of the Astronomical Society of London
Astrophys. J.	Astrophysical Journal
Atelier Phot.	Atelier des Photographen
Ateneo Ital.	L'Ateneo Italiano
Athenes Obs. Nat Ann	Annales de l'Observatoire National d'Athenes
Atlantis	The Atlantis, or Register of Literature and Science
Atti. Accad. Ital.	Atti dell'Accademia Italiana di Scienze
Atti. accad. Lincei	Atti della reale accademia dei Lincei, rendiconti, classe di scienze fisiche, mathematiche e naturali
Atti. Coll. Ing. Archit	Atti de Collegio degli Ingegneri ed Architetti in Milano
Atti. inst. incoragg.	Atti del R. instituto d'incoraggiamento di Napoli, Naples, Italy
Atti. R. Accad. Sci. Torino	Atti della Reale Accademia della Scienze di Torino
Atti Sci. Ital.	Riunione degli Scienziati Italiani
Atti Soc. Elvet.	Atti della Societa Elvetica delle Scienze Naturali
Aube, Mem. Soc. Agric.	Memoires de la Societe d'Agriculture, des Sciences, et des Lettres du department de l'Aube
Augsb. Naturhist. Ver. Ber.	Berichte des Naturhistorischen Vereins in Augsburg
Auk	The Auk. A Quarterly Journal of Ornithology
Ausland	Das Ausland
Aust. P.	Austrian Patent
Aust.-Hung. P	Austro-Hungarian Patent
Australasian Assoc. Rep	Report of the...Meeting of the Australasian Association for the Advancement of Science
Australasian J. Pharm.	Australasian Journal of Pharmacy, Melbourne
Australian Med. J.	Australian Medical Journal

Australia Med. Rec.	Medical Records of Australia
Australian P.	Australian P.
Australian Sugar J.	Australian Sugar Journal
Autun, Mem. Soc. Eduenne	Memoires de la Societe Eduenne
Auvergne, Ann. Sci.	Annales Scientifiques, Litteraires, et Industrielles de l'Auvergne
Auxerre, Bull. Soc. Sci.	Bulletin de la Societe des Sciences Historiques et Naturelles de l'Yonne
Badischen Aerzt. Verein. Mitth.	Mittheilungen des Badischen ärztlichen Vereins
Bah. P.	Bahamas Patent
Ballenstedt, Archiv.	Archiv für die neuesten Entdeckungen aus der Urwelt
Ballot, Mag. Landbouw.	Magazin voor Landbouw en Kruidkunde
Baltimore Med. Phys. Recorder	Baltimore Medical and Physical Recorder
Bamb. Naturf. Ges. Ber.	Bericht der naturforschenden Gesellschaft zu Bamberg
Barb. P.	Barbados Patent
Barcelona Acad. Bol.	Boletin de la Real Academia de Ciencias y Artes de Barcelona
Barcelona Acad. Mem.	Memorias de la Real Academia de Ciencias Naturales y Artes de Barcelona
Barrow Field Club Report	Barrow Naturalists' Field Club and Literary and Scientific Association. Annual Report and Proceedings
Basel, Ber.	Bericht über die Verhandlungen der Naturforschenden Gesellschaft in Basel
Batavia Genootsch. Verh.	Verhandlingen van het Bataviaasch Genootschap der Kunsten en Wetenschappen
Batavia, Natuur. Archief.	Natuur- en Geneeskundig Archief voor Nederlandsch-Indië
Batavia, Natuurk. Tijdschr.	Natuurkundig Tijdschrift voor Nederlandsch-Indië, uitgegeven door de Koninklijke Natuurkundige Vereeniging in Nederlandsch-Indië
Batavia, Notulen	Notulen van de Allgemeene en Bestuurs-Vergaderingen van het Bataviaasch Genootschap van Kunsten en Wetenschappen
Batavia Obs. Obsns.	Observations made at the (Royal) Magnetical and Meteorological Observatory at Batavia
Batavia, Tijdschr.	Tijdschrift voor Indische Taal-, Land-, en Volkenkunde
Batavia, Verh. Natuurk. Vereen.	Verhandlingen der Natuurkundige Vereeniging in Nederlandsch-Indië
Bath Micro. Soc. Minutes	Extracts from the Minutes of the Bath Microscopical Society
Bath Natur. Hist. Club. Proc.	Proceedings of the Bath Natural History and Antiquarian Field Club
Bath Soc. Agric. Letters	Letters and Papers of the Bath and West of England Society for the Encouragement of Agriculture, Arts, Manufactures, and Commerce
Baugew. Ztg.	Baugewerks-Zeitung
Baumgartner Zts.	Zeitschrift für Physik, Mathematik, und verwandte Wissenschaften
Bayer. Gewerbeztg.	Bayerische Gewerbezeitung
Bayer. Kunst. Gewerbebl.	Kunst und Gewerbeblatt (Poletechn. Verein Königreich Bayern)
Bayer, Landw. Ver. Erg.	Ergebnisse landwirthschaftlicher und agrikulturchemischer Versuche an der Station des General-Comite des Bayerischen Landwirthschaftlichen Vereines in München

Bayeux, Mem. Soc. Agric.	Memoires de la Societe d'Agriculture, Sciences, Arts, et Belles-Lettres de Bayeux
Bd. Trade J.	Board of Trade Journal
Beauvais, Soc. Acad. Mem.	Memoires de la Societe Academique d'Archeologie, Sciences et Arts du Department de l'Oise
Beitr. Anat. Physiol	See Eckhard
Beitr. Anthropol. Bayerns	Beiträge zur Anthropologie und Urgeschichte Bayerns. Organ der Munchener Gesellschaft fur Anthropologie, Ethnologie und Urgeschichte
Beitr. Biol. Pflanz.	Beiträge zur Biologie der Pflanzen
Beitr. Geophys.	Beiträge zur Geophysik. Abhandlungen aus dem Geographischen Seminar der Universität Strassburg. Beiträge zur Geophysik. Zeitschrift fur Physikalische Erdkunde
Beitr. Kryptog. Schweiz	Beiträge zur Kryptogamenflora der Schweiz
Beitr. Mecklenb. Aerzte	Beiträge Mecklenburgischer Aerzte zur Medicin und Chirurgie
Beitr. Morphol.	Beiträge zur Morphologie und Morphogenie. Untersuchungen aus dem Anatomischen Institut su Erlangen
Beitr. Naturk. Preussens	Beiträge zur Naturkunde Preussens. Herausgegeben von der Königlichen Physikalisch-Oekonomischen Gesellschaft zu Königsberg
Beitr. Paläont. Oesterr.-Ung.	Beiträge zur Paläontologie Oesterreich-Ungarns und des Orients
Beitr. Path. Anat.	Beiträge zur Pathologischen Anatomie und Physiologie. Beirtäge zur Pathologischen Anatomie und zur Allgemeinen Pathologie
Beitr. Physiol. Morphol.	Beiträge zur Physiologie und Morphologie Niederer Organismen.
Beitr. Russ Reich.	Beiträge zur Kenntniss des Russischen Reiches und der angrenzenden Länder Asiens
Belfast, Clin. Soc. Trans.	Transactions of the Clinical and Pathological Society of Belfast
Belfast Field Club Rep.	Annual Reports and Proceedings of the Belfast Naturalists' Field Club
Belfast Natur. Hist. Soc. Proc.	Proceedings of the Belfast Natural History and Philosophical Society
Belg. Horticole	La Belgique Horticole. Annales de Botanique et d'Horticulture
Belg. P.	Belgian Patent
Bengal Asiat. Soc. J.	Journal of the Asiatic Society of Bengal
Bengal Asiat. Soc. Proc.	Proceedings of the Asiatic Society of Bengal
Bengal Govt. Records	Selections from the Records of the Bengal Government
Bengal, Phot. Soc. J.	Journal of the Photographic Society of Bengal
Ber.	Berichte der Deutschen Chemischen Gesellschaft, Berlin
Ber. deut. bot. Ges.	Berichte der deutschen botanischen Gesellschaft
Ber. pharm. Ges.	Berichte der deutschen pharmazeutischen Gesellschaft
Ber. phys. Ges.	Berichte der deutschen physikalischen Gesellschaft
Ber. Sachs. Ges. Wiss.	Berichte über die Verhandlungen der Konigl. Sachs. Gesellschaft der Wissenschaften zu Leipzig
Ber. Veter. König. Sach.	Berichte über das Veterinärwesen im Königreich Sachsen
Berg. Hüttenm. Jahr.	Berg- und hüttenmannisches Jahrbuch
Berg. Huttenm. Ztg.	Berg- und hüttenmannische Zeitung

Bergens Mus. Aarb.	Bergens Museums Aarbog for...Afhandlinger og Aarsberetning udgivne af Bergens Museum
Berggeist	Der Berggeist
Berghaus, Ann.	Annalen der Erd-, Völker- und Staatenkunde
Berghaus, Zts. Erdk.	Zeitschrift für vergleichende Erdkunde
Berlin Afrik. Ges. Mitth.	Mittheilungen der Afrikanischen Gesellschaft in Deutschland
Berlin Akad. Abh.	Abhandlungen der k. Akademie der Wissenschaften zu Berlin
Berlin Akad. Monatsber.	Monatsberichte der k. Preussischen Akademie der Wissenschaften zu Berlin
Berlin Akad. Sitzber.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin
Berlin Ann. Telegr.	Annalen der Telegraphie
Berlin Astron. Jahr.	Berliner Astronomisches Jahrbuch
Berlin Bot. Gartens Jahr.	Jahrbuch des Königlichen Botanischen Gartens und des Botanischen Museums zu Berlin
Berlin Bot. Gartens Notizbl.	Notizblatt des Königl. Botanischen Gartens und Museums zu Berlin
Berlin Ent. Ges.	See Ill. Wschr. Ent.
Berlin Entom. Zts.	Berliner Entomologische Zeitschrift; herausg. von dem Entomologischen Verein in Berlin
Berlin Ges. Anthrop. Verh.	See Ztschr. Ethnol.
Berlin Ges. Erdk. Verh.	Verhandlungen der Gesellschaft für Erdkunde zu Berlin
Berlin Ges. Erdk. Zts.	See Berlin Zts. Erdk.
Berlin Ges. Geburtshlf. Gynäk.	See Zts. Geburtshlf. Gynäk.
Berlin Ges. Naturf. Freunde Mag.	Magazin der Gesellschaft Naturforschender Freunde zu Berlin, für die neuesten Entdeckungen in der gesammten Naturkunde
Berlin Ges. Naturf. Freunde N. Schr.	Neue Schriften derGesellschaft Naturforschender Freunde in Berlin
Berlin Ges. Naturf. Freunde Verh.	Verhandlungen der Gesellschaft Naturforschender Freunde zu Berlin
Berlin Ges. Psychiatr.	See Arch. Psychiatr.
Berlin Gesundheitsamt Biol. Abth. Arb.	Arbeiten aus der Biologischen Abtheilung für Land- und Forstwirthschaft am Kaiserlichen Gesundheitsamte
Berlin Ind. Ztg.	Industrie Zeitung, Berlin
Berlin Jahr. Pharm.	Berlinisches Jahrbuch für die Pharmacie und für die damit verbundenen Wissenschaften
Berlin Klin. Wochenschr.	Berliner klinische Wochenschrift
Berlin Mem. Acad.	Memoires de l'Academie Royale des Sciences de Berlin
Berlin Mitth. Ges. Naturf.	Mittheilungen aus den Verhandlungen der Gesellschaft Naturforschender Freunde zu Berlin
Berlin Monatsber.	Monatsberichte der K. Preuss. Akademie der Wissenschaften zu Berlin
Berlin Monatsber. Ges. Erdk.	Monatsberichte über die Verhandlungen der Gesellschaft für Erdkunde zu Berlin
Berlin Naturf. Freunde Sitzber.	Sitzungs-Berichte der Gesellschaft Naturforschender Freunde zu Berlin
Berlin Neue Zts. Geburtsk.	Neue Zeitschrift für Geburtskunde
Berlin Physiol. Ges. Verh.	See Arch. Anat. Physiol
Berlin Physik. Reichsanst. Abh.	Wissenschaftliche Abhandlungen der Physikalisch Technischen Reichsanstalt
Berlin Verh. Med. Ges.	Verhandlungen der Berliner medicinischen Gesellschaft

Berlin Zool. Mus. Mitth.	Mittheilungen aus der Zoologischen Sammlung des Museums für Naturkunde in Berlin
Berlin Zts. Erdk.	Zeitschrift der Gesellschaft für Erdkunde zu Berlin
Berlin Mitth.	Mittheilungen der Naturforschenden Gesellschaft in Bern
Berwick, Natur. Club Hist.	History of the Berwickshire Naturalists' Club
Berz. Jahr. Chem.	Berzelius Jahresberichte der Chemie
Besancon, Mem. Soc. Emul.	Memoires et Comptes Rendus de la Societe (Libre) d'Émulation du Doubs
Besancon, Seances Publ.	Seances publiques de l'Academie des Sciences, Arts, et Belles-Lettres de Besancon
Beton Eisen	Beton und Eisen
Betterave	Betterave
Beziers Soc. Sci. Bull.	Bulletin de la Société d'Etude des Sciences Naturelles de Beziers
Bianconi, Rep Ital.	Repertorio Italiano Per la Storia Naturale
Bibl. Anat.	Bibliographie Anatomique. Revue des Travaux en langue francaise. Anatomie. Histologie. Embryologie. Anthropologie
Bibl. Bot.	Bibliotheca Botanica. Abhandlungen aus dem Gesammtgebiete der Botanik
Bibl. Brit.	Bibliotheque Britannique, ou Recueil extrait des Ouvrages Anglais periodiques et autres; partie des Sciences et Arts
Bibl. Ital.	Giornale dell' I. R. Istituto Lomgardo di Scienze, Lettere ed Arti, e *Biblioteca Italiana*
Bibl. Math.	Bibliotheca Mathematica. Zeitschrift für Geschichte der Mathematik. Journal d'Histoire des Mathematiques. Bibliotheca Mathematica. Zeitschrift für Geschichte der mathematischen Wissenschaften
Bibl. Univ.	Bibliotheque Universelle des Sciences, Archives des Sciences Physiques et Naturelles
Bibl. Zool.	Bibliotheca Zoologica
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb
Bierbrauer	Der Bierbrauer
Bijdr. tot de Dierkunde	Bijdragen tot de Dierkunde
Biochem. Bull.	Biochemical Bulletin
Biochem. J.	The Bio-Chemical Journal
Biochem. Zentr.	Biochemisches Zentralblatt, Leipzig
Biochem. Zts.	Biochemische Zeitschrift
Biol. Bull.	Biological Bulletin
Biol. Zentr.	Biologisches Zentralblatt
Biophys. Zentr.	Biophysikalisches Zentralblatt, Leipzig
Birmingham Natur. Hist. & Micro. Soc. Trans.	See Midland Natlist Trans.
Birmingham Phil. Soc. Proc.	Proceedings of the Birmingham Philosophical Society
Blankenburg, Ber.	Berichte des Naturwissenschaftlichen Vereins des Harzes zu Blankenburg
Blätter Blech-Arb.	Deutsche Blatter fur Blecharbeiter
Blätter Kunstgew.	Blatter für Kunstgewerbe
Blätter Zuckerrüb.	Blätter für Zuckerrubenbau
Bleekrode, Nieuw Tijdschrift	Nieuw Tijdschrift gewijd aan alle takken van Volksvlijt, Nijverheid, Landbouw, Mijnwezen, Handel, Spoorwegen, Telegraphie en Scheepvaart
Blois, Mem. Soc. Sci.	Memoires de la Société des Sciences et des Lettres de Blois
Blois, Soc. Loir et Cher Mem.	Memoires de la Société des Sciences et Lettres de Loir et Cher

Boerhaave	Boerhaave
Böhm. Ges. Abh.	Abhandlungen der Königlich Böhmischen Gesellschaft der Wissenschaften
Böhm. Ges. Wiss. Jahr.	Jahresbericht der königl. böhm. Gesellschaft der Wissenschaften
Böhm. Monatschr. Ges. Mus.	Monatschrift des Gesellschaft des Vaterländischen Museums in Böhmen
Bol. P.	Bolivia Patent
Boll. chim. farm.	Bolletino chimico farmaceutico, Milan
Boll. estac. agr. Ciudad Juarez	Boletin de la estacion agricola experimental de Ciudad Juarez
Boll. ingen.	Boletin de ingenieros
Boll. Natur. Siena	Bollettino del Naturalista Collettore, Allevatore, Coltivatore
Bologna Accad. Sci. Mem.	Memorie della (R.) Accademi delle Scienze dell' Istituto di Bologna
Bologna, Mem. Inst. Naz. Ital.	Memorie dell'Istituto Nazionale Italiano
Bologna, Mem. Soc. Med.	Memorie della Societa Medica di Bologna
Bologna, Mem. Soc. Med. Chir.	Memorie della Societa Medico-chirurgica di Bologna
Bologna, Nov. Comment.	Novi Commentarii Academiae Scientiarum Instituti Bononiensis
Bologna, Opusc.	Opuscoli della Societa Medico-chirurgica di Bologna
Bologna, Opusc. Sci.	Opuscoli Scientifici
Bologna, Opusc. Sci. N. Coll.	Nuova collezione d'Opuscoli Scientifici
Bologna Rend.	Rendiconto delle Sessioni dell' Accademia Reale delle Scienze dell' Istituto di Bologna
Bombay, Agric. Hort. Soc. Proc.	Proceedings of the Agricultural and Horticultural Society of Western India
Bombay Govt. Records	Selections from the Records of the Bombay Government
Bombay, Med. Phys. Soc. Trans.	Transactions of the Medical and Physical Society of Bombay
Bombay Natur. Hist. Soc. J.	The Journal of the Bombay Natural History Society
Bombay, Roy. Asiat. Soc. J.	The Journal of the Bombay Branch of the Royal Asiatic Society
Bone, Acad. Hippone Bull.	Bulletin de l'Academie d'Hippone
Bonn, Corresp, Blatt Nat. Hist. Ver.	Correspondenzblatt des Naturhistorischen Vereins für Rheinland und Westphalen
Bonn, Niederrhein. Ges. Sitzber.	Sitzungsberichte der Niederrheinischen Gesellschaft für Natur- und Heilkunde zu Bonn
Bonn, Untersuch. Physiol. Lab.	Untersuchungen aus dem physiologischen Laboratorium zu Bonn
Bonn, Verh. Naturhist. Ver.	Verhandlungen des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Bonplandia	Bonplandia
Bordeaux, Acad. Sci. Seances Publ.	Seances publiques de l'Academie Royale des Sciences, Belles-Lettres, et Arts de Bordeaux
Bordeaux, Actes Acad. Sci.	Recueil des Actes de l'Academie des Sciences, Belles-Lettres, et Arts de Bordeaux
Bordeaux, J. Med.	Journal de Medecine de Bordeaux
Bordeaux, J. Med. Prat.	Journal de Medecine pratique, ou Recueil des Travaux de la Société de Medecine de Bordeaux
Bordeaux, Mem. Soc. Med. Chir.	Memoires et Bulletins de la Société Medico-Chirurgicale des Hopitaux et Hospices de Bordeaux
Bordeaux, Mem. Soc. Sci. Phys.	Memoires de la Société des Sciences Physiques et Naturelles de Bordeaux

Bordeaux, Soc Linn Actes	Actes de la Société Linneenne de Bordeaux
Bordeaux, Soc Linn. Bull	Bulletin d'Histoire Naturelle de la Société Linneenne Bordeaux
Bordeaux, Soc Med. Mem.	Memoires et Bulletins de la Société de Medecine et de Chirurgie de Bordeaux
Bordeaux, Soc Sci P.-V.	Proces-Verbaux des Seances de la Société des Sciences Physiques et Naturelles de Bordeaux
Bornemann, Der Ingenieur	Der Ingenieur
Boston J Phil.	The Boston Journal of Philosophy and the Arts
Boston J. Natur. Hist.	Boston Journal of Natural History
Boston Med Surg. J.	Boston Medical and Surgical Journal
Boston, Mem Amer Acad	Memoirs of the American Academy of Arts and Sciences
Boston, Mem Natur. Hist. Soc.	Memoirs read before the Boston Society of Natural History
Boston Pap. Soc. Natur. Hist.	Occasional papers of the Boston Society of Natural History
Boston, Proc Natur. Hist. Soc.	Proceedings of the Boston Society of Natural History
Boston Soc. Med Sci. J.	Journal of the Boston Society of Medical Sciences
Bot Centr.	Botanisches Centralblatt. Referirendes Organ für das Gesammtgebiet der Botanik des In- und Auslandes
Bot. Centr. Beihefte	Beihefte zum Botanischen Centralblatt
Bot. Cong. Proc.	The International Horticultural Exhibition and Botanical Congress: Report of Proceedings
Bot. Gaz.	The Botanical Gazette
Bot. Jahr. (Engler)	Botanische Jahrbucher, Engler, Leipzig
Bot. Mag., Tokyo	The Botanical Magazine, Tokyo
Bot. Notiser	Botaniska Notiser
Bot. Tidsskr.	Botanisk Tidsskrift udgivet af den Botaniske Forening i Kjobenhavn
Bot. Untersuch	Botanische Untersuchungen aus dem Physiologischen Laboratorium der landwirthschaftlichen Lehranstalt in Berlin
Bot. Untersuch (Brefeld's)	Untersuchungen aus dem Gesammtgebiete der Mykologie
Bot. Ver. Gesamtthüringen	See Jena Geogr. Ges. Mitth.
Botan. Ztg.	Botanische Zeitung
Bot. Zentr.	Botanisches Zentralblatt
Botaniste	Le Botaniste
Bouchardat, Archiv.	Archives de Physiologie, de Therapeutique, et d'Hygiene
Boue, J. Geol.	Journal de Geologie
Boulogne, Mem. Soc. Agric.	Memoires de la Société d'Agriculture, etc., de Boulogne-sur-Mer
Bourse cuirs Liege	Bourse aux cuirs de Liege, bulletin hebdomadaire
Brandenb. Bot. Ver. Verh.	Verhandlungen des botanischen Vereins fur die Provinz Brandenburg
Brass World	Brass World and Platers Guide, The
Braunk.	Braunkohle
Braunschw. Ver. Naturwiss. Jahr.	Jahresbericht des Vereins fur Naturwissenschaft zu Braunschweig
Braz. P.	Brazilian Patent
Bremen Abh.	Abhandlungen herausgegeben vom Naturwissenschaftlichen Verein zu Bremen
Brenn. Ztg.	Brennerei Zeitung
Brera, Giorn. Med. Prat.	Giornale di Medicina Pratica
Brera, Nuovi Comment.	Nuovi Commentari di Medicina

Brescia, Comment. Ateneo	Commentarj della Accademia di Scienze, Lettre, ed dell'Ateneo di Brescia
Breslau, Ann. Klin. Inst.	Annalen des Klinisch-chirurgischen Instituts auf der Universitat zu Breslau
Breslau, Bot Garten Arb.	Arbeiten aus dem Konigl Botanischen Garten zu Breslau
Breslau, Gewerbebl.	Breslauer Gewerbeblatt
Breslau, Jahr. Schles. Ver. Berg.	Jahrbuch des Schlesischen Vereins fur Berg- und Huttenwesen
Breslau, Schles. Ges. Jahr.	Jahresbericht des Akademischen Naturwissenschaftlichen Vereins zu Breslau
Breslau, Studien Physiol. Inst.	Studien des Physiologischen Instituts zu Breslau
Breslau, Zts. Klin Med.	Zeitschrift fur Klinische Medicin
Brest Soc Acad. Bull.	Bulletin de la Société Academique de Brest
Brewers J. (Lon)	Brewers Journal and Hop and Malt Trades Review, The (London)
Brewers J , N. Y.	Brewers Journal, New York
Brick	Brick
Brick J.	Brick, Pottery and Glass Journal
Brick and Clay Record	Brick and Clay Record
Brighton, Proc. Natur. Hist Soc.	Reports and Abstracts of the Proceedings of the Brighton and Sussex Natural History Society
Bristol Proc Nat. Soc.	Proceedings of the Bristol Naturalists' Society
Brit. Assoc Rep.	Report of the Meetings of the British Association for the Advancement of Science
Brit. Clay Worker	British Clay Worker, The
Brit. Food J.	British Food Journal
Brit. For Med. Chir. Rev.	British and foreign Medico-Chirurgical Review
Brit. Inst. Publ Health	See J. State Med
Brit. J. Almanac	British Journal of Photography Almanac
British J Dent. Sci.	The British Journal of Dental Science
Brit. J. Phot.	British Journal of Photography
Brit. Med J.	British Medical Journal
Brit. Mycol. Soc. Trans.	The British Mycological Society. Transactions
Brit. Pharm Confer. Proc.	Proceedings of the British Pharmaceutical Conference
Brit. Pharm Confer. Trans.	Year Book of Pharmacy, comprizing Abstracts of Papers With the Transactions of the British Pharmaceutical Conference
Brit. Colon Drug.	British and Colonial Druggist, London
Brit. Guiana Agr. Soc.	See Timehri
Brit. Guiana P.	British Guiana Patent
Brit. Hond. P.	British Honduras Patent
Brooklyn Entom. Soc. Bull.	Bulletin of the Brooklyn Entomological Society
Brosche, Zts	Zeitschrift fur Natur- und Heilkunde
Broussais, Ann.	Annales des la Medicine Physiologique
Brown-Sequard, J. Physiol.	Journal de la Physiologie de l'Homme et des Animaux
Brugnatelli, Giorn.	Giornale di Fisica, Chimica, e Storia Naturale
Brunn Verh.	Verhandlungen des Naturforschenden Vereines in Brunn
Brux Acad. Bull.	Bulletins de l'Academie Royale des Sciences, etc , de Belgique
Brux. Acad. Cent. Anniv.	Centieme Anniversaire de Foundation de l'Academie Royale de Belgique
Brux Acad Med Belg Bull	Bulletin de l'Academie Royale de Medecine Belgique
Brux. Acad Sci Mem.	Nouveaux memoires de l'Academie Royale, des Sciences et Belles-lettres de Bruxelles

Brux Actes Soc. Med.	Actes de la Société Medicale de Bruxelles
Brux. Ann. Soc. Entom. Belge	Annales de la Société Entomologique Belge
Brux. Ann. Soc. Malacol.	Annales de la Société Malacologique de Belgique
Brux. Ann Trav. Pub.	Annales des Travaux Publics de Belgique
Brux. Ann. Univ. Belg.	Annales des Universites de Belgique
Brux. Bull Belge Phot.	Bulletin Belge de la Photographie
Brux. Bull Soc. Bot.	Bulletins de la Société Royale de Botanique de Belgique
Brux Congr. Bot. Act.	Actes du Congres de Botanique horticole reuni a Bruxelles
Brux Congr. Bot. (C. R)	Congres de Botanique et d'Horticulture de 1880 tenu a Bruxelles
Brux. J. Med.	Journal de Medecine, de Chirurgie, et de Pharmacologie
Brux. J. Soc. Centr. Agric.	Journal de la Société Centrale d'Agriculture de Belgique
Brux. Mem. Couronn.	Memoires Couronnes et Memoires des Savants Entrangers
Brux. Mus. Congo Ann.	Etat Independant du Congo Annales du Musee du Congo, publiees par ordre du Secretaire d'Etat
Brux. Mus Hist. Natur. Ann.	Annales du Musee Royal d'Historie Naturelle de Belgique
Brux. Mus. Hist. Natur. Bull.	Bulletin du Musee Royal d'Histoire Naturelle de Belgique
Brux. Mus. Hist. Natur. Mem.	Memoires du Musee Royal d'Histoire Naturelle de Belgique
Brux. Soc. Agric. Journ.	Journal de la Société Centrale d'Agriculture de Belgique
Brux. Soc. Belge Micro. Ann.	Annales de la Société Belge de Microscopie
Brux. Soc. Belge Micro. Bull.	Bulletin (des Seances) de la Société Belge de Microscopie
Brux. Soc. Entom. Ann.	Annales de la Société Entomologique de Belgique
Brux. Soc. Entom. Mem.	Memoires de la Société Entomologique de Belgique
Brux. Soc. Linn. Bull.	Bulletin de la Société Linneenne de Bruxelles
Brux. Soc. Sci.	See Rev. Quest. Sci.
Brux. Soc. Sci. Ann.	Annales de la Société Scientifique de Bruxelles
Bucarest. Acad. Rom. Anal.	Analele Academiei Romane
Bucarest Soc. Sci. Bul.	Buletinul Societatii de Sciinte (Fizice, Fixica, Chimia si Mineralogia) din Bucuresci-Romania. Bulletin de la Société des Sciences, Bucarest-Roumanie
Buchholz	See Annab.-Buchh. Ver. Nat. Jber.
Buda, Evkonyvei	A' Magyar Tudos Tarsasag' Evkonyvei (Year Books of the Hungarian Scientific Association)
Buda, Palyamunkak.	Termeszettudomanyi Palyamunkak
Buda, Tudomanytar.	Tudomanytar Kozre bocsatja a' Magyar Tudos Tarsasag
Buffalo Bull.	Bulletin of the Buffalo Society of Natural Sciences
Builder	The Builder
Buitenzorg Inst. Bot. Bull.	's Lands Plantentuin Bulletin de l'Institut Botanique de Buitenzorg
Buitenzorg Jard. Bot Ann.	Annales du Jardin Botanique de Buitenzorg
Bull. Acad. Med.	Bulletin of the Academy of Medicine
Bull. Acad. roy. Belg.	Academie royale de Belgique; Bulletin de la Classes des Sciences
Bull. Acad. Sci., Cracow.	Bulletin international de l'Academie des Sciences de Cracovie

Bull. Acad. Sci., Petrograd	Bulletin de l'Academie Imperiale des Sciences de Petrograd
Bull. Amer. Inst. Min. Eng.	Bulletin American Institute of Mining Engineers
Bull. Amer. Pharm. Assoc.	Bulletin of the American Pharmaceutical Association
Bull. assoc. chim. sucr. dist.	Bulletin de l'association des chemists de sucrerie distillerie de France
Bull. Bur. Agric.	Bulletin of the Bureau of Agricultural Intelligence and of Plant Diseases
Bull. Bur. Chem. U. S. Dept. Agric.	Bulletins, Bureau of Chemistry, U. S. Department of Agriculture
Bull. Bur. Mines	Bureau of Mines Bulletin, Department of the Interior
Bull. Bur. Standards	Bulletin of the Bureau of Standards
Bull. Col. School Mines	Bulletin of the Colorado School of Mines
Bull. Dept. Agric. Jamaica	Bulletin of the Department of Agriculture, Jamaica
Bull. Dept. Agric. Trinidad	Bulletin of Agricultural Information, Department of Agriculture, Trinidad
Bull. Geol. Inst. Univ. Upsala	Bulletin of the Geological Institute of the University of Upsala
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America
Bull. Hyg. Lab.	Bulletins of the Hygienic Laboratory, United States Public Health and Marine Hospital Service
Bull. Imp. Inst.	Bulletin of the Imperial Institute, London
Bull. Iron Assoc.	Bulletin of the American Iron and Steel Association
Bull. Johns Hopkins Hosp.	Bulletin of Johns Hopkins Hospital
Bull. Mass. Inst. Tech.	Bulletin of the Massachusetts Institute of Technology
Bull. Med. Belge.	Bulletin Medical Belge.
Bull. Musee	Bulletin du Musee de l'industrielle de Belgique
Bull. Pharmacie	Bulletin de Pharmacie
Bull. Pharmacy	Bulletin of Pharmacy
Bull. Pharm. Sud-est	Bulletin de Pharmacie du Sud-est, Montpellier
Bull Sci. France Belg.	Bulletin Scientifique de la France et de la Belgique
Bull. Sci. Nord	Bulletin Scientifique, Historique et Litteraire du Department du Nord et des pays voisins
Bull. Sci. pharmacolog.	Bulletin des Sciences pharmacologiques
Bull. Soc. Bot. France	Bulletin de la Société Botanique de France
Bull. Soc. Bot. Belg.	Bulletin de la Société Royale de Botanique de Belgique
Bull. Soc. Chim.	Bulletin de la Société Chimique de France
Bull. Soc. Chim. Belg.	Bulletin de la Société Chimique de Belgique
Bull. Soc. Encourag.	Bulletin de la Société d'Encouragement
Bull Soc. franc. Mineral.	Bulletin de la Société Francaise de Mineralogie
Bull. Soc. franc. Phot.	Bulletin de la Société Francaise de Photographie
Bull. Soc. geol. France	Bulletin de la Société geologique de France
Bull. Soc. Ind. Amiens	Bulletin de la société industrielle d'Amiens
Bull. Soc. Ind. Marseille	Bulletin de la Société industrielle de Marseille
Bull. Soc. Ind. Minerale	Bulletin de la société de l'industrie minerale
Bull. Soc. Ind. Mulh.	Bulletin de la société industrielle de Mulhouse
Bull. Soc. Ind. Nord	Bulletin mensuel de la société industrielle du Nord
Bull. Soc. Ind. Rouen	Bulletin de la société industrielle de Rouen
Bull. Soc. internatl. elect.	Bulletin de la Société internationale des electriciens
Bull. Soc. Med. Amiens	Bulletin des Travaux de la Société Medicale d'Amiens
Bull. Soc. med. Gand	Bulletin de la Société de Medecine de Gand
Bull. Soc. Mycol	Bulletin de la Société Mycologique de France
Bull. Soc. pharm. Bord.	Bulletin de la société pharmacie de Bordeaux
Bull. Soc phot. Belg.	Bulletin de la Société photographique de Belgique
Bull. Soc. Romane Stiin	Buletinul societatii Romane de Stiinte
Bull. Soc. roy. pharm.	Bulletin de la société de pharmacie de Bruxelles royale
Bull. Soc. sci. med. Rennes	Bulletin de la société scientifique et medicale de l'ouest, Rennes

Bull. Soc. vaudoise	Bulletin de la Société vaudoise des Ingenieurs et des Architects
Bull. Torrey Bot. Club	Bulletin of the Torrey Botanical Club, New York
Bull. Vulc. Ital.	Bullettino del Vulcanismo Italiano (e di Geodinamica generale)
C. A.	Chemical Abstracts
Cabanis, J. Ornithol.	Journal fur Ornithologie
Cadiz, Period. Mens. Cien.	Periodico mensual de Ciencias matematicas y fisicas
Caen, Acad. Mem.	Memoires de l'Academie des Sciences, Belles Lettres, et Arts de Caen
Caen, Bull. Soc. Linn. Normandie	Bulletin de la Société Linneene de Normandie
Caen, Mem. Soc. Linn. Normandie	Memoires de la Société Linneenne de Normandie
Caen, Travaux	Precis des Travaux de la Société d'Agriculture, &c. de Caen
Calcutta, J. Natur. Hist.	The Calcutta Journal of Natural History
Calcutta, Quart. J.	Quarterly Journal of the Medico-Physical Society
Calcutta Roy. Bot. Gard. Ann.	Annals of the Royal Botanic Garden, Calcutta
Calcutta, Trans. Med. Phys. Soc.	Transactions of the Medical and Physical Society of Calcutta
Cal. Acad. Bull.	Bulletin of the California Academy of Sciences
Cal. Acad. Mem.	Memoirs of the California Academy of Sciences
Cal. Acad. Natur. Sci. Proc.	Proceedings of the Californian Academy of Natural Sciences
Cal. Acad. Pap.	Occasional Papers of the California Academy of Sciences
Cal. Min. Bur. Bull.	California State Mining Bureau. Bulletin
Cal. Min. Bur. Rep.	(California State Mining Bureau). Report of the State Mineralogist
Calvados, Mem. Soc. Linn.	Memoires de la Société Linneenne du Calvados
Cambrai, Mem. Soc. Emul.	Memoires de la Société d'Emulation de Cambrai
Cambridge Mem. Analyt. Soc.	Memoirs of the Cambridge Analytical Society
Cambridge Mus. Comp. Zool. Bull.	Proceedings of the Museum of Comparative Zoology at Harvard College, Cambridge, Mass.
Cambr. Ornith. Club Bull.	Bulletin of the Nuttall Ornithological Club. A Quarterly Journal of Ornithology
Cambridge Phil. Soc. Proc.	Proceedings of the Cambridge Philosophical Society
Cambridge Phil. Soc. Trans.	Transactions of the Cambridge Philosophical Society
Cambridge, Studies Physiol. Labor	Studies from the Physiological Laboratory in the University of Cambridge
Camera Oscura	La Camera Oscura; rivista periodica universale dei progressi della Fotografia
Can.	Canadian—Canada
Can., Bot. Soc. Ann.	Annals of the Botanical Society of Canada
Can. Chem. J.	The Canadian Chemical Journal
Can. Drug.	Canadian Druggist
Can. Eng.	Canadian Engineer, The
Can. Entom.	The Canadian Entomologist
Can. Entom. Soc. Rep.	First Annual Report on the Noxious Insects of the Province of Ontario
Can. Inst. Proc.	Proceedings of the Canadian Institute (Toronto, being a continuation of "The Canadian Journal of Science, Literature and History")
Can. Inst. Trans.	Transactions of the Canadian Institute
Can. J.	The Canadian Journal of Industry, Science, and Art

Can Naturalist	The Canadian Naturalist and Geologist, and Proceedings of the Natural History Society of Montreal
Can P.	Canadian Patent
Can Pat Off Rec	Canadian Patent Office Record
Can Pharm J	Canadian Pharmaceutical Journal and Pharmacal Gazette
Can Rec Sci	The Canadian Record of Science, including the Proceedings of the Natural History Society of Montreal, and replacing the Canadian Naturalist
Can Roy Soc Proc Trans	Proceedings and Transactions of the Royal Society of Canada
Canestrini	See Archivio Zool
Canestrini, Archiv	Archivio per la Zoologia, l Anatomia, e la Fisiologia
Cannes Soc Mem	Memoires de la Société des Sciences Naturelles (et Historiques), des Lettres et des Beaux-Arts de Cannes, et de l'arrondissement de Grasse
Cantu, Cronaca	Cronaca
Caout Gutta p	Caoutchouc et la Gutta-percha
Caradoc Field Club Trans.	Transactions of the Caradoc and Severn Valley Field Club
Cardiff Natur Soc Trans	Cardiff Naturalists' Society Report and Transactions
Carinthia	See Karnten
Carl, Rep Physik	Repertorium für Experimental Physik, etc (Rep der Physik)
Carlsberg Lab	See under Kiobenh
Carlsruhe	See Karlsruhe
Carlsruhe, Verh Naturwiss Ver.	Verhandlungen des Naturwissenschaftlichen Vereins
Carloinisches Medicq-Chirurgisches Institut.	See under Stockh Physiol Lab Mitth
Carus, Zool Anzeiger	Zoologischer Anzieger
Casopis	Casopis pro Pestovani Mathematiky a Fysiky (Journal for the Advancement of Mathematics and Physica)
Casopis Cesketho Lekarn	Casopis Cesketho Lekarnitura
Casper Vierteljahrssch	Vierteljahrsschrift fur gerichtliche und offentliche Medicin
Casper Wochensch	Wochenschrift fur die gesammte Heilkunde
Cassel Jahr	Jahresbericht, dann Bericht, uber die Thatigkeit des Vereins fur Naturkunde in Cassel
Cassier s Mag.	Cassiers's Magazine
Castings	Castings
Catania Atti Accad Gioen	Atti dell'Accademia Gioenia di Scienze Naturali di Catania
Catania Boll Accad Gioen	Bollettino delle Sedute della Accademia Gioenia
Cattaneo Bibl. di Farm	Biblioteca di Farmacia, Chimica, etc.
Cattaneo Giorn Farm.	Giornale di Farmacia
Cell. Ind.	Die Celluloid Industrie
Cellule	La cellule
Cement	Cement
Cement Age	Cement Age
Cement Eng. News	Cement and Engineering News
Cement Record	Cement Record
Centr Agrik Chem.	Central-Blatt fur Agrikulturchemie und rationellen Wirthschafts-Betrieb Referirendes Organ fur naturwissenschaftliche Forschungen in ihrer Anwendung auf die Landwirthschaft
Centr Allg Path.	Centralblatt fur allgemeine Pathologie

Centr. Bakt.	Centralblatt für Bacteriologie und Parasitenkunde
Centr. Med. Wiss.	Centralblatt fur die medicinischen Wissenschaften
Centr. Mineral	Centralblatt fur Mineralogie, Geologie und Palaeontologie
Centr. Papierfabr.	Centralblatt fur Papierfabrikation
Centr. Path.	Centralblatt fur Allgemeine Pathologie und Pathologische Anatomie
Centr. Physiol.	Centralblatt für Physiologie
Centr. Text. Ind.	Centralblatt für die Textil-Industrie
Centr. Zuckerind.	Centralblatt für die Zuckerindustrie
Centrztg. Optik	Central-Zeitung fur Optik und Mechanik (Elektrotechnik und verwandte Berufszweige)
Ceramique	Ceramique, La
Cette Stat. Maritime	See Montpellier Inst. Zool. Trav.
Cey. P.	Ceylon Patent
Chamb. Comm. J.	Chamber of Commerce Journal
Chambery Mem. Acad. Savoie.	Memoires de la Societe Academique de Savoie.
Charente-Inf. Soc. Sci. Ann.	Academie de la Rochelle. Societe des Sciences Naturelles de la Charente-Inferieure. Annales
Charkoff.	See Kharkov.
Charleston Med. Journ.	Charleston Medical Journal and Review
Charleston South J. Med.	The Southern Journal of Medicine
Chem. Age	Chemical Age
Chem. Centr.	Chemisches Centralblatt (1830–1906).
Chem. Coll. Reports	Reports of the Royal College of Chemistry, and Researches conducted in the Laboratories
Chem. Drug.	Chemist and Druggist, London
Chem. Drug. Australasia	Chemist and Druggist of Australasia
Chem. Eng.	Chemical Engineer
Chem. Gaz.	Chemical Gazette, The
Chem. Ind.	Chemische Industrie
Chem. Listy	Chemicke Listy
Chem. News	Chemical News
Chem. Pharm. Centr. Blatt.	Chemisch-pharmaceutisches Central-Blatt
Chem. Rev.	The Chemical Review
Chem. Rev. Fett-Harz-Ind.	Chemische Revue uber die Fett-und Harz-Industrie
Chem. Tech. Mitth.	Elsner's Chemisch-Technische Mittheilungen
Chem. Tech. Rep.	Chemisch-Technisches Repertorium (Jacobsen 1862–1901)
Chem. Tech. Neuzeit	Chemische Technologie der Neuzeit
Chem. Tech. Übers.	Chemisch-Technische Übersicht (supplement to Chem. Ztg.)
Chem. Tech. Ztg.	Chemiker-und Techniker-Zeitung
Chem. Trade J.	Chemical Trade Journal and Chemical Engineer
Chem. Weekbl.	Chemisch Weekblad
Chem. World	Chemical World, The
Chem. Zentr.	Chemisches Zentralblatt (1907–)
Chem. Ztg.	Chemiker-Zeitung
Chem. Ztg. Rep.	Repertorium der Chemiker Zeitung
Chem. Zts.	Chemische Zeitschrift
Chemist	The Chemist
Chemnitz Ber.	Bericht der Naturwissenschaftlichen Gesellschaft zu Chemnitz
Cherbourg, Mem. Soc. Acad.	Memoires de la Société Academique de Cherbourg
Cherbourg, Mem. Soc. Sci.	Memoires de la Société Imperiale des Science Naturelles de Cherbourg

Cherbourg Soc. Sci. Natl. Mem.	Memoires de la Société Nationale des Sciences Naturelles et Mathematiques de Cherbourg
Chester Soc. Sci. Proc.	Proceedings of the Chester Society of Natural Science (and Literature)
Chicago Acad. Sci. Bull.	Bulletin of the Chicago Academy of Sciences
Chicago Acad. Sci. Bull. Nat. Hist. Surv.	The Chicago Academy of Sciences. Bulletin...of the Natural History Survey
Chicago Acad. Sci. Trans.	Transactions of the Chicago Academy of Sciences
Chicago Entom. Soc. Mem.	Occasional Memoirs of the Chicago Entomological Society
Chicago Field Columb. Mus. Publ.	Publications of the Field Columbian Museum
Chile, Anales Univ.	Anales de la Universidad de Chile
Chile P.	Chilean Patent
Chili Soc. Sci. Act.	Actes de la Société Scientifique du Chili (Actas de la Sociedad Cientifica de Chile)
Chim. et Ind.	Chimie et Industrie
Chimiste	Chimiste, Le
Christiania, Forh.	Forhandlinger i Videnskabs-Selskabet i Christiania
Christiania, Norsk Mag.	Norsk Magazin for Laegevidenskaben
Christiania Skr. (Math.-Nat. Kl.)	Skrifter udgivne af Videnskabsselskabet i Christiania. Mathematisk-naturvidenskabelig Klasse
Christiania, Univers. Lab.	Das chemische Laboratorium der Universität Christiania
Chron. ind.	Chronique de l'industrie
Chur, Jahresber. Naturf. Gesell.	Jahresbericht der Naturforschenden Gesellschaft von Graubündten in Chur
Ciment	Ciment, Le
Cincin. Soc. Natur Hist. Jl.	The Journal of the Cincinnati Society of Natural History
Cistula Entom.	Cistula Entomologica
Civil Eng. Inst. Trans.	Transactions of the Institution of Civil Engineers
Civil Eng. J.	The Civil Engineer and Architect's Journal, etc.
Civilingenieur	Der Civilingenieur
Clay Worker	Clay Worker, The
Clermont, Mem. Acad. Sci.	Memoires de l'Academie des Sciences, Belles Lettres, Arts de Clermont-Ferrand
Cleveland Med. J.	Cleveland Medical Journal
Clin. Soc. Trans.	Transactions of the Clinical Society of London
Coblentz, Jahr. bot. Ver.	Jahresbericht des botanischen Vereines am Mitten und Niederrheine, mit botanischen Abhandlungen
Cohn, Beitr. Biol. Pflanz.	Beiträge zur Biologie der Pflanzen
Coimbra, Inst.	O Instituto, journal scientifico et letterario
Coimbra, Soc. Broter. Bol.	Sociedade Broteriana. Boletim Anual
Col. P.	Colombian Patent
Collegium	Collegium (Scientific technical supplement to Ledermarkt)
Colliery Guardian	Colliery Guardian and Journal of the Iron and Coal Trades
Colmar Soc. Hist. Natur. Bull.	Bulletin de la Société d'Histoire Naturelle de Colmar
Colombia, Contrib.	Contribuciones de Colombia a las Ciencias i a las Artes
Colombo	See Ceylon
Colorado Sci. Soc. Proc.	Proceedings of the Colorado Scientific Society
Comment. Fauna &c. Ven. Trent.	Commentario della Fauna, Flora e Gea del Veneto e Trentino
Compt. rend.	Comptes rendus hebdomadaires des Seances de l'Academie des Sciences

Compt. rend Assoc. Franc	Association Francaise pour l'Avancement des Sciences. Compte Rendu de la le (-12e) Session; 1872–83
Compt. rend. minerale	Comptes rendus de la Société de l'industrie minerale
Compt. rend. Soc. biol.	Comptes rendus des seances et memoires de la Société de biologie, Paris
Compt. rend. trav lab. Carlsberg	Comptes rendus du travaux du laboratoire de Carlsberg
Concrete	Concrete
Concrete Age	Concrete Age
Concrete Constr. Eng.	Concrete and Constructional Engineering
Concrete Eng.	Concrete Engineering (no longer published separately. Combined with Cement Age)
Conegliano Scuola Vit. Enol. Ann.	Annali della R. Scuola di Viticoltura e di Enologia in Conegliano
Conegliano Scuola Vit. Enol. N. Rassegna	Nuova Rassegna di Viticoltura de Enologia della R. Scuola di Conegliano
Conegliano Scuola Vit. Enol Riv.	La Rivista. Periodico (quindicinale, Organo) della R. Scuola di Viticoltura e di Enologia (e del Comizio Agrario) di Conegliano
Cong. P.	Congo Free State Patent
Congr. Anthropol Compt. Rend.	Congres international d'Anthropologie et d'Archeologie prehistoriques. Comptes Rendus
Congr. Bot. Crittog. Atti	Societa Crittogamologica Italiana. Atti del Congresso Nazionale di Botanica Crittogamica in Parma
Congr. Bot. Int. Atti	Atti del Congresso Internazionale di Genova
Congr. Int. Bot. Bull.	Bulletin du Congres International de Botanique et d'Horticulture reuni a St. Petersbourg...
Congr Internatl. Hortic. Bull.	Bulletin du Congres International d'Horticulture a Bruxelles
Congr. Internatl. Med. Atti	Atti dell' XI. Congresso Medico Internazionale
Congr Internatl. Med. C. R	Comptes-Rendus du XII Congres International de Medecine
Congr Internatl Sci Med. C. R.	Congres Periodique International des Sciences Medicales Compte-Rendu
Congr. Internatl. Zool (C. R.)	Congres International de Zoologie
Connecticut, Acad. Mem.	Memoirs of the Connecticut Academy of Arts and Sciences
Connecticut Acad Trans.	Transactions of the Connecticut Academy of Arts and Sciences
Contrib. Biol Veg	Contribuzioni alla Biologia Vegetale
Copenhagen	See Kjobenhavn.
Copenhagen	See Congr. Int. Sci Med C. R., 1884
Copenhague, Resumé	Résumé du Bulletin de la Société Royale Danoise des Sciences
Cordoba Acad. Bol.	Boletin de la Academia Nacional de Ciencias Exactas existente en la Universidad de Cordoba
Cordoba Acad. Ci. Act	Actas de la Academia Nacional de Ciencias en Cordoba
Corn Trade J.	Corn Trade Journal
Cornwall, J. Roy. Inst.	Journal of the Royal Institution of Cornwall
Cornwall Poly. Soc Rep.	Royal Cornwall Polytechnic Society, Annual Report
Cornwall, Poly. Soc. Trans.	Reports and Transactions of the Royal Geological Society of Cornwall
Corresp. Blatt. Schweiz. Aerzte	Correspondenz-Blatt für Schweizer Aerzte
Corresp. Blatt Zahn.	Correspondenzblatt fur Zahnärzte
Cosmos	Cosmos Revue Encyclopedique hebdomadaire

Costa, Corrisp. Zool.	Corrispondenza Zoologica, destinata a diffondere nel regno delle Due Sicilie tutto cio che si va discuoprendo entro e fuori Europa (e vice-versa), ris guardante la Zoologia in generale
Cotteswold Club Proc.	Proceedings of the Cotteswold Naturalists' Field Club
Cracovie Acad. Sci. Bull	Bulletin International de l'Academie des Sciences de Cracovie
Cracow	See Krakow
Crell. Ann.	Chemische Annalen fur die Freunde der Naturlehre, etc.
Crichton, Russ. Sammlung.	Russische Sammlung für Naturwissenschaft und Heilkunst
Cron. med. mex.	Cronica medica mexicana, Mexico
Croydon Micro. Club Proc.	Proceedings and Transactions of the Croydon Microscopical and Natural History Club
Croydon Micro. Club Rep	...Report and Abstract of Proceedings of the Croydon Microscopical (and Natural History) Club
Cuba P.	Cuban Patent
Cuba, Rep. Fis. Nat.	Repertorio fisico-naturale de la isla de Cuba
Cuir	Cuir, Le
Cumberland Assoc. Trans.	Transactions of the Cumberland and Westmorland Association for the Advancement of Literature and Science
Cuyper, Rev. Univ.	Revue Universelle des Mines, de la Metallurgie, &c.
D'Alton u. Burm. Ztg. Zool.	Zeitung fur Zoologie, Zootomie, und Palaeozoologie
Dan. Biol. Stat. Rep.	Report of the Danish Biological Station to the Home Department (Board of Agriculture)
Dan. P.	Danish Patent
Danzig, Neu. Schrift.	Neueste Schriften der Naturforschenden Gesellschaft in Danzig
Danzig, Schrift.	Schriften der Naturforschenden Gesellschaft in Danzig
Darmst. Beitr. Geol.	Beitrage zur Geologie des Grossherzogthums Hessen und der angrenzenden Gegenden
Darmst. Ver. Erdk. Notiz.	Notizblatt des Vereins fur Erdkunde zu Darmstadt und des Mittelrheinischen Geologischen Vereins
Davenport Acad. Proc.	Proceedings of the Davenport Academy of Natural Sciences
Dax Soc. Borda Bull.	(Bulletin de la) Société de Borda, Dax (Landes)
Delft Ecole Poly. Ann.	Annales de l'Ecole Polytechnique de Delft
Delhi, Med. J.	Quarterly Medical and Surgical Journal for the North-West Provinces
Denison Univ. Sci. Lab. Bull.	Bulletin of (the Scientific Laboratories of) Denison University
Dent. Cosmos	Dental Cosmos, Philadelphia
Dent. Digest	The Dental Digest, Chicago
Dent. Rev.	The Dental Review
Deut. Amer. Apoth. Ztg.	Deutsch-Amerikanische Apotheker Zeitung, New York
Deut. Amer. Gewerbeztg.	Illustrierte Deutsch-Amerikanische Gewerbe und Industrie-Zeitung (Newark, N. J.)
Deut. Arch Klin. Med.	Deutsches Archiv. fur Klinische Medizin
Deut. Bot. Ges. Ber.	Berichte der Deutschen Botanischen Gesellschaft
Deut. Bot. Monats.	Deutsche Botanische Monatsschrift
Deut. Buchdr. Ztg.	Deutsche Buchdruker-Zeitung
Deut. Eisenbahn Ztg.	Zeitung des Vereins Deutscher Eisenbahn-Verwaltungen
Deut. Elektro. Ges.	See Zts. Elektroch.

Deut Entom Zts	Deutsche Entomologische Zeitschrift (formerly *Berliner Entomologische Zeitschrift*)
Deut Geol Ges Zts	Zeitschrift der Deutschen Geologischen Gesellschaft
Deut Gerber Ztg	Deutsche Gerber Zeitung
Deut Ind Ztg	Deutsche Industrie Zeitung
Deut Klinik	Deutsche Klinik
Deut Mechan Ztg	Deutsche Mechaniker-Zeitung
Deut med Wochenschr	Deutsche medizinische Wochenschrift
Deut. Monats	Deutsche Monatshefte
Deut Naturf Ber.	Amtlicher Bericht der Versammlung Deutscher Naturforscher und Aerzte
Deut Naturf Festschr	Festschrift fur die 59. Versammlung Deutscher Naturforscher und Aerzte
Deut Naturf. Tagebl	Tageblatt der Versammlung Deutscher Naturforscher und Aerzte
Deut. Naturf. Versamml Ber.	Bericht uber die Versammlung der Deutschen Naturforscher und Aerzte
Deut. Poly Ztg	Allgemeine Deutsche Polytechnische Zeitung (H. Grothe)
Deut. Phys Ges Verh	Verhandlungen der Deutschen Physikalischen Gesellschaft
Deut. Tech. Ztg	Deutsche Techniker Zeitung
Deut. Topfer Ziegl Ztg	Deutsche Topfer und Ziegler Zeitung
Deut. Vierteljahrschr Oeff. Gesundh.	Deutsche Vierteljahrsschrift fur Gesundheitspflege
Deut. Zool. Ges.	See Zool Anz
Deut. Zool. Ges. Verh	Verhandlungen der Deutschen Zoologischen Gesellschaft
Deut Zts Chirurg.	Deutsche Zeitschrift fur Chirurgie
Deut Zts Thiermed	Deutsche Zeitschrift fur Thiermedicin und vergleichende Pathologie
Deut. Zuckerind	Deutsche Zuckerindustrie
Devon Assoc. Trans	Transactions of the Devonshire Association for the Advancement of Science, Literature and Art
Devon & Cornwall Natur Hist Soc	See Plymouth Inst Trans
Diamant Ztg	Diamant, Glas Industrie Zeitung
Dietet Hyg Gaz	Dietetic and Hygienic Gazette, The
Dijon, Acad. Sci Mem	Memoires de l'Academie des Sciences, Arts et Belles Lettres de Dijon
Dijon, J Agric	Journal d'Agriculture de la Cote d Or
Dijon, Seances Acad.	Seances publiques de l'Academie des Sciences, Arts et Belles-Lettres de Dijon
Dinant, Soc Natur. Bull	Bulletin de la Société des Naturalistes Dinantais
Dingl Poly.	Dinglers Polytechnisches Journal
Donders, Archiv	Archiv fur die Hollandischen Beitrage zur Natur- und Heilkunde
Dorpat, Archiv	Archiv fur die Naturkunde Liv , Esth , und Kurlands
Dorpat, Biol. Naturk.	Biologische Naturkind
Dorpat, Naturf Ges.	See Arch Nat (Dorpat)
Dorpat, Naturwiss. Abh	Naturwissenschaftliche Abhandlungen aus Dorpat
Dorpat Pharm Inst Arb	Arbeiten des Pharmakologischen Institutes zu Dorpat
Dorpat Sitzber	Sitzungsberichte der Naturforscher-Gesellschaft bei der Universitat (Jurjew) Dorpat
Dorpat Schr	Schriften herausgegeben von der Naturforscher Gesellschaft bei der Universitat (Jurjew) Dorpat
Dorset Field Club Proc	Proceedings of the Dorset Natural History and Antiquarian Field Club

Douai Mem. Soc. Agric.	Memoires de la Société d'Agriculture, de Sciences, et d'Arts, seant a Douai
Doubs Soc. Emul. Mem.	Memoires de la Société d'Emulation du Departement du Doubs
Dove Rep. Physik.	Repertorium der Physik. Enthalterid eine vollständige Zusammenstellung der neuern Fortschritte dieser Wissenschaft
Dresden Ausz. Protokol.	Auszüge aus den Protokollen der Gesellschaft fur Natur- und Heilkunde in Dresden
Dresden Denkschr. Naturwiss. Ges. Isis.	Denkschriften der Naturwissenschaftlichen Gesellschaft Isis zu Dresden
Dresden Entom. Ver. "Iris" Corresp.-Bl.	See Iris
Dresden Isis Festschr.	Festschrift der Naturwissenschaftlichen Gesellschaft Isis in Dresden
Dresden Isis Sitzber.	Sitzungsberichte und Abhandlungen der Naturwissenschaftlichen Gesellschaft Isis in Dresden
Dresden, Jahr. Natur. Heilk.	Jahresberichte fur 1858–60 v. d. Gesellschaft für Natur- und Heilkunde in Dresden
Dresden, Mitth. Poly. Schule	Mittheilungen der K. Sachs. Polytechnischen Schule
Dresden, Schr. Ges. Mineral.	Auswahl aus den Schriften der unter Werner's Mitwirkung gestifteten Gesellschaft fur Mineralogie
Dresden, Sitzber. Natur. Heilk.	Sitzungsberichte der Gesellschaft fur Natur- und Heilkunde
D. R. P.	German Patent (Deutsches Reichs-Patent)
Drug. Circ.	Druggist's Circular
Drug Topics	Drug Topics, New York
Dublin, Geol. Soc. J.	Journal of the Geological Society of Dublin
Dublin, Hosp. Gaz.	Dublin Hospital Gazette
Dublin J. Med. Chem. Sci.	Dublin Journal of Medical and Chemical Science
Dublin J. Med. Sci.	The Dublin Journal of Medical Science
Dublin Med. Trans.	Dublin Medical Transactions
Dublin Micro. Club	See Irish Natur.
Dublin, Natur. Hist. Soc. Proc.	Proceedings of the Natural History Society of Dublin
Dublin Natur. Field Club	See Irish Natur.
Dublin, Pathol. Soc. Proc.	Proceedings of the Pathological Society of Dublin
Dublin Quart. J.	The Dublin Quarterly Journal of Science
Dublin Quart. J. Med.	Dublin Quarterly Journal of Medical Science
Dublin, Roy. Soc. J.	Journal of the Royal Dublin Society
Dublin Soc. J., Dublin Soc. Trans.	Transactions and Journal of the Dublin Society
Dublin Soc. Sci. Proc.	The Scientific Proceedings of the Royal Dublin Society
Dublin Soc. Sci. Trans.	The Scientific Transactions of the Royal Dublin Society
Dublin, Zool. Bot. Assoc. Proc.	Proceedings of the Dublin University Zoological and Botanical Association
Dudley, Geol. Soc. Proc.	Transactions of the Dudley and Midland Geological and Scientific Society
Dumfr. Gallow. Soc. Trans.	The Transactions and Journal of Proceedings of the Dumfriesshire and Galloway Natural History and Antiquarian Society
Dunkerque, Mem. Soc. Encour.	Memoires de la Société Dunkerquoise pour l'Encouragement des Sciences, des Lettres, et des Arts
Durham Univ. Phil. Soc. Proc.	Proceedings of the University of Durham Philosophical Society

Dyer, Calico Ptr	Dyer, Calico Printer, Bleacher, Finisher, and Textile Review
Dzondi, Aeskulap	Aeskulap
Eastbourne Natur. Hist Soc. Papers (& Trans)	Papers (Transactions) of the Eastbourne Natural History Society
Eastbourne Natur. Hist. Soc. Proc	The Sixth Annual Report of the Eastbourne Natural History Society
Eastbourne Natur Hist. Soc. Trans.	Transactions of the Eastbourne Natural History Society
Echange	l'Echange Organe (Mensuel) des Naturalistes de la Region Lyonnaise . .
Eckhard, Beitr.	Beitrage zur Anatomie und Physiologie
Eclairage Elect	l'Eclairage Electrique Revue (hebdomadaire) d(el)'Electricite
Eclect. Med. J , Cincin	Eclectic Medical Journal, Cincinnati
Econ. Geol	Economic Geology
Ecu. P	Ecuador Patent
Edinb. Bot. Soc. Proc.	Proceedings of the Botanical Society of Edinburgh for the years 1855–56
Edinb Bot. Soc. Trans	Transactions of the Botanical Society of Edinburgh
Edinb. Field Club Trans.	Transactions of the Edinburgh Naturalists' Field Club
Edinb , Fish Bd Rep.	Annual Report of the Fishery Board for Scotland
Edinb. J. Med Sci	Edinburgh Journal of Medical Science
Edinb. J. Natur Geogr Sci.	The Edinburgh Journal of Natural and Geographical Science
Edinb J Sci	The Edinburgh Journal of Science
Edinb Med. Chir Soc Trans.	Transactions of the Medico-Chirurgical Society of Edinburgh
Edin Med J	Edinburgh Medical Journal
Edinb. Mem Wern Soc	Memoirs of the Wernerian Natural History Society
Edinb. Monthly J Med. Sci.	Edinburgh Monthly Journal of Medical Science
Edinb Natur. Soc Trans.	Transactions of the Edinburgh Field Naturalists' and Microscopical Society, instituted as the Edinburgh Naturalists' Field Club
Edinb. N Phil J	The Edinburgh New Philosophical Journal
Edinb. Phil. J.	The Edinburgh Philosophical Journal
Edinb. Plin. Soc Trans	Transactions of the Plinian Society
Edinb. Proc. Phys Soc.	Proceedings of the Royal Physical Society of Edinburgh
Edinb. Roy Coll Physns Lab. Rep.	Reports from the Laboratory of the Royal College of Physicians, Edinburgh
Edinb. Roy. Soc Proc	Proceedings of the Royal Society of Edinburgh
Edinb. Roy. Soc Trans	Transactions of the Royal Society of Edinburgh
Edinb. Trans. Scot. Soc Arts	Transactions of the Royal Scottish Society of Arts
Eisen Ztg	Eisen Zeitung
Ekaterinburg	See Iekaterinenb.
Elberfeld Naturwiss, Ver Jahr.	Jahres-Bericht des Naturwissenschaftlichen Vereins in Elberfeld
Elec. Rev.	The Electrical Review
Elec. Soc. Trans.	The Transactions and Proceedings of the London Electrical Society
Elec. Telegr. Rev	The Electric Telegraph Review
Elec. World	Electrical World
Electrician	The Electrician
Electricite	PElectricite
Electrochem. Met. Ind.	Electrochemical and Metallurgical Industry

Elektrochem Zts	Elektrochemische Zeitschrift
Elektrotech Zts	Electrotechnische Zeitschrift
Elliott Soc J.	Journal of the Elliott Society of Natural History
Elliott Soc Proc	Proceedings of the Elliott Society of Natural History
Elsner, Mitth	See Chem. Tech Mitth.
Emden Naturf. Ges Jahr.	.. Jahresbericht der Naturforschenden Gesellschaft in Emden
Emden Naturf Ges Schr.	Kleine Schriften der Naturforschenden Gesellschaft in Emden
Eng.	Engineering
Eng Contr.	Engineering and Contracting
Eng. Digest	Engineering Digest
Eng Mag	Engineering Magazine, The
Eng Mining J (Eng Min. J.)	Engineering and Mining Journal, The
Eng. News	Engineering News
Eng Record	Enginering Record, Building Record and Sanitary Engineer
Engineer	Engineer, The
Engineers' J.	The Engineers' Journal and Railway Gazette of India and the Colonies
Engineers Soc Trans	Society of Engineers. Transactions
Engl Mech.	English Mechanic
Engler, Bot Jahr.	Botanische Jahrbucher fur Systematik, Pflanzengeschichte und Pflanzengeographie
Engrais, L'	Engrais, L'
Entom. Annual	The Entomologist's Annual
Entom. Mag.	The Entomological Magazine
Entom. Medd (Kjobenh.)	Entomologiske Meddelelser udgivne af Entomologisk Forening
Entom Month Mag.	The Entomologist's Monthly Magazine
Entom. Nachr.	Entomologische Nachrichten
Entom Record	The Entomologist's Record and Journal of Variation
Entom Soc. Trans	The Transactions of the Entomological Society of London
Entom. Tidskr.	Entomologisk Tidskrift pa Foranstaltande af Entomologiska Foreningen i Stockholm
Entomologica Amer	Entomologica Americana
Entomologist	The Entomologist
E P.	English (British) Patent
Epicure	Epicure, The
Epidem. Soc. Trans.	Transactions of the Epidemiological Society of London
Epinal (Vosges) Ann.	Annales de la Société d'Emulation du departement des Vosges
Erdel. Muz -Egyl. Ertek.	Az Erdelyi Muzeum-Egylet Kiadvanyai Ertekezesek. (Publications of the Transylvanian Museum Association. Memoirs)
Erdmann, Sveriges Geol. Undersok.	Sveriges geologiska Undersokning, pa offentlig bekostnad, utford under Ledning af A. Erdmann
Erfurt, Abh. Akad. Wiss.	Abhandlungen der Kurfurstlich Mainzer Akademie nutzlicher Wissenschaften zu Erfurt
Erfurt, Akad. Jahr.	Jahrbucher der koniglichen Akademie gemeinnutziger Wissenschaften zu Erfurt
Erfurt, Denkschr.	Denkschrift der Akademie gemeinnütziger Wissenschaften in Erfurt
Erfurt, Nova Acta	Nova Acta Academiae Electoralis Moguntinae Scientiarum utilium quae Erfurti est.

Ergeb. Physiol.	Ergebnisse der Physiologie, Wiesbaden
Erlangen, Abh.	Abhandlungen der Physikalisch-medicinischen Societät in Erlangen
Erlangen Anat. Inst.	See Bietr. Morphol.
Erlangen, Mitth. Phys. Med. Soc.	Wissenschaftliche Mittheilungen der Physikalisch-medicinischen Societät zu Erlangen
Erlangen Phys. Med. Soc. Sitzber.	Sitzungsberichte der Physikalisch-Medizinischen Societät zu (in) Erlangen
Erythea	Erythea. A Journal of Botany, West American and General
Essex Field Club Proc.	Journal of Proceedings of the Essex Field Club
Essex Field Club Spec. Mem.	Essex Field Club Special Memoirs
Essex Field Club Trans.	Transactions of the Essex Field Club
Essex Inst. Bull.	Bulletin of the Essex Institute
Essex Inst. Commun.	Communications read before the Essex Institute
Essex Inst. Proc.	Proceedings of the Essex Institute
Essex Natur. Hist. Soc. J.	Journal of the Essex County Natural History Society
Essex Natlist.	The Essex Naturalist
Essig. Ind.	Deutsche Essigindustrie
Etudes Gites Mineraux	See France Gites Min. Etudes
Eure, Bull. Acad. Ebroic.	Bulletin de l'Academie Ebroicienne
Eure, J. Agric.	Journal d'Agriculture, de Medicine et des Sciences accessoires
Eure, Recueil Trav.	Recueil des Travaux de la Société Libre d'Agriculture, des Sciences, des Arts et des Belles-Lettres du departmente de l'Eure
Eure, Soc. Agric. Bull.	Bulletin de la Société d'Agriculture, des Sciences, et des Arts du departement de l'Eure
Eure, Soc. Agric. Recueil	Recueil de la Société d'Agriculture, Sciences, Arts, et Belles-Lettres du departement de l'Eurs
Evkönyv	A' Magyar Tudos Tarsasag' Evkönyvei
Exner. Rep.	Repertorium der Physik.
Exper. Sta. Rec.	Experiment Station Record
Eyr	Eyr, et Medicinisk Tidsskrift
Fachgenosse	Fachgenosse, Der
Falaise, Mem. Soc. Acad.	Memoires de la Société Academique des Sciences, &c., de Falaise
Farben Ztg.	Farben Zeitung
Färb. Ztg.	Färber Zeitung (Lehne's)
Fechner Centr.	Centralblatt für Naturwissenschaften und Anthropologie
Fechner, Rep.	Repertorium der Experimental-Physik.
Fed. Inst. Min. Engin. Trans.	Transactions of the Federated Institution of Mining Engineers
Fer.	Ferrum, Halle
Ferussac, Bull. Sci. Math.	Bulletin des Sciences Mathematiques, Astronomiques, Physiques, et Chimiques par le Baron de Ferussac
Ferussac, Bull. Sci. Natur.	Bulletin des Sciences Naturelles et de Geologie
Feuille Jeunes Natur.	Feuille des Jeunes Naturalistes
Field Mus. Natur. Hist.	Field Museum of Natural History, Chicago, Publication
Fij. P.	Fiji Islands Patent
Fin. P.	Finland Patent
Finistere Soc. Sci. Bull.	Bulletin de la Société d'Etudes Scientifiques du Finistere
Finlande Soc. Geogr.	See Fennia
Finska Läk. Sällsk. Handl.	Finska Läkare Sällskapets Handlingar
Finska Vet.-Soc.	See Helsingfors, Bidrag. Helsingfors, Öfvers

Firenze Accad. Georgofili Atti	Atti della Reale Accademia Economico-Agraria dei Georgofili di Firenze
Firenze, Ann. Mus Fis	Annali del R. Museo di Fisica e Storia Naturale
Firenze, Ann. Mus Imp.	Annali del Museo Imperiale di Fisica e Storia Naturale di Firenze
Firenze Congr Bot Atti	Atti del Congresso Internazionale Botanico tenuto in Firenze nel mese di Maggio 1874
Firenze, Mem. Soc Ital.	See Modena
Firenze, Opusc Sci	Collezione d'Opuscoli scientifici.
Firenze R. Inst. Pubbl	Pubblicazioni del R Istituto di Studi Superiori Pratici e di Perfezionamento in Firenze
Firenze Soc. Georgofili Atti	Atti della (Real) Societa Economica di Firenze ossia de' Georgofili
Firenze Soc. Studi Geogr. Boll.	See Riv Geogr Ital
Flora	Flora oder Allgemeine Botanische Zeitung
Flore Jardins	Annales d'Horticulture et de Botanique, ou Flore des Jardins du Royaume des Pays-Bas
Flore Serres	Flore des Serres et des Jardins de l'Europe
Florence	See Firenze
Flörke, Repert	Repertorium des neuesten und wissenwurdigsten aus der gesammten Naturkunde
Foldt. Közlon	Foldtani Kozlony, Havi folyoirat kiadja a Magyarhoni Foldtani Tarsulat
Folia Clin.	Folia clinica chimico et miscroscopica
Folia haematol.	Folia haematologica
Folia Therap. Lond	Folia Therapeutica, London
Forbes, Med. Rev	The British and Foreign Medical Review, or Quarterly Journal of Practical Medicine and Surgery
Forsch. Agr.-Phys	Forschungen auf dem Gebiete der Agrikultur-Physik
Förster, Allg. Bauztg	Allgemeine Bauzeitung
Fortschr. Chem.	Fortschritte der Chemie, Physik und Physikalischen chemie
Fortschr. Med.	Fortschritte der Medicin.
Fortschr. Phys.	Die Fortschritte der Physik.
Fortschr. Rontgenstr.	Fortschritte auf dem Gebiete der Rontgenstrahlen
Fortschr. Theerfarben-Fabrikation	Fortschritte der Theerfarbenfabrikation und ver wendter Industriezweige
Foundry	Foundry, The
F. P.	French Patent
France, Congr. Med. Chir.	Congres Medico-Chirurgicale de France
France, Congr. Sci.	Sessions des Congres Scientifiques de France
France Gites Miner. Etudes	Etudes des Gites Mineraux de la France
France, Inst. Provinces Annuaire	Annuaire de l'Institut des Provinces et des Congres Scientifiques de France
France, Inst. Provinces Mem.	Memoires de l'Institut des Provinces de France. Sciences physiques et naturelles
France Soc. Agric. Bull.	Bulletin des Seances de la Société Nationale d'Agriculture de France
France Soc. Agric. Mem.	Memoires publies par la Société Nationale d'Agriculture de France
France Soc. Bot. Bull.	Bulletin de la Société Botanique de France
France Soc. Entom.	See Abeille., Paris, Soc. Ent. Ann., Paris, Soc. Ent. Bull., Rev. Ent.
Franc Soc. Miner. Bull.	Bulletin de la Société Mineralogique de France. Bulletin de la Société Francaise de Mineralogie. (Ancienne Société Mineralogique de France)
France Soc. Zool.	See Paris, Caus. Sci.
France Soc. Zool. Bull.	Bulletin de la Société Zoologique de France

France Soc. Zool. Mem.	Memoires de la Société Zoologique de France
Frankfurt	See Senckenberg
Frankfurt, Jahr. Phys. Ver.	Jahrbuch zur Verbreitung naturwissenschaftlicher Kenntnisse, veranstaltet vom Physikalischen Verein zu Frankfurt a/Main
Frankf. Ver. Pflege Phot.	See Wien, Photogr. Correspond.
Frankfurt, Zool. Garten	Der Zoologische Garten Frankfurt a/M.
Frankfurter Zts. Pathol.	Frankfurter Zeitschrift für Pathologie
Franzós. Ann.	Franzosische Annalen für die allgemeine Naturgeschichte, Physik, &c.
Freiberg, Jahr. Berg Hütt.	Jahrbuch fur den Berg- und Hüttenmann. Herausg. von der Konigl. Berg-Akademie zu Freiberg
Freiburg, Beitr	Beiträge zur Rheinischen Naturgeschichte
Freiburg, Ber	Berichte uber die Verhandlungen der Naturforschenden Gesellschaft zu Freiburg i. B.
Freie K.	Freie Kunste
Frelon	Le Frelon. Journal d'Entomologie descriptive
Fries, Bot. Notiser	Botaniska Notiser
Froriep, Notizen	Notizen aus dem Gebiete der Natur- und Heilkunde
Fühling's Ztg.	Fuhlings landwirtschaftliche Zeitung
Gac. ind.	La Gaceta industrial
Gand, Ann Soc Agric.	Annales de la Société Royale d'Agriculture et de Botanique
Gand, Ann. Soc. Med.	Annales de la Société de Medecine de Gand
Gand, Bull. Soc. Med.	Bulletin de la Société de Medecine de Gand
Gard, Apercu Trav.	Notice ou Apercu analytique des Travaux de l'Academie Royale du Gard
Gard, Mem. Acad.	Memoires de l'Academie du Gard
Gard, Notice Trav. Acad.	Notice des Travaus del'Academie du Gard
Garden & Forest	Garden and Forest. A Journal of Horticulture, Landscape Art and Forestry
Gardeners Chron.	The Gardeners Chronicle
Garnett, Ann. Phil.	Annals of Philosophy, Natural History, Chemistry &c.
Garten-Flora	Garten-Flora
Garten-Ztg.	Neue allgemeine Deutsche Garten- und Blumenzeitung
Gartenwelt	Gartenwelt, The
Gas World	Gas World, The
Gaz	Le Gaz
Gazz. del. Clin.	Gazzetta della Cliniche
Gazz. med. ital lomb.	Gazzetta medica italiana lombardia, Milano
Gazz. Chim. Ital.	Gazzetta Chimica Italiana
Geelong Field Natur. Club	See Wombat
Gehlen J.	Journal fur dei Chemie und Physik
Gendrin, Trans. Med.	Transactions Medicales
Geneeskundig Mag.	Geneeskundig Magazijn
Geneve, Archiv.	See Archives Sci. Phys. Nat.
Geneve, Bull. Soc. Ornith Suisse.	Bulletin de la Societe Ornithologique Suisse
Geneve Conserv. Bot. Annuaire	Annuaire du Conservatoire du Jardin Botanique de Geneve
Geneve, Inst. Natl. Bull.	Bulletin de l'Institut National Genevois
Geneve. Inst. Natl. Mem.	Memoires de l'Institut National Genevois
Geneve, Mus. Hist. Natur. Ann.	See Rev. Suisse Zool.
Geneve, Recueil Trav. Soc. Med.	Recueil des Travaux de la Société Medicale de Geneve
Geneve, Soc. Geogr. Mem.	Memoires de la Société de Geographie de Geneve

Geneve, Soc Phys. Mem.	Memoires de la Société de Physique et d'Histoire Naturelle de Geneve
Genie civ.	Genie Civil
Genova	See Congr. Bot. Int. Atti 1892
Genova, Ann Mus. Phys.	Annali del Museo Civico di Storia Naturale
Genova, Giorn.	Giornale degli Studiosi di Lettere, Science, arti e Mestieri
Genova, Mem. Accad.	Memoire dell'Accademia Imperiale delle Scienze di Genova
Genova, Mem. Ist. Ligure.	Memorie dell' Istituto Ligure
Genova, Mem. Soc. Med. Emul.	Memorie della Societa Medica di Emulazione di Genova
Genova Mus. Civ. Ann.	Annali del Museo Civico di Storia Naturale di Genova
Genova Mus. Zool. Anat. Comp Boll.	Bollettino dei Musei di Zoologia e Anatomia Comparata della R. Universita di Genova
Genova, Soc. Ligust Atti	Atti della Societa Ligustica di Scienze Naturali e Geografiche
Genova Univ. Atti	Atti della R. Universita di Genova
Geogr. Soc. J.	Journal of the Royal Geographical Society of London
Geogr. Soc. Proc.	Proceedings of the Royal Geographical Society and Monthly Record of Geography
Geogr. Soc. Suppl. Pap.	Royal Geograhical Society. Supplementary Papers
Geol. Mag.	Geological Magazine
Geol. Survey, Can	Geological Survey, Canada
Gera, Naturwiss. Jahr.	Jahresbericht der Gesellschaft von Freunden der Naturwissenschaften in Gera, nebst Nachrichten uber den Naturwissenschaftlichen Verein in Schleiz
Gerber	Der Gerber
Germar, Mag Entom	Magazin der Entomologie
Germar, Zts Entom	Zeitschrift fur die Entomologie
Gergonne, Ann. Math.	Annales de Mathematique
Gesundh. Ing.	Gesundheits-Ingenieur
Gew. Ztg.	Wieck's Gewerbezeitung
Gewerbebl Schw.	Schweizerisches Gewerbeblatt
Gewerbebl Wurt	Gewerbeblatt aus Wurttemberg
Gewerbeh.	Gewerbehalle
Gewerks Ztg.	Oesterreichische Gewerkszeitung
Giessen, Oberhess. Ges. Ber.	Berichte der Oberhessischen Gesellchaft für Natur- und Heilkunde
Gievel, Zts.	See Zts. Gesammt. Naturwiss.
Gilbert, Ann. Phys	See Ann Phys.
Gill. Tech. Micro. Repos.	Technical and Microscopical Repository
Giorn. Arcad.	Giornale Arcadico di Scienze
Giorn. farm. chim.	Giornale de farmacia, di chimica
Giorn. Gen. civ.	Giornale del Genio civile
Giron. Ist. Lomb.	See Bibl. Ital.
Giorn. Mineral. Crist. Petr.	Giornale di Mineralogia, Cristallografia e Petrografia
Gironde Comm. Meteorol.	See Bordeaux Soc. Sci. Mem.
Gironde, J. Med.	Journal Medical de la Gironde
Gistl, Faunus	Faunus
Glasgow. Inst. Engin. Trans.	Transactions of the Institution of Engineers and Shipbuilders in Scotland
Glasgow Med. Chir. Soc. Trans.	Transactions of the Medico-Chirurgical Society of Glasgow
Glasgow Med. J.	Glasgow Medical Journal
Glasgow Natur. Hist. Soc. Proc. & Trans.	Proceedings and Transactions of the Natural History Society of Glasgow
Glasgow Path. Clin. Soc. Trans.	Transactions of the Glasgow Pathological and Clinical Society

Glasgow Phil. Soc. Proc.	Proceedings of the Philosophical Society of Glasgow
Glashütte	Glashutte, Die
Glas-Ind.	Glas-Industrie, Die
Gleanings Sci.	Gleanings in Science
Globe	See Geneve Soc. Geogr. Mem.
Glückauf	Gluckauf; Berg- und Huttenmannische-Zeitschrift
Good Roads	Good Roads
Goodsir, Ann. Anat. Physiol.	Annals of Anatomy and Physiology
Gordon Coll. Phot. Assoc.	See Wombat.
Görlitz, Abh.	Abhandlungen der Naturforschenden Gesellschaft zu Görlitz
Götheborg, Handl.	Gotheborgs Kongl. Vetenskaps och Vitterhets Samhälles Handlingar
Götheborg, Nya Handl.	Nya Handlingar af Kongl. Vettenskaps och Vitterhets Samhallet i Gotheborg
Göttingen, Abh.	Abhandlungen der Koniglichen Gesellschaft der Wissenschaften zu Gottingen
Göttingen, Comment.	Commentationes recentiores Societatis, etc.
Göttingen, Nachr.	Nachrichten von der Georg-Augusts Universitat und der Konigl. Gesellschaft der Wissenchaften zu Gottingen
Göttinger Studien	Gottinger Studien
Göttingen, Studien Ver.	Studien des Göttingischen Vereins Bergmännischer Freunde
Gräfe, J. Chir. Augenheilk.	Journal der Chirurgie und Augen-Heilkunde
Graph. Mitth.	Schweizer graphische Mitteilungen
Graubünden Naturf. Ges. Jahr.	Jahresbericht der Naturforschenden Gesellschaft Graubundens
Gravenhage, Athenaeum	Athenaeum
Gravenhage, Inst. Ingen. Tijdschr.	Tijdschrift van het Koninklijk Instituut van Ingenieurs
Gravenhage, Inst. Ingen. Uittrek.	Uittreksels uit Vreemde Tijdschriften voor de Leden van het Koninklijk Instituut van Ingenieurs
Gravenhage, Inst. Ingen. Verh.	Verhandelingen van het Koninklijk Instituut van Ingenieurs
Gravenhage, Inst. Ingen. Verslag.	K. Instituut van Ingenieurs. Algemeen Verslag van de Werkzaamheden en Notulen der Vergaderingen
Gravenhage, Tijdschr.	Tijdschrift voor Entomologie, door de Nederlandsche Entomologische Vereeniging
Graves, Natur. J.	The Naturalists' Journal and Miscellany
Graz Bot. Inst. Mitth.	Mittheilungen aus dem Botanischen Institute zu Graz
Graz, Unters. Physiol. Histol.	Untersuchungen aus dem Institute fur Physiologie und Histologie
Great. Brit. Phil. Soc.	See Victoria Inst. J.
Greifswald Naturwiss. Ver. Mitth.	See Neu-Vorpommern Mitth.
Grenoble, Acad. Delph. Bull.	Bulletin de l'Academie Delphinale, ou Société des Sciences et Arts de Grenoble
Grevillea	Grevillea, a Quarterly Record of Cryptogamic Botany and its Literature
Groningen, Ann. Acad.	Annales Academiae Groninganae
Gruithuisen, Neue Analekt.	Neue Analekten fur Erd- und Himmels-kunde
Grunert Archiv.	Archiv fur Mathematik und Physik
Grunert, Meteor. Optik	Beiträge zur meteorologischen Optik, etc.
Guat. P.	Guatemala Patent

Guia Minero	Guia del Minero: Periodico cientifico, industrial y mercantil
Guillemin, Archiv. Bot.	Archives de Botanique, ou Recueil Mensuel de Memoires originaux, etc.
Gummi-Ztg.	Gummi-Zeitung
Günsburg, Zts. Klin. Med.	Zeitschrift fur klinische Medizin, mit dem Verein für physiologische Heilkunde in Breslau
Gurlt, Mag. Ges. Thierheilk.	Magazin für die gesammte Thier-Heilkunde
Guy's Hosp. Rep.	Guy's Hospital Reports
Haarlem Kolon. Mus. Bull.	Bulletin van het Koloniaal Museum te Haarlem
Haarlem, Mus. Teyler Archiv.	Archives du Musee Teyler
Haarlem, Natuurk. Verh. Maatsch. Wet.	Natuurkundige Verhandelingen van de (Bátaafsch) Hollandsche Maatschappij der Wetenschappente Haarlem
Haaxman, Tijdschr.	Tijdschrift voor Wettenschappelijke Pharmacie, etc.
Habana Acad. Anales.	Anales de la (Real) Academie de Ciencias Medicaes Fisicas y Naturales de la Habana
Haeser, Archiv. Med.	Archiv fur die gesammte Medicin
Hage	See Gravenhage
Hahnemann. Month.	Hahnemannian Monthly, Philadelphia
Haidinger, Abh.	Naturwissenschaftliche Abhandlungen
Haidinger, Ber.	Berichte uber die Mittheilungen von Freunden der Naturwissenschaften in Wien
Hainaut Soc. Mem.	Memoires et Publications de la Société des Sciences, des Arts et des Lettres du Hainaut
Hall, Bijdragen	Bijdragen tot de Natuurkundige Wetenschappen
Halle, Abr. Naturwiss. Ver.	Abhandlungen des Naturwissenschaftlichen Vereins fur Sachsen und Thüringen in Halle
Halle aux cuirs, La	Halle aux cuirs, La
Halle, Jahr. Naturwiss. Ver.	Jahresbericht des Naturwissenshaftlichen Vereins in Halle
Halle Kryptog. Lab.	See Beitr. Physiol. Morphol.
Halle, Naturf. Ges. Abh.	Abhandlungen der Naturforschenden Gesellschaft zu Halle
Halle, Naturf. Ges. Ber.	Bericht der Naturforschenden Gesellschaft zu Halle
Halle, Naturf. Ges. Neu. Schr.	Neue Schriften der Naturforschenden Gesellschaft zu Halle
Halle, Zts. Ges. Naturwiss.	Zeitschrift für die gesammten Naturwissenschaften
Hamburg, Abh. Geb. Naturwiss.	Abhandlungen aus dem Gebiete der Naturwissenschaften
Hamburg Bot. Ges.	See Bot. Centrbl.
Hamburg, Mitth.	Mittheilungen aus den Verhandlungen der Naturwissenschaftlichen Gesellschaft in Hamburg
Hamb. Mus. Ber.	Naturhistorisches Museum zu Hamburg. Berichte
Hamb. Mus. Jahr.	Jahresbericht uber das Naturhistorische Museum zu Hamburg
Hamb. Mus. Mitth.	Mittheilung aus dem Naturhistorischen Museum in Hamburg
Hamb. Naturwiss. Ver. Abh.	Abhandlungen aus dem Gebiete der Naturwissenschaften herausgegeben vom Naturwissenschaftlichen Verein in Hamburg
Hamb. Ver. Naturwiss. Unterh. Verh.	Verhandlungen des Vereins für Naturwissenschaftliche Unterhaltung zu Hamburg
Hamb. Wiss. Anst. Jahr.	Jahrbuch der Hamburgischen Wissenschaftlichen Anstalten

Hampshire Field Club Pap. & Proc.	Papers and Proceedings of the Hampshire Field Club
Hannover Architekt.-Ver. Zts.	Zeitschrift des Architekten- und Ingenieur-Vereins zu Hannover. Zeitschrift für Architektur und Ingenieurwesen
Hannover Jahr.	...Jahresbericht der Naturhistorischen Gesellschaft zu Hannover
Hannöverische Ann.	Hannöverische Annalen für die gesammte Heilkunde
Harlem Soc. Holland. Sci.	See Arch. Neerland
Hartford, Trans.	Transactions of the Natural History Society of Hartford
Harvard Mus. Zool. Mem.	Memoirs of the Museum of Comparative Zoology at Harvard College
Harvard Mus. Zool. Bull.	Bulletin of the Museum of Comparative Zoology at Harvard College, in Cambridge
Harz, Naturwiss. Ver. Ber.	Berichte des Naturwissenschaftlichen Vereins des Harzes zu Blankenburg
Havre, Cercle Bot.	Cercle pratique d'Horticulture et de Botanique de l'arrondissement du Havre: Bulletins
Haw. P.	Hawaiian Patent
Haye	See Congr. Int. Hyg. C. R., 1884
Heart	Heart
Hedwigia	Hedwigia. Ein Notizblatt für Kryptogamische Studien nebst Repertorium für Kryptogamische Literatur. Hedwigia. Organ für (specielle) Kryptogamenkunde (und Phytopathologie) nebst Repertorium fur (Kryptogamische) Literatur.
Heidelb. Jahr. Lit.	Jahrbücher der Literatur. Verhandlungen des Naturhistorisch-Medicinischen Vereins zu Heidelberg
Heidelb. Naturhist. Med. Festschr.	Festchrift zur Feier des funfhundertjahrigen Bestehens der Ruperto-Carola dargebracht von dem Naturhistorisch-Medicinischen Verein zu Heidelberg
Heidelb. Naturhist. Med. Verh.	Verhandlungen des Naturhistorisch-Medicinischen Vereins au Heidelberg
Heidelb., Verh.	Verhandlungen der in Heidelberg versammelten Augenärzte
Heis, Wochenschr.	Wochenschrift für Astronomie, Meteorologie, und Geographie
Heller, Archiv.	Archiv fur physiologische und pathologische Chemie und Mikroskopie
Helsingfors, Acta Soc. Sci. Fenn.	Acta Societatis Scientiarum Fennicae
Helsingfors, Bidrag Finlands Natur o. Folk.	Bidrag till kannedom om Finlands Natur och Folk, utgifna af Finska Vetenskaps-Societeten
Helsingfors, Bidrag Finlands Naturkänn.	Bidrag till Finlands Naturkännedom, Etnografi och Statistik, utgifna af Finska Vetenskaps-Societeten
Helsingfors, Faun. Flor. Fenn. Acta.	Acta Societatis pro Fauna et Flora Fennica
Helsingfors, Fauna Flora Fenn. Medd.	Meddelanden af Societas pro Fauna et Flora Fennica
Helsingfors, Faun. Flor. Fenn. Notiser	Notiser ur Sällskapets pro Fauna et Flora Feennica Forhandlingar
Helsingfors, Öfvers, Finaka Vet. Soc.	Öfversigt af Finska Vetenskaps-Societatens Förhandlingar
Helv. Chim. Acta	Helvetica Chimica Acta
Henle und Pfeufer, Zts.	See Zeitschrift für rationelle Medicin
Hermannstader Verh.	Verhandlungen und Mittheilungen des Siebenbürgischen Vereins fur Naturwissenschaften in Hermannstadt

Hermbstätt, Archiv.	Archiv der Agriculturchemie für denkende Landwirthe
Hermstadt, Bull.	Bulletin des Neuesten und Wissenwürdigsten aus der Naturwissenschaft, etc.
Hermbstadt, Museum	Museum des Neuesten und Wissenwürdigsten aus dem Gebiete der Naturwissenschaft, der Künste, der Fabriken, der Manufakturen, der technischen Gewerbe, der Landwirthschaft, der Produktenwaaren und Handelskunde, und der burgerlichen Haushaltung, &c.
Hertha	Hertha
Herts. Natur. Hist. Soc. Trans.	Transactions of the Hertfordshire Natural History Society and Field Club
Hessen, Naturhist. Verg.	Verhandlungen des Naturhistorischen Vereins für das Gross herzogthum Hessen und Umgebung
Heusinger, Zts.	Zeitschrift für die organische Physik
Hide and Leather	Hide and Leather
High Wycombe Natur. Hist. Mag.	The Quarterly Magazine of the High Wycombe Natural History Society
Highland Soc. Trans.	Transactions of the Highland and Agricultural Society of Scotland with an abstract of the Proceedings
Hildesheim Roemer-Mus. Mitth.	Mittheilungen aus dem Roemer-Museum Hildesheim
Himly, Bibl. Ophthalm.	Bibliothek für Ophthalmologie
Hippone	See Bone
Hisinger, Afh.	Afhandlingar i Fysik, Kemi, och Mineralogie
Hobart Town	See Tasmania
Hoeven en Vriese, Tijdschr.	Tijdschrift voor Natuurlijke Geschiedenis en Physiologie
Hoff, Mag.	Magazin fur die gesammte Mineralogie, Geognosie, etc.
Hoffman, Phytogr. Blatt.	Phytographische Blatter
Holl. P.	Holland Patent
Holländ, Beitr.	Hollandsiche Beiträge zu den anatomischen und physiologischen Wissenscaften
Holländ, Mag.	Hollandisches Magazin der Naturkunde
Holmesdale Natur. Hist. Club Proc.	Proceedings and Annual Reports of the Holmesdale Natural History Club, Reigate, for the years 1865–67
Homme	L'Homme: Journal illustre des Sciences Anthropologiques
Hooker, Bot. Miscell.	The Botanical Miscellany
Hooker, Comp. Bot. Mag.	Companion to the Botanical Magazine
Hooker, Lond. J. Bot.	London Journal of Botany
Hoppe, Bot. Taschenb.	Neues Botanisches Taschenbuch für die Anfänger dieser Wissenschaft und der Apothekerkunst
Horae Soc. Entom. Rossicae	Horae Societatis Entomologicae Rossicae variis sermonibus Rossicae usitatis
Horkel, Archiv.	Archiv. für die thierische Chemie
Horn, Archiv. Med.	Archiv. fur praktische Medizin und Klinik
Horn's Phot. J.	Horn's photographisches Journal
Hornschuch, Archiv.	Archiv Skandinavischer Beiträge zur Naturgeschichte
Horolog. J.	The Horological Journal
Hortic. Soc. J.	Journal of the Royal Horticultural Society of London
Hortic. Soc. Trans.	Transactions of the Horticultural Society of London
Hufeland, J. Arzn.	Journal der practischen Arzneikunde
Humboldt.	Humboldt. Monatsschrift für die Gesamten Naturwissenschaften
Humming Bird	The Humming Bird. .... scientific, artistic and industrial Review

Hongkong P.	Hongkong Patent
Hung. P.	Hungarian Patent
Hutm. Ztg.	Deutsche Hutmacher-Zeitung
Hyg. Congr.	See Congr. Int. Hig. Act.; Congr Int. Hyg. C. R.; Int. Congr. Hyg. Arb.; Int. Congr. Hyg. Trans.
Hyg. Rundschau.	Hygienische Rundschau. Berlin
Hyg. viande	Hygiene de la viande et du lait, L'
Iekaterinenb., Soc. Oural. Bull.	Bulletin de la Société Ouralienne d'Amateurs des Sciences Naturelles
Il Berico	Il Berico
Il Cimento	Il Cimento
Il. Giamb-Vico	Il Giambattista-Vico
Il Progresso	Il Progresso delle Scienze, Lettere, ed Arti.
Il Subalpino	Il Subalpino, Giornale di Scienze
Il Tempo	Il Tempo, Giornale Italiano di Medicina
Ill. Insects Rep.	...Report of the State Entomologist.. on the Noxious and Beneficial Insects of the State of Illinois
Ill. Lab. Natur. Hist. Bull.	Bulletin of the Illinois State Laboratory of Natural History
Ill. Mus. Natur. Hist. Bull.	Bulletin.. of the Illinois State Museum of Natural History
Illiger, Magazin	Magazin für Insektenkunde
Illumin. Engin. (London)	Illuminating Engineer (London), The
Illust. Hortic.	Illustration horticole; journal special des Serres et des Jardins
Illust. landw. Ztg.	Illustr· rte landwirtschaftliche Zeitung
Illust. Off. J.	Illustrated Official Journal, The (Patents)
Illust. Wochenschr. Entom.	Illustrierte Wochenschrift für Entomologie. Internationales Organ für alle Interessen der Insektenkunde. Offizielles Organ der Berliner Entomologischen Gesellschaft
Impr.	L'imprimerie
Ind. Chim.	Industria chimica
Ind. lait.	L'Industrie laitiere
Ind. Text.	L'industrie textile
Ind. Ztg.	Deutsche Industrie Zeitung
Index Med.	Index Medicus, Washington
India Agric. Soc. J.	Journal of the Agricultural and Horticultural Society of India
India, Agric. Soc. Proc.	Proceedings of the Agricultural and Horticultural Society of India
India Agric. Soc. Trans.	Transactions of the Agricultural and Horticultural Society of India
India Bot. Surv. Records	Records of the Botanical Survey of India
India Dept. Agric.	India Department of Agriculture, Publications
India, Govt. Records (For. Dept.)	Selections from the Records of the Government of India. (Foreign Department)
India, Govt. Records (Home Dept.)	Selections from the Records of the Government of India
India P.	Indian Patent
India Rev.	India Review and Journal of Foreign Science and the Arts
India Rub. J.	India Rubber Journal
India Rub. World	India Rubber World
Indian Ann.	Indian Annals of Medical Science
Indian J. Med. Phys. Sci	Indian Journal of Medical Science
Indian Med. Gaz.	The Indian Medical Gazette, a monthly record of Medicine, &c.

Indian Meteorol. Mem.	Indian Meteorological Memoirs: being occasional Discussions and Compilations of meteorological data relating to India and the neighboring countries
Indian Mus. Notes	Indian Museum Notes
Industrieztg. Ungarn	Industriezeitung für Ungarn
Ingenieur	Der Ingenieur
Inghirami, Opuscoli	Nuova Collezione di Opuscoli e Notizie di Scienze
Innsbruck, Jahr.	Jahresbericht der k. k. Ober-Realschule zu Innsbruck
Innsbruck Naturwiss. Med. Ber.	Berichte des Naturwissenschaftlich-medizinischen Vereines in Innsbruck
Innsbruck, Neue Zts.	Neue Zeitschrift des Ferdinandeums für Tirol
Innsbruck, Zts. Ferdinandeums	Zeitschrift des Ferdinandeums fur Tirol und Voralberg
Inst.	L'Institut
Inst. Act. J.	Journal of the Institute of Actuaries (and Assurance Magazine)
Inst. Brewing Trans.	Transactions of the Institute of Brewing
Inst. Civ. Eng. Proc.	Minutes of the Proceedings of the Institution of Civil Engineers
Inst. Egypt. Bull.	Bulletin de l'Institut Egyptien
Inst. Egypt. Mem.	Memoires (ou Travaux originaux) presentes (et lus) a l'Institut Egyptien
Inst. Elect. Engin. J.	Journal of the Institution of Electrical Engineers
Inst. Mechan. Engin. Proc.	Institution of Mechanical Engineers. Proceedings
Inst. Min. Eng. Trans.	Transactions of the Institution of Mining Engineers
Inst. Min. Met. Trans.	Transactions of the Institution of Mining and Metallurgy
Inst. Solvay Trav.	Institut Solvay. Travaux de Laboratoire
Intell. Observer	The Intellectual Observer
Intl. Beitr. Path. Therap.	Internationale Beiträge zur Pathologie und Therapie, die Ernährungsstorungen, Stoffwechsel und Verdauungkrankheiten
Intl. Congr. Appl. Chem.	International Congress of Applied Chemistry
Intl. Congr. Hyg. Trans.	Transactions of the International Congress of Hygiene and Demography
Intl. Congr Zool Proc.	Proceedings International Congress of Zoology
Intl. Entom Ver.	See Zürich, Soc. Ent.
Intl. Med. Congr. Trans.	Transactions of the International Medical Congress
Intl. Med. Congr. Verh.	Verhandlungen des Internationalen Medicinischen Congresses
Intl. J. Anat.	Monthly International Journal of Anatomy and Histology (Physiology).
Intl. Mschr. Anat.	See Intl. J. Anat.
Intl. Sugar J.	International Sugar Journal, The
Intl. Zentr. Baukeram. Glasind.	Internationales Zentralblatt für Baukeramik und Glasindustrie
Intl. Zts. Metallog.	Internationale Zeitschrift für Metallographie
Invent. Rec.	Inventor's Record, The
Iowa Acad. Sci. Proc.	Proceedings of the Iowa Academy of Sciences
Iowa Univ. Lab. Natur. Hist. Bull.	Bulletin from the Laboratories of Natural History of the State University of Iowa
Ireland, Coll. Physicians Trans.	Transactions of the Association of Fellows and Licentiates of the King's and Queen's College of Physicians in Ireland
Ireland, Inst. Civ. Eng. Trans.	The Transactions of the Institute of Civil Engineers of Ireland

Ireland Roy. Soc. Ant. Proc. & Pap.	See Dublin, Roy. Soc. Ant. Ir. Jl.
Ireland Zool. Soc.	See Irish Natlist
Iris	Correspondenz-Blatt des Entomologischen Vereins Iris zu Dresden. Iris, Dresden. Deutsche Entomologische Zeitschrift herausgegeben von der Gesellschaft Iris zu Dresden in Verbindung mit der Deutschen Entomologischen Gesellschaft zu Berlin.. Fortsetzung des "Correspondenz-Blattes des Entomologischen Vereins Iris."
Irish Acad. Cunningham Mem.	Royal Irish Academy. Cunningham Memoirs
Irish Acad. Proc.	Proceedings of the Royal Irish Academy
Irish Acad. Trans.	The Transactions of the Royal Irish Academy
Irish Natur.	The Irish Naturalist: a monthly Journal of general Irish Natural History
Iron	Iron
Iron Age	Iron Age
Iron Coal Trades Rev.	Iron Coal Trades Review
Iron Steel Inst. J.	The Journal of the Iron & Steel Institute
Iron Steel Inst. Trans.	Transactions of the Iron and Steel Institute
Isenflamm, Beitr. Zergelied.	Beitrage fur die Zergliederungskunst
Isere Soc. Bull.	Bulletin de la Société de Statistique, des Sciences naturelles et des Arts industriels du Departement de l'Isere
Isle of Man Natur. Hist. & Antiq. Soc.	See Yn Lioar Manninagh
Ital. P.	Italian Patent
Italia, Soc. Bot. Bull.	Bullettino della Societa Botanica Italiana
Italia Soc. Crittog. Atti	Atti della Societa Crittogamologica Italiana
Italia Soc. Crittog. Comment.	Commentario della Societa Crittogamologica Italiana
Italia Soc. Crittog. Mem.	Memorie della Societa Crittogamologica Italiana
Italia, Soc. Entom. Bull.	Bullettino della Societa Entomologica Italiana
Italia, Soc. Zool. Boll.	Bollettino della Societa Zoologica Italiana
Ithaca, Cornell Univ. Bull. Amer. Paleont.	Bulletins of American Paleontology
J.	Journal
J. A. C. S.	Journal of the American Chemical Society
J. Adv. Therap.	Journal of Advanced Therapeutics, New York
J Agric.	The (Quarterly) Journal of Agriculture
J. agric. Hort.	Journal de l'Agriculture, le Horticulture, etc.
J. Agric. Prat.	Journal d'Agriculture pratique, etc.
J. Agric. Sci.	Journal of Agricultural Science
J. agric. Soc.	Journal of the Agricultural Society
J. Agric. Tropicale	Journal d'Agriculture tropicale
J. allied Soc.	Journal of the Allied Societies (Dental)
J. Amer. Lea. Chem. Assoc.	Journal of the American Leather Chemists' Association
J. Amer. Med. Assoc.	Journal of the American Medical Association
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association
J. Amer. Soc. Mechan. Eng.	Journal of the American Society of Mechanical Engineers
J. Anal. Chem.	The Journal of Analytical (and Applied) Chemistry
J. Anat.	Journal de l'anatomie de la Physiologie normales et pathologiques de l'homme et des animaux
J. Anat. Physiol.	The Journal of Anatomy and Physiology
J. Appl. Chem.	Journal of Applied Chemistry

J. Appl. Micr.	Journal of Applied Microscopy
J. Assoc. Eng. Soc.	Journal of the Association of Engineering Societies
J. Biol. Chem.	Journal of Biological Chemistry
J. Bot.	Journal de Botanique
J. Buchdr.	Journal für Buchdruckerkunst
J. C. S.	Journal of the Chemical Society, London
J. Camera Club	Journal of the Camera Club
J. Can. Min. Inst.	Journal of the Canadian Mining Institutes
J. Chem. Met. Soc. South Af.	Journal of the Chemical, Metallurgical and Mining Society of South Africa
J. chim. med.	Journal de chimie medicale, de pharmacie et de toxicologie
J. chim. phys.	Journal de chimie, physique, electrochemie, thermochimie, radiochimie, mechanique, chimie, stoichiometrie
J. Chir.	Journal de Chirurgie
J. Chir. Augenheilk.	Journal der Chirurgie und Augenheilkunde
J. Coll. Agric. Imp. Univ. Tokyo	Journal of the College of Agriculture, Imperial University of Tokyo
J. Comp. Path. Therap.	The Journal of Comparative Pathology and Therapeutics
J Conch.	The Journal of Conchology
J. ecole poly.	Journal de l'Ecole polytechnique
J. Entom.	Journal of Entomology, descriptive and geographical
J. Exp. Med.	Journal of Experimental Medicine
J. Exp. Zool.	Journal of Experimental Zoology, The
J. fabr. sucre	Journal des fabricants de sucre
J. Frank. Inst.	Journal of the Franklin Institute
J Gasbeleucht	Journal fur Gasbeleuchtung
J. Gaslighting	Journal of Gas Lighting
J. Gen. Physiol.	Journal of General Physiology
J Genie Civ.	Journal du Genie Civil des Sciences et des Arts
J. Geol.	Journal of Geology
J. Goldschm.	Journal der Goldschmiedekunst und verwandter Gewerbe
J. Heb. Med.	Journal Hebdomadaire de Medecine
J. Heb. Sci. Med.	Journal Hebdomadaire des Progres des Sciences et Institutions Medicales
J. Home Econ.	Journal of Home Economics, The
J. Hygiene	Journal of Hygiene
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry
J. Indian Archipel.	Journal of the Indian Archipelago and Eastern Asia
J. Infect. Dis.	Journal of Infectious Diseases
J. Inst. Brewing	Journal of the Institute of Brewing
J. Inst. Metals	Journal of the Institute of Metals
J. Intl. Anat.	See Int. J. Anat.
J. Invent.	Journal des Inventeurs
J. Landw.	Journal fur Landwirtschaft
J. Med. Chir. Pharm.	Journal de Medecine, Chirurgie, Pharmacie
J. Med. Paris	Journal de medicine de Paris
J. Med. Research	Journal of Medical Research
J. Microgr.	Journal de micrographie
J. Micro. Sci.	Quarterly Journal of Microscopical Science
J. Mines	Journal des Mines, ou Recueil de Memoires sur l'exploitation des Mines, et sur les Sciences et les Arts qui s'y rapportent
J. mines met.	Journal des mines et de metallurgie
J. Morphol.	Journal of Morphology

J. Mus. Godeffroy	Journal des Museum Godeffroy. Geographische, Ethnographische und Naturwissenschaftliche Mittheilungen
J. Mycol.	The Journal of Mycology
J. N. Engl. Water Works Assoc.	Journal New England Water Works Association
J. Opthalmol.	Journal d'Ophthalmologie
J. Ornith.	Journal fur Ornithologie
J. Papier	Journal de Fabricants de Papier, fonde et publie par L. Piette
J. Path. Bact.	The Journal of Pathology and Bacteriology
J. Petrole	Journal du petrole
J. Pharm.	Journal de Pharmacie
J. Pharm. Anvers	Journal de Pharmacie d'Anvers
J. Pharm. Chim.	Journal de Pharmacie et de Chimie
J. Pharm. Elsass-Lothringen	Journal de pharmacie von Elsass-Lothringen
J. Pharm. Soc. Japan	Yakagakuzasshi (Journal of the pharmaceutical society of Japan)
J. Pharmacol.	Journal of Pharmcology and Experimental Therapeutics
J. Phot. Suppl.	Journal of Photographic Supplies
J. Phot. Soc.	Journal of the Photographic Society
J. Phys.	Journal de Physique theorique et appliquee
J. Phys. Chem.	The Journal of Physical Chemistry
J. Phys. Chim.	Journal de Physique, de Chimie, et de l'Histoire Naturelle
J. Physiol.	The Journal of Physiology
J. physiol. path. gen.	Journal de physiologie et de pathologie general, Paris
J. prakt. Chem.	Erdmann's Journal fur praktische Chemie
J. Psychol. Med.	Journal of Psychological Medicine and Mental Pathology
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society
J. Roy. Astron. Soc. Canada	Journal of the Royal Astronomical Society of Canada
J. Roy. Inst. Pub. Health	Journal of the Royal Institute of Public Health
J. Roy. San. Inst.	Journal of the Royal Sanitary Institute
J. Roy. Soc. N. S. Wales	Journal of the Royal Society of New South Whales
J. Roy. U. S. Inst.	Journal Royal United Service Institution
J. Russ. Phys. Chem. Soc.	Journal of the Russian Physical Chemical Society
J. S. C. I.	Journal of the Society of Chemical Industry
J. Savants	Journal des Savants
J. Sci.	The Journal of Science
J. sci. math. physi. nat.	Journal de sciencias mathematicas, physicas naturaes
J. Soc. Arts	Journal of the Royal Society of Arts
J. Soc. Dyers Col.	Journal of the Society of Dyers and Colorists
J. soc. pharm. Anvers	Journal de pharmacie, organe de la société de pharmacie d'Anvers
J. Soc. Telegr. Eng.	Journal of the Society of Telegraphic Engineers
J. State Med.	The Journal of State Medicine
J. suisse chim. pharm.	Journal suisse de chimie et pharmacie
J. Travel	The Journal of Travel and Natural History
J. Trop. Med.	The Journal of Tropical Medicine
J. U. S. Artill.	Journal of the United States Artillery
J. Univ. Med.	Journal universel et hebdomadaire de Medecine et de Chirurgie pratiques et des Institutions medicales
J. Univ. Sci. Med.	Journal Universel des Sciences Medicales
J. Wash. Acad. Sci.	Journal of the Washington Academy of Sciences
J. Western Soc. Eng.	Journal of the Western Society of Engineers

Jaarb. Mijnw. Nederl. Ind.	Jaarboek van het Mijnwezen in Nerderlandsch Oost-Indie
Jahr. = Jahresbericht	Jahrbuch
Jahr. Agrik.-Chem.	Jahresbericht über die Fortschritte der Agrikulturchemie mit besonderer Berücksichtigung der Pflanzenchemie und Pflanzenphysiologie
Jahr. Berg- u. Hüttenw.	Jahrbuch fur das Berg- und Hüttenwesen im Königreiche Sachsen
Jahr. Kinderheilk.	Jahrbuch für Kinderheilkunde und physische Erziehung
Jahr. Chem.	Jahresbericht der Chemie (Liebig-Kopp)
Jahr. Gähr. Organ.	Jahresbericht über die Fortschritte in der Lehre von den Gährungs-Organismen (Koch)
Jahr. Mineral.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie
Jahr. Mineral Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie, und Palaeontologie, Beilage-Band
Jahr. Pharm.	Jahresbericht der Pharmacie
Jahr. Phot.	Jahrbuch der Photographie (Eder)
Jahr. Phot. Reprod.	Jahrbuch für Photographie und Reproduktiontechnik
Jahr. Phy. Ver. Frankfurt	See Frankfurt, Jahr. Phys. Ver.
Jahr. Physiol.	Jahresbericht über die Fortschritte der Physiologie
Jahr. Radioactiv. Electronik.	Jahrbuch der Radioaktivität und Electronik
Jahr. rein. Chem.	Jahresbericht der reinen Chemie
Jahr. Tier-Chem.	Jahresbericht uber der Fortschritte der Tier-Chemie
Jahr. wiss. Bot.	Jahrbucher fur wissenschaftliche Botanik
Jamaica Inst. J.	Journal of the Institute of Jamaica
Jamaica P.	Jamaica Patent
Jamaica Soc. Arts. Trans.	Transactions of the Jamaica Society of Arts
Jamain, Archives Ophthalm.	Archives d'Ophthalmolgie
Jap. P.	Japanese Patent
Jardine, Mag. Zool. Bot.	The Magazine of Zoology and Botany
Jena Ann. Acad.	Annales Academiae Jenensis
Jena Ann. Phys. Med.	Die Jenaischen Annalen für Physiologie und Medicin
Jena Ann. Soc. Mineral	Annalen der Societät fur die gesammte Mineralogie zu Jena
Jena Denkschr.	Denkschriften der Medicinisch-Naturwissenschaftlichen Gesellschaft zu Jena
Jena Geogr. Ges. Mitth.	Mittheilungen der geographischen Gesellschaft (für Thuringen) zu Jena
Jena Sitzber	Sitzungsberichte der Jenaischen. Gesellschaft für Medicin und Naturwissenschaft
Jena Zts.	Jenaische Zeitschrift fur Naturwissenschaft herausgegeben von der Medicinisch-naturwissenschaftlichen Gesellschaft zu Jena
Jern-Kontoret's Ann.	Jern-Kontoret's Annaler
Johns Hopkins Biol. Lab. Mem.	Memoirs from the biological laboratory of the Johns Hopkins University
Johns Hopkins Biol. Lab. Stud.	Johns Hopkins University. Studies from the Biological Laboratory
Johns Hopkins Univ. Circ.	The Johns Hopkins University Circulars
Jura, Trav. Soc. Emul.	Travaux de la Société d'Émulation du Department du Jura
Jurjew	See Dorpat
Just's bot. Jahr.	Just's botanischer Jahresbericht, Leipzig and Berlin
Kali	Kali

Kampen, Mag.	Magazin voor Wetenschappen, Kunsten, &c.
Kan. Acad. Sci. Trans.	Transactions of the....annual meeting of the Kansas Academy of Science
Kan. Univ. Quart.	The Kansas University Quarterly
Karlsruhe Bact. Inst. Arb.	Arbeiten aus dem bacteriologischen Institut der technischen Hochschule zu Karlsruhe
Karlsruhe Naturwiss. Ver. Verh.	Verhandlungen des Naturwissenschaftlischen Vereins in Karlsruhe
Kärnten, Berg-Verein, Zts.	Zeitschrift des Berg- u. Hüttenmännischen Vereins für Kärnten
Kärnten Landesmus. Jahr.	Jahrbuch des naturhistorischen Landes-Museums von Kärnten
Kärnten, Zts.	Zeitschrift des berg- und hüttenmännischen Vereines fur Kärnten
Karsten	See Botan. Untersuch.
Karsten, Archiv.	Archiv fur Mineralogie, Geognosie, Bergbau, und Hüttenkunde
Kassel Ver. Naturk. Ber.	Bericht des Vereins für Naturkunde zu Cassel
Kassel Ver. Naturk. Festschr.	Festschrift des Vereins für Naturkunde zu Cassel zur Feier seines Fünfzigjahrigen Bestehens
Kastner, Archiv. Chem.	Archiv. für Chemie und Meteorologie
Kastner, Archiv. Naturlehre	Archiv. für die gesammte Naturlehre
Kazan Soc. Phys.-Math. Bull.	Bulletin de la Société Physico-Mathematique de Kazan
Kazan Soc. Natur. Proc.	Proceedings of the Physico-Mathematical Section of the Society of Naturalists of the Imperial University of Kazan
Kazan Soc. Natur. Trans.	Transactions of the Society of Naturalists of the Imperial University of Kazan
Kazan Univ. Bull.	Bulletin of the Imperial University of Kazan
Kazan Univ. Mem.	Scientific Memoirs of the Imperial University of Kazan
Kekule, Krit. Zts. Chem.	Kritische Zeitschrift für Chemie, Physik, und Mathematik; see also Zts. Chem.
Keram. Rundschau	Keramische Rundschau
Kew Bull.	Royal (Botanic) Gardens, Kew. Bulletin of Miscellaneous Information
Kharkov. Math. Soc. Commun.	Communications de la Société Mathematique de Kharkov
Kiel. Mitth. Ver. Elbe.	Mittheilungen des Vereins nördlich der Elbe zur Verbreitung naturwissenschaftlicher Kenntnisse in Kiel
Kiel, Physiol. Inst. Arb.	Arbeiten aus dem Kieler physiologischen Institut
Kiel, Schr.	Schriften der Universität zu Kiel
Kiel Univ. Mineral. Inst. Mitth.	Mittheilungen aus dem Mineralogischen Institut der Universität Kiel
Kiev Soc. Natur. Mem.	Memoires de la Société des Naturalistes de Kiev
Kiöbenh. Bot. For.	See Bot. Tidsskr.
Kiöbenh. Bot. For. Festskr.	Festskrift, udgivet af den Botaniske Forening i Kiöbenhavn i Anledning af dens Halvhundredaars fest, den 12 April, 1890
Kiöbenh. Bot. For. Medd.	Meddelelser fra den Botaniske Forening i Kjobenhavn
Kiöbenh. Carlsb. Lab. Medd.	Meddelelser fra Carlsberg Laboratoriet
Kiöbenh. Dansk. Vid. Selsk. Afh.	Det Kongelige Danske Videnskabernes Selskabs naturvidenskabelige og mathematiske Afhandlinger

Kiöbenh., Dansk. Vid. Selsk. Skrift.	Det Kongelige Danske Videnskabernes Selskabs Skrifter. Naturvidenskabelig og Mathematisk Afdeling
Kiöbenh. Ent. For.	See Ent. Medd. (Kiobenh.)
Kiöbenh., Oversigt	Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlinger og dets Medlemmers Arbejder i Aaret 1874(–83)...samt. med en Résumé du *Bulletin de l'Academie Royale Danoise des Sciences et des Lettres* pout l'annee 1874(–83)
Kiobenh., Reg. Soc. Med Acta.	Acta Regiae Societatis Medicae Havniensis
Kiobenh., Vidensk. Forh.	Videnskabelige Forhandlinger ved Sioelland Stifts Landemde
Kiöbenh, Vidensk. Meddel.	Videnskabelige Meddelelser fra den Naturhistoriske Forening i Kjobenhavn
K. K. Ges. Aerzte	See Med. Jahr.
Klausenburg	See Kolozsvar
Kliniek	Kliniek
Klug, Jahr. Insect.	Jahrbucher der Insectenkunde, etc.
Koll Chem. Beihefte	Kolloidchemische Beihefte
Kolloid-Zts.	Kolloid-Zeitschrift
Kolozsvar Orvos-Termesz. Tars. Ertes.	Ertesito a "Kolozsvari Orvos-Termeszettudomanyi Tarsulat" -nak az ... orvosi, termeszettudomanyi szakuleseirol ..... Proceedings of the Medical and natural history sections of the Klausenburg Medical and Natural History Society
K Svenska Vet-Akad.	Kongl Svenska Vetenskaps-Akademiens Handlingar
Konigsb. Archiv.	Konigsberger Archiv fur Naturwissenschafften und Mathematik
Konigsb. Med. Jahr.	Konigsberger medicinische Jahrbücher; herausgegeben von dem Verein fur wissenschaftliche Heilkunde zu Konigsberg
Königsb. Schr.	Schriften der physikalisch-okonomischen Gesellschaft zu Konigsberg in Preussen
Kosmos (Lwow)	Kosmos Czasopismo polskiego Towarzystwa przyrodnikow imienia Kopernika. (Cosmos. The Journal of the Polish Society Naturalists founded in honor of Copernicus)
Krain Mus.-Ver. Mitth	See Laibach, Mus.-Ver. Krain Mitth.
Krakow Akad. (Mat.-Przyrod) Pam.	Pamietnik Akademii Umiejetnosci w Krakowie. Wydzial Matematyczno-Przyrodniczy. (Memoires of the Academy of Science in Cracow. Section of Mathematics and Natural Science)
Krakow Akad. (Mat -Przyrod) Rozpr.	Rozprawy i Spawozdania z Posiedzen Wydzialu Matematyczno-Przyrodniczego Akademii Umiejetnosci. (Proceedings of the Section of Mathematics and Natural Science of the Academy of Science)
Krakow, Akad. (Mat - Przyrod) Rozpr. & Spraw.	Rozprawy i Sprawozdania z Posiedzen Wydzialu Matematyczno-Przyrodniczego Akademii Umiejetnosci. (Proceedings of the Section of Mathematics and Natural Science of the Academy of Science)
Krakow Kom. Fizyogr. Spraw.	Akademija Umiejetnosci w Krakowie. Sprawozdanie Komisyi Fizyograficznej .... (Academy of Science in Cracow. Report of the Physiographical Commission)
Krakow, Roczn. Tow. Nauk.	Rocznik Towarzystwa Naukowego z Uniwersytetem Jagiellonskim Zlaczonego
Krakau, Untersuch. Path Anat.	Untersuchungen aus dem Pathologisch-Anatomischen Institute in Krakau

Kreutzer's Jahr. Phot.	Kreutzer's Jahresbericht der Photographie
Kristiania, Geogr. Selsk. Arb.	Det Norske Geografiske Selskabs Arbog
Kristiania, Norw. Mar. Investig. Rep.	Report on Norwegian Fishery and Marine Investigations
Kroyer, Naturhist. Tidssk.	Naturhistorisk Tidsskrift
Kühn-Archiv.	Kühn-Archiv. (formerly Berichte aus dem physiologischen Laboratorium und der Versuchsanstalt des Landwirtschaftlichen Instituts der Universitat Halle
Kult. Ing.	Der Kultur-Ingenieur (F. Dunkelberg)
Kunst	Kunstoffe
Lab. Club. Trans.	Transactions of the Laboratory Club
Laboratory	The Laboratory
Laibach, Jahr. Gymnas.	Jahresbericht des k. k. Ober-Gymnasiums in Laibach
Laibach, Jahr. Realschule	Jahresbericht der k. k. selbständigen Unter-Realschule zu Laibach
Laibach, Jahresh.	Jahresheft des Vereins des Krainischen Landes Museums in Laibach
Laibach, Mus.-Ver. Krain Mitth.	Mittheilungen des Museal-Vereins für Krain
Lancet	The Lancet, London
Landb. Cour.	Landbouw-Courant
Landshut Bot. Ver Ber.	Bericht des Botanischen Vereines in Landshut
Landw. Centr.	Landwirthschaftliches Centralblatt fur Deutschland
Landw Jahr.	Landwirthschaftliche Jahrbucher Zeitschrift fur wissenschaftliche Landwirthschaft und Archiv des Königlich Preussischen Landes-Oekonomie-Kollegiums
Landw. Jahr. Schweiz	Landwirtschaftliches Jahrbuch der Schweiz
Landw. Presse	Landwirtschaftliche Presse
Landw. Versuchs-Stat.	Die landwirthschaftlichen Versuchs-Stationen
Landw Ztg.	Landwirtschaftliche Zeitung
Laon, Soc. Acad. Bull.	Bulletin de la Société Academique de Laon
Laurent Ann Anat.	Annales Francaises et Etrangeres d'Anatomie et de Physiologie, appliquees a la Medecine et a l'Histoire Naturelle
Laurent Gerhardt, Compt. rend.	Comptes rendus Mensuels des Travaux Chemiques
Lausanne, Bull. Soc. Med.	Bulletin de la Société Medicale de la Suisse Romande
Lausanne, Bull. Soc Vaud.	Bulletin des Seances de la Société Vaudoise des Sciences Naturelles
Lausitz. Monatschr.	Lausitzische (und neue Lausitzische) Monatschrift Organ der Oberlausitzischen Gesellschaft der Wissenschaften
Leather	Leather
Leather Mfr.	Leather Manufacturer
Leather Tr. Rev.	Leather Trades Review
Leather World	Leather World, The
Lederind.	Lederindustrie (Deutsche Gerber-Zeitung)
Ledermarkt	Ledermarkt, Der. (See also Collegium)
Leeds, Trans. Phil Soc.	Transactions of the Philosophical and Literary Society of Leeds
Leicester, Lit. Phil Soc. Selection	Selection of Papers, of the Literary and Philosophical Society of Leicester
Leicester Soc. Rep.	Leicester Literary and Philosophical Society ..Report of the Council
Leicester Soc. Trans.	Transactions of the Leicester Literary and Philosophical Society

Leide	See Leyden
Leiiden, Ann. Acad.	Annales Academiae Lugduno-Batavae
Leiden, Tijdschr. Entom.	Tijdschrift voor Entomologie
Leipzig, Abh. Jablon. Ges.	Abhandlungen bei Begründung der k. Sächsischen Gesellschaft der Wissenschaften am Tage der zweihundertjährigen Geburtsfeier Leibnizens
Leipzig, Abh. Math. Phys.	Abhandlungen der Mathematisch-Physischen Classe der Koniglich Sächsischen Gesellschaft der Wissenschaften
Leipzig, Arbeit. Physiol. Anst.	Arbeiten aus der physiologischen Anstalt zu Leipzig
Leipzig, Astron. Ges. Viertelj.	Vierteljahrsschrift der Astronomischen Gesellschaft
Leipzig, Ber. Math. Phys.	Berichte über die Verhandlungen (Math. Phys. Classe) der Königlich Sächsischen Gesellschaft der Wissenschaften zu Leipzig
Leipz. Färb. Ztg.	Leipziger Farber- und Zeugdrucker-Zeitung
Leipzig Jablon. Preisschr.	Preisschriften gekront und herausgegeben von der furstlich Jablonowski' schen Gesellschaft zu Leipzig
Leipzig, Monatschr. Text. Ind.	Leipziger Monatsschrift für Textil Industrie
Leipzig, Naturf. Ges. Sitzber.	Sitzungsberichte der Naturforschenden Gesellschaft zu Leipzig
Leipzig, Physiol. Anst. Arb.	Arbeiten aus der Physiologischen Anstalt zu Leipzig
Leipzig, Schr. Naturf. Ges.	Schriften der Naturforschenden Gesellschaft zu Leipzig
Leipzig, Verh. Med. Ges.	Verhandlungen der Medicinischen Gesellschaft
Leyden Mus. Notes	Notes from the Leyden Museum
Leo, Mag.	Magazin fur Heilkunde und Naturwissenschaft in Pohlen
Leoben, Berg. u. Hütt. Jahr.	Berg- und Hüttenmannisches Jahrbuch der k. k. Montan. Lehranstalten zu Leoben und Pribram
Leonhard Bronn	See Neues Jahr. Mineral
Leonhard Bronn, Jahr.	Jahrbuch fur Mineralogie, Geognosie, Geologie, und Petrefaktenkunde
Leonhard Bronn, Neu. Jahr.	Neues Jahrbuch fur Mineralogie, Geognosie, Geologie und Petrefaktenkunde
Leonhard, Taschenbuch	Taschenbuch für die gesammte Mineralogie
Leonhard, Zts.	Zeitschrift für Mineralogie
Leopold.-Carol. Deutsch. Akad. Naturf.	See Ac. Nat. Curios. Nova Acta. Leopoldina
Leopoldina	Leopoldina. Amtliches Organ der Kaiserlichen Leopoldino-Carolinischen Deutschen Akademie der Naturforscher
Letters on Brewing	Letters on Brewing
Les Mondes	Revue hebdomadaire des Sciences et de leurs application
Licht.	Licht: Zeitschrift für Photographie· herausgegeben vom Photographischen Verein. zur Berlin
Liege, Ann. Acad.	Annales Academiae Leodiensis
Liege Assoc. Ingen. Annu.	See Rev. Univ. Mines
Liege, Mem. Soc. Emul.	Memoires de la Société Libre d'Émulation de Leiege
Liege, Mem. Soc. Sci.	Memoires de la Société (Royale) des Sciences de l'Agriculture, et des Arts a Liege
Leige Lab. Fredericq Trav.	Universite de Liege. Institut de Physiologie. Travaux du Laboratoire de Leon Fredericq
Lille Inst. Zool. Trav.	Travaux de l'Institut Zoologique de Lille et du Laboratoire de Zoologie Maritime de Wimereux (Pas-de-Calais). Travaux de la Station Zoologique de Wimereux

Lille Mem. Soc.	Memoires de la Société (Imperiale) des Sciences, de l'Agriculture et des Arts de Lille
Lille, Mem. Soc. Sci.	Memoires de la Société (Royale) des Sciences, etc., a Lille
Lille, Seances Publ.	Seances Publiques de la Société des Amateurs
Lille, Trav.	Recueil des Travaux de la Société d'Amateurs des Sciences, de l'Agriculture, et des Arts a Lille
Lille, Trav. Mem.	Travaux et Memoires de l'Universite de Lille
Lima, Mem. Cien. Nat.	Memorias de Ciencias Naturales y de Industrial (Lima)
Limbourg, Soc. Sci. Bull.	Bulletin de la Société Scientifique et Litteraire du Limbourg
Limoges, Assises	Assises scientifiques de Limoges (Institut des Provices de France)
Lindblom, Bot. Notiser	Botaniska Notiser
Linn	Linnaea: ein Journal für die Botanik
Linn Entom.	Linnaea Entomologica
Linn. Soc. J.	The Journal of the Linnean Society. Botany and Zoology
Linn. Soc. Trans.	The Transactions of the Linnean Society of London
Linn. Soc. Proc.	Proceedings of the Linnean Society of London
Linneska Samf. Handl.	Linneska Samfundets Handlingar for ar 1832
Linz, Ber.	Bericht über das Museum Francisco-Carolinum in Linz
Lisboa, Acad. Sci. Mem.	Historia e Memorias da Academia Real das Sciencias de Lisboa
Lisboa, Actas	Actas das Sessoes da Academia Real das Sciencias de Lisboa
Lisboa, Ann.	Annaes das Sciencias e Lettras
Lisboa, J. Math. Sci.	Jornal de Sciencias Mathematicas, Physicas e Naturaes publicado sob os Auspicios da Academia Real das Sciencias de Lisboa
Litterar. Annal.	Litterarische Annalen der gesammten Heilkunde
Liverpool Biol. Soc. Proc.	Proceedings and Transactions of the Liverpool Biological Society
Liverpool, Lit. Phil. Soc. Proc.	Proceedings of the Literary and Philosophical Society of Liverpool
Liverpool Mar. Biol. Comm.	See Liverpool Biol. Soc. Proc.; Liverpool Biol. Soc. Proc. & Trans.; Liverpool Lit. Phil. Soc. Proc.
Liverpool Med. Chir. J.	Liverpool Medico-Chirurgical Journal
Liverpool School Trop. Med. Mem.	Liverpool School of Tropical Medicine. Memoirs
Liverpool. Thompson Yates Lab. Rep.	The Thompson Yates Laboratories Report
Loc. Gov. Bd. Rep. (Med. Off.)	...Annual Report of the Local Government Board. Supplement containing the Reports of the Medical Officer
London	See Int. Congr. Hyg. Trans., 1891; Int. Congr. Zool. Proc. 1898
London, Ann. Med. Surg.	Annals of Medicine and Surgery, Records of the occurring Improvements, &c.
London, Cryst. Soc. Proc.	Proceedings of the Crystallological Society
London Elec. Soc. Proc.	Proceedings of the London Electrical Society
London, Fed. Inst. Brewing J.	Journal of the Federated Institutes of Brewing containing the Transactions of the various Institutes
London J. Med.	London Journal of Medicine
London, Med. Phys. J.	The Medical and Physical Journal
London, Med. Soc. Trans.	Transactions of the Medical Society of London

London, Obstet. Soc. Trans.	Transactions of the Obstetrical Society of London
London, Odont. Soc. Trans.	Transactions of the Odontological Society of London
London Path. Soc. Trans.	Transactions of the Pathological Society of London
Lond. Phot. Soc.	London Photographic Society
London Phys. Soc. Proc.	Proceedings of the Physical Society of London
London Physiol. J.	London Physiological Journal
London Poly. Rev.	The London Polytechnic Review and Magazine
London, Poly. Mag.	Polytechnic Magazine and Journal of Science, Letters, and Fine Arts
London, Sci. Soc. Proc.	Proceedings of the Scientific Society of London
London, Soc. Imp. Med. Trans.	Transactions of the Society for the Improvement of Medical and Chirugical Knowledge
Lotos	Lotos, Jahrbuch fur Naturwissenschaft im Auftrage der Vereines "Lotos"
Lousiana Planter	Louisiana Planter and Sugar Maufacturer, The
Louvaine, Ann. Acad.	Annales Academiae Lovaniensis
Lowell Obs. Ann.	Annals of the Lowell Observatory
Lucca, Atti Accad.	Atti della R. Accademia Lucchese di Scienze, Lettere, et Arti
Lumière	La Lumière; Revue de la Photographie
Lumière elec.	Lumière electrique, La
Lund, Acta Univ.	Acta Universitatis Lundensis. Lunds Iniversitets Ars-skrift. Afdelningen for Mathematik och Naturvetenskap
Lund Bot. För.	See Bot. Centrbl.; Bot. Notiser
Lund, Phys. Sallsk. Tidskr	Physiografiska Sallskapets Tidskrift
Lüneb., Denkschr.	Denkschriften des naturwissenschaftlichen Vereins fur das Fusrtenthum Luneburg
Lüneb., Jahr. Naturwiss. Ver.	Jahresbericht über die Thatigkeit des naturwissenschaftlichen Vereins in Luneburg
Lüneb. Jheft. Naturwiss. Ver.	Jahreshefte des Naturwissenschaftlichen Vereins fur das Fürstentum Luneburg
Luxemb., Inst. Roy. Publ.	Publications de l'Institut Royal Grand-Ducal de Luxembourg: Section des Sciences Naturelles
Luxemb. P.	Luxembourg Patent
Luxemb. Soc. Bot. Rec. Mem. Trav.	Recueil des Memoires et des Travaux publies par la Société Botanique du Grant-Duche de Luxembourg
Luxemb. Soc. Sci. Natur.	Société des Sciences Naturelles du Grand-Duche de Luxembourg
Lyon	Lyon scientifique et industriel
Lyon, Acad. Sci. Mem.	Memoires de l'Academie des Sciences, Belles-Lettres, et Arts de Lyon
Lyon Mus. Hist. Natur. Archiv.	Archives du Museum d'Histoire naturelle de Lyon
Lyon Soc. Agric. Ann.	Annales de la Société d'Agriculture, Histoire naturelle et Arts utiles de Lyon. Annales de la Société d'Agriculture, Sciences et Industrie de Lyon
Lyon Soc. Bot. Ann.	Annales de la Société Botanique de Lyon
Lyon, Soc. Linn. Ann.	Annales de Socétié Linneenne de la Lyon
Lyon, Soc. Linn. Compt. rend.	Comptes Rendus des Travaux de la Société de Medecine
Lyon, Soc. Sci. Med. Mem.	Memoires et Comptes-Rendus de la Société des Sciences Medicales de Lyon
Lyon Univ. Ann.	Annales de l'Universite de Lyon
Maandbl. Natuurweten.	Maandblad voor Natuurwetenschappen, uitgegeven door de Sectie voor Natuurwetenschappen van het Gennotschap ter Bevordering van Natuur-, Genees- en Heelkunde te Amsterdam

Maclurian Lyceum, Contrib.	Contributions of the Maclurian Lyceum to the Arts and Sciences
Macon Acad. Ann.	Annales de l'Academie de Macon. Société des Arts, Sciences, Belles-Lettres et (d')Agriculture (de Saone-et-Loire)
Macon, Soc. Agric. Compt. rend.	Comptes Rendus des Travaux de la Société d'Agriculture Sciences, et Belles-Lettres
Macon Soc. Compt. rend.	Compte Rendu des Travaux de la Société (d'Agriculture), des Sciences, Arts et Belles-lettres, de Macon
Madras J.	The Madras Journal of Literature and Science
Madras Quart. J.	Madras Quarterly Journal of Medical Science
Madrid	See Congr. Int. Hig. Act. 1898
Madrid Acad. Cien. Mem.	Memoires de la Real Academia de Ciencias Exactas, Fisicas y Naturales de Madrid
Madrid, Anales Hist. Natur.	Anales de Historia Natural
Madrid, Anales Minas	Anales de Minas
Madrid, Anuar.	Anuario del Real Observatorio de Madrid
Madrid, Bol.	Boletin Oficial del Ministerio de Comercio
Madrid, Ingen. Ind. Anales	Anales de la Asociacion de Ingenieros Industriales
Madrid, Mem.	Memorias de la Real Academia de Ciencias
Madrid, Revista	Revista de los Progresos de las Ciencias exactas, fisicas, y naturales
Madrid, Soc. Hist. Natur. Anales	Anales de la Sociedad Espanola de Historia Natural
Mag. Gesammt. Thierheilk.	Magazin fur die gesammte Thierheilkunde
Mag. Natur. Hist.	The Magazine of Natural History, and Journal of Zoology, Botany, Mineralogy, Geology, and Meteorology
Mag. Natur. Phil.	The Magazine of Natural Philosophy
Mag. Naturvid.	Magazin for Naturvidenskaberne
Mag. Zool.	Magasin de Zoologie
Magdeb. V. Ver. Abh. Naturwiss.	Abhandlungen des Naturwissenschaftlichen Vereins zu Magdeburg
Magdeb. V. Ver. Festschr. Naturwiss.	Festschrift zur Feier des 25 jahrigen Stiftungstages des Naturwissenschaftlichen Vereins zu Magdeburg
Magdeb. V. Ver. Jahr. Abh. Naturwiss.	Jahresbericht und Abhandlungen des naturwissenshaftlichen Vereins in Magdeburg.
Magendie, J. Physiol.	Journal de Physiologie, experimentale et pathologique
Magyar Akad. Ertes. (Math. Termesz.)	Magyar Akademiai Ertesitó. A mathematikai, es Termeszettudomanyi osztalyok kozlonye. (Report of the Hungarian Academy. Communications of the Mathematical and Natural Science Sections)
Magyar Boripar	Magyar Boripar
Magyar Nemzeti Muzeum	See Termr. Fuz.
Magyar Termt. Tars.	See Termt. Kozlon.
Magyar Tud. Akad. Ertes.	A Magyar Tudomanyos Akademia Ertesitoje. (Report of the Hungarian Academy of Science) Akademiai Ertesito a Magyar Tud. Akademia Megbizasabol. (Report by the Committee of the Hungarian Academy of Science)
Magyar Tud. Akad. Ertek. (Math.)	Ertekezesek a Mathematikai Tudomanyok körebol. Kiadja a Magyar Tudomanyos Akademia. (Memoirs in the Mathematical Sciences. Published by the Hungarian Academy of Science)

Magyar Tud. Akad. Ertek. (Termt.)	Értekezesek a Termeszettudomanyok korebol. Kiadja a Magyar Tudomanyos Akademia. (Memoirs in the Natural Sciences. Published by the Hungarian Academy of Science)
Magyar Tud. Akad. Evk.	A Magyar Tudomanyos Akademia Evkönyvei. (Annals of the Hungarian Academy of Science)
Maine Loire Soc. Mem. Acad.	Memoires de la Société Academique de Maine et Loire
Majocchi, Ann Fis. Chim.	Annali di Fisica, Chimica, etc.
Malpighia	Malpighia. Rassegna mensuale di Botanica
Malta P.	Malta Patent
Malvern Field Club Trans.	The Transactions of the Malvern Naturalists' Club
Manufact. and Build.	The Manufacturer and Builder
Manchester, Engin. Proc.	Proceedings of the Manchester Institution of Engineers
Manchester, Lit. Phil Soc. Mem.	Memoirs of the Literary and Philosophical Society of Manchester
Manchester, Lit. Phil Soc. Proc.	Proceedings of the Literary and Philosophical Society of Manchester
Manchester Micro. Soc. Trans.	Manchester Microscopical Society. Transactions and Annual Report
Manchester, Owens Coll. Biol. Lab. Stud.	Studies from the Biological Laboratories of the Owens College
Manchester, Owens Coll. Stud. Biol.	Studies in Biology from the Biological Department of the Owens College
Mannheim, Jahr.	Jahresbericht des Mannheimer Vereins für Naturkunde
Mans, Soc. Agric. Bull.	Bulletin de la Société d'Agriculture, etc., de la Sarthe
Mans, Soc. Bull.	Bulletin de la Société (Royale) d'Agriculture, Sciences et Arts du Mans
Mans, Soc. Roy. Trav.	Analyse des Travaux de la Société (Royale) des Arts du Mans
Marburg, Ges. Naturwiss. Schr.	Schriften der Gesellschaft zur Beförderung der gesammten Naturwissenschaften zu Marburg
Marianini	See Mem. Fis. Sperim.
Marne, Soc. Agric. Compte Annuel	Compte annuel et Sommaire des Travaux de la Société Agricole, etc., du departement de la Marne
Marne, Soc. Agric. Seance	Seance publique de la Société d'Agriculture, etc., du departement de la Marne
Marseille, Ann. Sci.	Annales de Sciences et de l'Industrie du midi de la France
Marseille Fac. Sci. Ann.	Annales de la Faculte des Sciences de Marseille
Marseille Lab. Zool. Mar. Trav.	See Marseille Mus. Ann.
Marseille, Mem. Acad.	Memoires publies par l'Academie de Marseille
Marseille, Mem. Soc. Emul.	Memoires de la Société d'Émulation de la Provence
Marseille Mus. Ann.	Annales du Musee d'Histoire naturelle de Marseille
Maschin.-Constr.	Der praktische Maschinen-Construkteur (W. Uhland)
Maschinenb.	Der Maschinenbauer
Mass. Bd. Health Report	Annual Report of the State Board of Health, Lunacy and Charity of Massachusetts. Annual Report of the State Board of Health of Massachusetts
Mass Insects Report	..Annual Report on the Injurious and Beneficial Insects of Massachusetts
Mass. Med. Soc. Commun.	Massachusetts Medical Society's Communications
Mat. grasses	Le Matieres grasses
Maurice, Soc. Hist. Natur. Rapp.	Septieme Rapport Annuel sur les Travaux de la Société d'Histoire Naturelle de l'Ile Maurice

Mauritius, Meteorol. Soc. Proc.	Proceedings, &c., of the Meteorological Society of Mauritius
Mauritius, Meteorol. Soc. Trans.	Transactions of the Meteorological Society of Mauritius
Mauritius P.	Mauritius Patent
Mauritius Roy. Soc. Trans.	Transactions de la Société Royale des Arts et des Sciences de Maurice
Meaux, Bull. Soc. Archeol.	Bulletin de la Société d'Archeologie, Sciences, Lettres et Arts du dept. de Seine et Marne
Mechan. Engin. Inst. Proc.	Institution of Mechanical Engineers. Proceedings
Meckel, Archiv.	Archiv fur Anatomie und Physiologie
Meckel, Deut. Archiv	Deutsches Archiv. für die Physiologie
Med. Assoc. J.	Journal edited for the Provincial Medical and Surgical Association
Med. Bot. Soc. Trans.	Transactions of the Medico-Botanical Society of London
Med. Chem. Unters.	Medicinish-chemische Untersuchungen; aus dem Laboratorium fur angewandte Chemie zu Tubingen
Med. Chir. Soc. Proc.	Proceedings of the Royal Medical and Chirurgical Society of London
Med.-Chir. Trans.	Medico-Chirurgical Transactions
Med. Chir. Ztg.	Medicinisch-chirurgische Zeitung
Med. Congr.	See Congr. Int. Med. C. R., Congr. Int. Sci. Med. C. T., Congr. Med. Int. Atti., Int. Med. Congr. Trans, Int. Med. Congr. Verh.
Med. Jahr.	Medizinische Jahrbücher, von der K. K. Gessellschaft in Wien
Med. Klinik.	Medizinische Klinik
Med. naturwiss. Archiv.	Medizinisch-naturwissenschaftliches Archiv.
Med. Off. India Sci. Mem.	Scientific Memoirs by Medical Officers of the Army of India
Med. Phys. J.	The Medical and Physical Journal
Med. Rec.	The Medical Record, N. Y.
Med. Times	The Medical Times, London
Med. Trans.	Medical Transactions
Med. Wochenschr.	Medizinische Wochenschrift
Med. Ztg. Russ.	Medicinische Zeitung Russlands
Medd. Gronland	Meddelelser om Gronland
Medd. K. Vetenskapsakad. Nobel-inst.	Meddelanden från K. Vetenskapsakademiens Nobel-institut
Meisner, Ann.	Annalen der allgemeinen Schweizerischen Gesellschaft fur die gesammten Naturwissenschaften
Meisner, Anzeiger	Naturwissenschaftlicher Anzeiger der Allgemeinen Schweizerischen Gesellschaft fur die gesammten Naturwissenschaften
Melbourne	See Victoria
Mem. accad. Lincei	Memorie della r. accademia dei Lincei, Classe di scienze fisiche, mathematiche e naturali
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino
Mem. Chem. Soc.	Memoirs and proceedings of the Chemical Society of London prior to 1848
Mem. Coll. Sci. Eng. Kyoto	Memoirs of the College of Science and Engineering, Kyoto Imperial University
Mem. Fis. Sperim.	Memorie di Fisica sperimental
Mem. Imp. Mineral. Soc. Petrograd	Memoirs of the Imperial Mineralogical Society of Petrograd
Mem. Lepidopt., St. Petersb.	Memoires sur les Lepidopteres

Mem. Manch. Lit. Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society
Mem. Med. Milit.	Recueil de Memoires de Medecine, de Chirurgie et de Pharmacie Militaires
Mem. poud. salp.	Memorial des poudres et salpetres
Mem. rev. soc. cien. "Antonio Alzate"	Memorias y revista de la sociedad cientifica "Antonio Alzate"
Mem. Soc. Ing. civ.	Memoires et Compte-Rendu des travaux de la Société des Ingenieurs Civils, etc.
Mem. Soc. Nat. Kiev.	Memoirs of the Society Nat. Kiev.
Mem. Valdarnesi	Memorie Valdarnesi
Mende, Soc. Agric. Bull.	Bulletin de la Société d'Agriculture, Industrie, Sciences, et Arts de departement de la Lozere
Mende, Soc. Agric. Mem.	Memoires et Analyses des Travaux de la Société d'Agriculture, Commerce, Sciences, et Arts de la ville de Mende, departement de la Lozere
Merck's Ann. Rep.	Merck's Annual Report
Merck's Archiv.	Merck's Archives, New York
Messenger Math.	The Messenger of Mathematics
Met.	Metallurgical-Metallurgia
Met. Chem. Eng.	Metallurgical and Chemical Engineering
Met. ital.	Metallurgia italiana, La
Met. Rev.	The Metallurgical Review
Metal Ind.	The Metal Industry
Metal Tech.	Metal Technik
Metall. Ind. Ztg.	Deutsche Metall-Industrie-Zeitung
Metallarb.	Der Metallarbeiter
Metallurgie	Metallurgie
Metaxa, Ann. Med. Chir.	Annali medico-chirurgici.
Metz Acad. Mem.	Memoires de l'Academie (Imperiale) de Metz
Metz, Assises	Assises scientifiques de Metz (Institut des Provinces de France)
Metz, Seance Gen.	Société des Lettres, Sciences, Arts, et Agriculture de Metz
Metz Soc. Hist. Natur. Bull.	Bulletin de la Société d'Histoire naturelle de Metz
Mex.	Mexican, Mexico, Mexicane
Mex. P.	Mexican Patent
Mex. Mus. Anales	Anales del Museo Nacional de Mexico
Mex. Registro Trim.	Registro trimestre, o Coleccion de Memorias de Historia, Literatura, Ciencias, etc., por una Sociedad de Literatos
Mex. Soc. "Alzate" Mem.	Memorias de la Sociedad Cientifica "Antonio Alzate"
Mexique Archiv. Comm. Sci.	Archives de la Commission Scientifique du Mexique, publiees sous les auspices du Ministere de l'Instruction Publique
Meyer Bros Drug.	Meyer Brothers Druggist, St. Louis
Meyer Jahr. Chem.	R. Meyer's Jahrbuch der Chemie
Michigan, Fish Comm. Report	Biennial Report of the State Board of Fish Commissioners. (Contains the Michigan Fish Comm. Bull.)
Micro. J.	Quarterly Journal of Microscopical Science
Micro. Soc. J.	Journal of the Royal Microscopical Society
Micro. Soc. Trans.	Transactions of the Microscopical Society of London
Midl. Drug.	Midland Druggist and Pharmaceutical Review
Midl. Med. Surg. Rep.	Midland Medical and Surgical Reporter
Midl. Quart. J. Med. Sci.	The Midland Quarterly Journal of Medical Sciences
Milano, Ann. Scienz.	Annali di Scienze e Lettere

Milano, Atti Ginnas.	Atti dell' I. R. Ginnasio Liceale Convitto Longone in Milano
Milano, Atti Ist. Lomb.	Atti dell' I. R. Istituto Lombardo di Scienze, Lettere, ed Arti
Milano, Atti Soc. Ital.	Atti della Societa Italiana di Scienze Naturali
Milano, Cagnola Atti	Atti della Fondazione Scientifica Cagnola dalla sua istituzione in poi.
Milano, Giorn. Soc. Incor.	Giornale della Societa d'Incorragiamento delle Scienze, etc., stabilita in Milano
Milano, Ist. Lomb. Adunanze	Solenni Adunanze del R. Istituto Lombardo di Scienze e Lettere
Milano, Ist. Lomb. Rapporti	Rapporti sui Progressi delle Scienze del R. Istituto Lombardo di Scienze
Milano, Ist. Lomb. Rend.	Rendiconti dell' Istituto Lombardo di Scienze e Lettere—Classe di Scienze matematiche e naturali
Milano, Mem. Ist. Lomb.	Memorie dell' I. R. Istituto Lombardo di Scienze, etc.
Milano, Mem. Ist. Lomb. Veneto	Memorie dell' I. R. Istituto del regno Lombardo-Veneto
Milch. Zentr.	Milchwirtschaftliches Zentralblatt
Milch Ztg.	Milch Zeitung
Min Eng. World	Mining and Engineering World
Min. J.	The Mining Journal
Min. Rev.	Mining Review, a Monthly Record of Geology
Min. Sci.	Mining Science
Min. Sci. Press	Mining and Scientific Press
Min. Smelt. Mag.	The Mining and Smelting Magazine: a monthly review of Practical Mining, Quarrying, and Metallurgy
Min. Soc. J.	See Min. Mag
Mineral. Mag.	The Mineralogical Magazine and Journal of the Mineralogical Society of Great Britain and Ireland
Mineral. Mitth.	Mineralogische Mittheilungen
Mineral. Petr. Mitth.	(Tschermak's) Mineralogische und Petrographische Mittheilungen
Mines and Minerals	Mines and Minerals
Minn. Acad. Sci. Bull.	Bulletins of the Minnesota Academy of Natural Sciences
Minn. Acad. Sci. Pap.	The Minnesota Academy of Natural Sciences at Minneapolis, Minn. Occasional Papers
Minn. Bot. Stud.	Geological and Natural History Survey of Minnesota. Minnesota Botanical Studies
Miquel, Bull.	Bulletin des Sciences Physiques et Naturelles en Neerlande
Misc. Ent.	Miscellanea Entomologica
Mitau, Quatember	Die Quatember
Mitth. Artil. Geniew.	Mittheilungen über Gegenstände des Artillerie- und Genie-wesens
Mitth. Böhmen. Archit. Ing. Ver.	Mittheilungen des Architekten und Ingenieur Vereins im Königreiche Böhmen
Mitth. Centralst. Wiss.-tech. Unters.	Mittheilungen aus der Centralstelle für wissenschaftlichtechnische Untersuchungen
Mitth. Gewerbever. Nassau	Mittheilungen für den Gewerbeverin für Nassau
Mitth. Kais. Gesundhts.	Mittheilungen aus dem Kaiserlichen Gesundheitsamte, Berlin
Mitth. Königl. Materialprüfungsamt	Mitteilungen aus dem Königlichen Material prüfungsamt zu Gross Lichterfelde West
Mitth. Hannov. Gewerbever.	Mittheilungen des Gewerbevereins für Hannover

Mitth. Lebensm. Hyg.	Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene veröffentlicht vom Schweizer Gesundheitsamt
Mitth. Malerei	Technische Mitteilungen für Malerei
Mitth. königl. Prüfungsans. Wasser-versorgung	Mitteilungen aus der königlichen Prüfungsanstalt für Wasser-versorgung und Abwässer beseitung zu Berlin
Mitth. Tech. Gew. Mus.	Mitteilungen aus dem Technischen Gewerbe Museum
Mitth. Techn. Versuchsamtes	Mittheilungen des k. k. Technischen Versuchsamtes
Mitth. Zool. Sta. Neapel	Mittheilungen aus der zoologischen Station zu Neapel. etc.
Mo. Insects Report	Annual Report on the Noxious, Beneficial and other Insects, of the State of Missouri, made to the State Board of Agriculture
Mod. Sugar Planter	Model Sugar Planter, The
Modena, Accad. Sci. Mem.	Memorie della Regia Accademia di Scienze, Lettere ed Arti di Modena
Modena, Annu. Soc. Natur.	Annuario della Societa dei Naturalisti in Modena
Modena Atti Soc. Natur.	Atti della Societa dei Naturalisti di Modena
Modena, Mem. Soc. Ital.	Memorie di Matematica e di Fisica della Societa Italiana delle Scienze
Modena, Relazione	Relazione delle Adunanze della R. Accademia di Scienze, Lettere, ed Arti di Modena, nell' Anno Academico 1842–43
Moigno, Annu. Cosmos	Annuaire du Cosmos
Mois chim. electrochim.	Mois chimique et electrochimique, Le
Mois min. met.	Mois minier et metallurgique, Le
Mois sci. ind.	Mois scientifique et industriel, Le
Moleschott, Unters.	Untersuchungen zur Naturlehre des Menschen und der Thiere
Moll, Ann.	Annalen der Berg- und Hüttenkunde
Moll, Efemeriden	Efemeriden der Berg- und Huttenkünde
Moll, Jahr. Berg.	Jahrbucher der Berg- und Hüttenkunde
Moll, Neue Jahr.	Neue Jahrbücher der Berg- und Huttenkunde
Mon. ceram. verr.	Moniteur de la ceramique de la verrerie et journal du ceramiste et du chaufournier (reuins)
Mon. cord.	Moniteur de la cordonnerie
Mon. fils. tiss.	Moniteur des fils et tissus
Mon. Ind.	Moniteur Industriel
Mon. Ind. Belge	Moniteur Industriel Belge
Mon. Pap.	Moniteur Papeterie
Mon. Sci.	Moniteur Scientifique (Quesneville)
Mon. teint.	Moniteur de la teinture des apprets et de l'impression des tissus
Monats.	Monatshefte fur Chemie und verwandte Theile anderer Wissenschaften. Gesammelte Abhandlungen aus den Sitzungsberichten der kaiserlichen Akademie der Wissenschaften
Monats. Dermatol.	Monatshefte für praktische Dermatologie
Monatsbl. Hannover Gewerbever.	Monatsblatt des Gewerbevereins für Hanover
Monatschr. Text.-Ind.	Leipziger Monatsschrift fur Textil-Industrie
Monatschr. Zahn.	Monatschrift für Zahnärzte
Montevideo Mus. Nac. Anales	Anales del Museo Nacional de Montevideo
Monthly Amer. J. Geol.	The monthly Journal of Geology and Natural Science
Monthly Archiv. Med. Sci.	Monthly Archives of the Medical Sciences

Monthly Cons. & Trade Report	The monthly Consular and Trade Reports
Montpellier, Acad. Proces-Verb.	Extraits des Proces-Verbaux des Seances de l'Academie des Sciences et Lettres
Montpellier, Acad. Sci. Mem.	Academie des Sciences et Lettres de Montpellier
Montpellier Inst. Zool. Trav.	Travaux originaux du Laboratoire Zoolique de la Faculte des Sciences de Montpellier et de la Station Maritime de Cette
Montpellier, Mem. Acad. Sect. Med.	Memoires de l'Academie des Sciences et Lettres: Section de la Medecine
Montpellier, Recueil. Bull.	Recueil des Bulletins publies par la Société Libre des Sciences, etc.
Montreal Natur. Hist. Soc. Proc.	See Canad. Rec. Sci.
Montreal Pharm. J.	Montreal Pharmaceutical Journal
Montsouris	See under Paris
Morphol. Arb.	Morphologische Arbeiten
Morphol. Jahr.	Morphologisches Jahrbuch
Moscou	See Congr. Int. Anthrop. C. R. 1892, Congr. Int. Med. C. R. 1897, Congr. Int. Zool. (C. R.) 1892
Moscou, Comment. Soc. Phys. Med.	Commentationes Societatis Physico-Medicae apud Universitatem Mosquensem institutae
Moscou, Soc. Natur. Bull.	Bulletin de la Société Impeiiale des Naturalistes
Moscou, Soc. Natur. Mem.	Memoires de la Société Imperiale des Naturalistes de Moscou
Moscou, Soc. Natur. Nouv. Mem.	Nouveaux Memoires de la Société Imperiale des Naturalistes de Moscou
Moscow Soc. Sci. Bull.	Bulletin of the Imperial Society of Lovers of Natural Science, Anthropology and Ethnography, in connection with the Imperial University of Moscow
Moscow Univ. Mem. (Natur. Hist.)	Scientific Memoirs of the Imperial University of Moscow. Natural History Section
Moscow Univ. Mem. (Phys.-Math.)	Scientific Memoirs of the Imperial University of Moscow. Physico-Mathematical Section
Moselle, Bull. Soc. Hist. Natur.	Bulletin de la Société d'Histoire Naturelle du departement de la Moselle
Moselle, Trav. Soc. Sci. Med.	Expose des Travaux de la Société des Sciences Medicales de la Moselle
Mov. Pict. World	Moving Picture World
Mulder, Archief.	Natuur- en Scheikundig Archief.
Mulder, Scheik. Verh.	Scheikundige Verhandelingen en Onderzoekingen
Müller, Archiv.	Archiv. für Anatomie, Physiologie, und wissenschaftliche Medicin.
München, Akad. Abh.	Abhandlungen der Mathematisch-Physikalisch Classe der königlich Bayerischen Akademie der Wissenschaften
München, Akad. Sitzber.	Sitzungsberichte der Mathematisch-Physikalischen Classe der k. B. Akademie der Wissenschaften München
München Bot. Ver.	See Bot. Centrbl.
München, Bull. Akad.	Bulletin der k. Akademie der Wissenschaften
München, Denkschr.	Denkschriften der Königl. Baierischen Akademie der Wissenschaften zu München
München, Entom. Ver. Mitth.	Mittheilungen des Münchener Entomologischen Vereins
München, Gelehrte Anz.	Gelehrte Anzeigen

München Ges. Morphol. Physiol. Sitzber.	Sitzungsberichte der Gesellschaft für Morphologie und Physiologie in München
München, Naturwiss. Tech. Comm. Abh.	Abhandlungen der naturwissenschaftlichtechnischen Commission bei der Königl. Baierischen Akademie
München Phot. Ges.	See Wien, Photogr. Correspond.
Munchen, Sitzber.	Sitzungsberichte der Königl. Baierischen Akademie der Wissenschaften zu Munchen
München Thierarznei-Schule Jahr.	Jahresbericht der k. Central-Thierarznei-Schule in Munchen
Munchen Thierärztl. Hochschule Jahr.	Jahresbericht der k. Thierärztlichen Hochschule in Munchen
München, Zts. Archit.	Zeitschrift des Bayerischen Architekten- und Ingenieur-Vereins
Munic. Engin.	Municipal Engineer
Munic. J. Engin.	Municipal Journal and Engineer
Münster, Abh. Aerzt. Ges.	Abhandlungen und Beobachtungen der ärztlichen Gesellschaft zu Münster
Museum Senckenb.	Museum Senckenbergianum
Must. Ztg.	Leipziger Färber Zeitung (Farberei Musterzeitung)
N. Brunsw. Natur. Hist. Soc. Bull.	Bulletin of the Natural History Society of New Brunswick
N. England Bot. Club	See Rhodora
N. Engl. Eng.	New England Engineer, The
N. England J. Med.	New England Journal of Medicine and Surgery.
N. Erf. Erfahr.	Neuste Erfindungen und Erfahrungen
N. Hampshire San. Bull.	New Hampshire Sanitary Bulletin
N. Haven	See Connecticut
N. Idea	New Idea (The), Detroit
N. Med. Phys. J.	New Medical and Physical Journal
N. Mex. Agric. Coll. Bull.	New Mexico Agricultural College. Experiment Station. Las Crues, N. M. Bulletin. New Mexico College of Agriculture and the Mechanic Arts. Agricultural Experimental Station Bulletin
N. Orleans Med. Surg. J.	New Orleans Medical and Surgical Journal
N. Orleans Proc.	Proceedings of the New Orleans Academy of Sciences
N. Russ. Soc. Natur. Mem.	Memoirs of the New Russian Society of Naturalists
N. S. Wales, Acclim. Soc. Report	Annual Reports (3, 6, and 7) of the Acclimatisation Society of N. S. W.
N. S. Wales Dept. Mines Report	Annual Report of the Department of Mines (and Agriculture), New South Wales
N. S. Wales, Entom. Soc. Trans.	The Transactions of the Entomological Society of New South Wales
N. S. Wales Linn. Soc. (Macleay Mem. Vol.)	Linnean Society of New South Wales. The Macleay Memorial Volume
N. S. Wales, Linn. Soc. Proc.	The Proceedings of the Linnean Society of New South Wales
N. S. Wales P.	New South Wales Patent
N. S. Wales, Phil. Soc. Trans.	Transactions of the Philosophical Society of New South Wales
N. S. Wales, Roy. Soc. J.	Journal and Proceedings of the Royal Society of New South Wales
N. S. Wales, Roy. Soc. Trans.	Transactions of the Royal Society of New South Wales
N. Y. Acad. Ann.	Annals of the New York Academy of Sciences, late Lyceum of Natural History
N. Y. Acad. Mem.	New York Academy of Sciences. Memoirs
N. Y. Acad. Trans.	Transactions of the New York Academy of Sciences. Late Lyceum of Natural History

N. Y. Acad. Med. Bull.	Bulletin of the New York Academy of Medicine
N. Y. Acad. Med. Trans.	Transactions of the New York Academy of Medicine
N. Y. Agric. Soc. Trans.	Transactions of the New York State Agricultural Society
N. Y. Bot. Club Bull.	Bulletin of the Torrey Botanical Club
N. Y. Entom. Soc. J.	Journal of the New York Entomological Society
N. Y. Insects Report	Report on the Noxious, Beneficial and other Insects of the State of New York
N. Y. J. Med.	New York Journal of Medicine and the Collateral Sciences
N. Y. Linn. Soc. Trans.	Transactions of the Linnaean Society of New York
N. Y. Lit. Phil. Soc. Trans.	Transactions of the Literary and Philosophical Society of New York
N. Y Lyceum Ann.	Annals of the Lyceum of Natural History of New York
N. Y. Lyceum, Proc.	Proceedings of the Lyceum of Natural History in the City of New York
N. Y. Med. J.	New York Medical Journal
N. Y. Med. Repos.	Medical Repository of New York
N. Y. Med. Soc. Trans.	Transactions of the Medical Society of the State of New York
N. Y. Mus Bull.	University of the State of New York. Bulletin of the New York State Museum
N. Y. Mus. Mem.	Memoirs of the New York State Museum
N. Zeal. Inst. Trans.	Transactions and Proceedings of the New Zealand Institute
N. Zeal. Inst. Min. Engin. Trans.	Transactions of the New Zealand Institute of Mining Engineers
N. Zeal. J. Sci.	The New Zealand Journal of Science
N. Zeal. P.	New Zealand Patent
N. Zeal. Pap. & Rep.	New Zealand. Papers and Reports relating to Minerals and Mining
Nachr. König. Ges.	Nachrichten von der königlichen Gesellschaft der Wissenschaften zu Göttingen. (Mathematische-physikalische Klasse)
Nancy, Acad. Stanislas. Mem.	Academie de Stanislas. Memoires de la Société (Royale) des Sciences, etc., de Nancy
Nancy Soc. Sci. Bull.	Bulletin de la Société des Sciences de Nancy
Nancy Soc. Sci. Mem.	Memoires de la Société (Royale) des Sciences, Lettres, et Arts de Nancy
Nancy Soc. Sci. Trav.	Precis analytique des Travaux de la Société (Royale) des Sciences, Arts, et Agriculture de Nancy
Nantes J. Med.	Journal de la Section de Medecine de la Société Academique du departement de la Loire Inferieure
Nantes, Ann. Soc. Acad.	Annales de la Société Academique de Nantes et du departement de la Loire Inferieure
Nantes Soc. Sci. Natur. Bull.	Bulletin de la Société des Sciences naturelles de l'Ouest de la France
Napoli Accad. Aspir. Ann.	Annali della Accademia degli aspiranti Naturalisti
Napoli Accad. Atti	Atti della Reale Accademia delle Scienze Fisiche e Matematiche
Napoli Accad. Pontan. Atti	Atti dell' Accademia Pontaniana
Napoli Accad. Sci. Atti	Atti della Reale Accademia della Scienze e Belle Lettere; Sezione della Societa R. Borbonica
Napoli Accad. Sci. Mem.	Memorie della R. Accademia della Scienze
Napoli Giorn. Mat.	See Giornale di Matemat.
Napoli, Atti Ist. Incorr.	Atti del Real Istituto d'Incorraggiamento alle Scienze Naturali di Napoli

Napoli Lucifero	Il Lucifero
Napoli Mus.	Museo di Letteratura e Filosofia
Napoli, Ann. Mus. Zool.	Annuario del Museo Zoologico della R. Universita di Napoli
Napoli Rend.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche. (Sezione della Societa Reale di Napoli)
Napoli Soc. Natur. Boll.	Bollettino della Societa di Naturalisti in Napoli
Natl. Assoc. Retail Drug, Notes	The Journal of the National Association of Retail Druggists, Chicago
Natl. Disp.	National Dispensatory
Natl. Drug.	National Druggist
Natl. Eclect. Med. Assoc. Quart.	The National Eclectic Medical Association Quarterly, Cincinnati
Natl. Glass Budget	National Glass Budget
Natl. Inst. Bull.	Bulletin of the Proceedings of the National Institution for the Promotion of Science
Natur. Can.	Le Naturaliste Canadien. Bulletin de Recherches, Observations et Decouvertes se rapportant a l'Histoire naturelle du Canada
Natur. Sicil.	Il Naturalista Siciliano. Giornale di Scienze Naturali
Natur. J.	The Naturalists' Journal
Naturaleza	La Naturaleza. Periodico cientifico de la Sociedad Mexicana de Historia Natural
Naturalist (Yorks)	The Naturalist: Journal of the West Riding Consolidated Naturalists' Society
Naturaliste	Le Naturaliste
Nature	Nature
Naturf.	Der Naturforscher
Natur. Hist. Review	The Natural History Review and Quarterly Journal of Science
Naturhist. Notizen	Naturhistorische und chemisch-technische Notizen nach den neuesten Erfahrungen
Naturhist. Tidsskr.	Naturhistorisk Tidsskrift
Naturwiss. Umschau Chem. Ztg.	Naturwissenschaftliche Umschau der Chemiker-Zeitung
Natuurk Tijdschr.	Natuurkundige Tijdschrift, inhoudende Phijsica, Chemie, Pharmacie, Nat. Hist., &c., uitg. van wege het Genootschap: "Tot nut en vergenoegen," te Arnhem.
Nauche, J. Galvan.	Journal du Galvanisme, de Vaccine, etc.
Naval Archit. Trans.	Transactions of the Institution of Naval Architects
Naval Sci.	Naval Science: a Quarterly Magazine for promoting the improvement of Naval Architecture, Marine Engineering, Steam Navigation, and Seamanship
Neapel Zool. Sta., Fauna & Flora	Fauna und Flora des Golfes von Neapel und der angrenzenden Meeres-Abschnitte herausgegeben von der Zoologischen Station zu Neapel
Neapel Zool. Sta. Mitth.	Mittheilungen aus der Zoologischen Station zu Neapel
Nebraska Univ. Stud.	University Studies. Published by the University of Nebraska
Nederl. Archiv.	See Selenka
Nederl. Archief Natuurk.	Nederlandsch Archief voor Genees-en Natuurkunde
Nederl. Bot. Ver. Versl. en Meded.	See Nederl. Kruidk. Arch.
Nederl. Dierk. Ver. Tijdschr.	Tijdschrift der Nederlandsche Dierkundige Vereeniging
Nederl. Entom. Ver.	See Tijdschr. Ent.

Nederl. Kruidk. Archief.	Nederlandsch Kruidkundig Archief
Nederl. Lancet	Nederlandsch Lancet. Tijdschrift aan de praktische Chirurgie, etc.
Nederl. Tijdschr. Dierkunde	Nederlandsch Tijdschrift voor de Dierkunde, uitgegeven door het koninklijk Zoologisch Genootschap Natura Artis Magistra te Amsterdam
Nederl. Tijdschr. Geneesk.	Nederlandsch Tijdschrift voor Geneeskunde, tevens orgaan der Nederlandsche Maatschappij tot de Bevordering der Geneeskunst
Neuchatel Soc. Sci. Bull.	Bulletin de la Société des Sciences Naturelles de Neuchatel
Neues Bergmänn J.	Neues bergmännisches Journal
Neues Jahr. Min.	Neues Jahrbuch für Mineralogie Geologie und Palaeontologie
Neues Lausitz. Mag.	Neues Lausitizisches Magazin; unter Mitwirkung der Oberlausitzischen Gesellschaft der Wissenschaften
Neue med.-chir. Ztg.	Neue medicinisch-chirurgische Zeitung
Neues Nord. Archiv.	Neues nordisches Archif fur Natur und Arzneikunde, verfasst von einer Gesellschaft nordischer Gelehrten
Neue Preuss. Provinz. Blätt.	Neue Preussische Privinzial-Blätter
Neu-Vorpommern Mitth.	Mittheilungen aus dem naturwissenschaftlichen Vereins für Neu-Vorpommern und Rugen in Greifswald
Newbury Field Club Trans.	Transactions of the Newbury District Field Club
Newcastle Chem. Soc. Trans.	Newcastle-upon-Tyne Chemical Society. Transactions
Newf. P.	Newfoundland Patent
Newman. Entom.	The Entomologist
Newport Natur. Hist. Soc. Proc.	Proceedings of the Newport Natural History Society
Nicholson J.	Journal of Natural Philosophy, Chemistry, and the Arts
Nick.	The Nickelodeon
Niederl. Archiv. Zool.	Niederländisches Archiv. für Zoologie
Niederösterr. Gewerb-Ver. Verh.	Verhandlungen des Niederösterreichischen Gewerbe-Vereins
Niederrhein. Ges. Naturk. Sitzber.	Sitzungsberichte der Niederrheinischen Gesellschaft für Natur- und Heilkunde zu Bonn
Niederrhein. Ges. Organ.	Organ fur die gesammte Heilkunde; herausgegeben von der Niederrheinischen Gesellschaft für Natur- und Heilkunde zu Bonn
Nieuw Archief Wisk.	Nieuw Archief voor Wiskunde
Nimes Soc. Sci. Bull.	Bulletin de la Société d'Etude des Sciences Naturelles de Nimes
Nor. Amer. Med. Chir. Rev.	The North-American Medico-Chirurgical Review
Nor. Eng. Inst. Min. Engin. Trans.	North of England Institute of Mining and Mechanical Engineers. Transactions
Nor. Staff. Field Club Rep.	(The) North Staffordshire (Naturalists') Field Club (and Archaeological Society). Annual Report (and Transactions)
Nord. Braband, Handel. prov. Genoots.	Handelingen van het provinciaal Genootschap van Kunsten en Wetenschappen in Nord Braband
Nord France Soc. Linn. Bull.	Bulletin de la Société Linneenne du Nord de la France
Nord France Soc. Linn. Mem.	Memoires de la Société Linneenne du Nord de la France

Nord, Mem. Soc. Agric.	See Douai
Nord, Soc. Agric. Seance Publ.	Seance Publique de la Société d'Agriculture, Sciences, et Arts, etc., du departement du Nord
Nordamerik. Monatsber.	Nordamerikanischer Monatsbericht fur Natur- und Heilkunde
Norddeut. Landwirth	Der norddeutsche Landwirth
Nordisches Archiv.	Nordisches (u. Neues Nordisches) Archiv. für Naturkunde und Arzneiwissenschaft
Norf. Norw. Natur. Soc. Trans.	Transactions of the Norfolk and Norwich Naturalists' Society
Normandie	See Caen
Normandie Soc. Linn. Bull.	Bulletin de la Société Linneenne de Normandie
Normandie Soc. Linn. Mem.	Memoires de la Société Linneenne de Normandie
Normandie Soc. Linn. Seance Publ.	Seance Publiques de la Société Linneenne de Normandie
Norsk Tidsk. Vid. Litt.	Norsk Tidskrift for Videnskab og Litteratur.
Norske Videnskab. Skrift.	Det Kongelige Norske Videnskabersselskabs Skrifter i det 19 de Aarhundrede
Northampton Natur. Hist. Soc. J.	Journal of the Northampton(shire) Natural History Society and Field Club
Northern J. Med.	Northern Journal of Medicine
Northumb. Natur. Hist. Soc. Trans.	Transactions of the Natural History Society of Northumberland, Durham, and Newcastle-upon-Tyne
Northwestern Drug.	Northwestern Druggist (The), Minneapolis
Norw. P.	Norwegian Patent
Notarisia	Notarisia. Commentarium Phycologicum. La Notarisia. Commentario Ficologico Generale. Parte speciale della Rivista Neptunia
Notices of Judgment, U. S. Dept. Agric.	Notices of Judgment, U. S. Department of Agriculture
Notiz Archit. Ver. Niederrhein	Notizblatt des Architekten und Ingenieur Vereins fur Niederrhein und Westfalen
Notiz. Riga	Notizblatt des technischen Vereins zu Riga
Nouv. Ann. Math.	Nouvelles Annales de Mathematiques
Nouv. Archiv. Miss. Sci.	Nouvelles Archives des Missions Scientifiques et Litteraires
Nouv. remedes	Nouveaux remedes, Paris
Nova Acta Acad. Nat. Curios	Novorum Actorum Academiae Caesareae Leopoldino-Carolinae Germanicae Naturae Curiosorum
Nova Scotia Inst. Sci. Proc. & Trans.	(The) Proceedings and Transactions of the Nova Scotian Institute of (Natural) Science
Nova Scotia, Trans. Lit. Sci. Soc.	Transactions of the Literary and Scientific Society of Nova Scotia
Novitates Zool.	Novitates Zoologicae. A Journal of Zoology in connection with the Tring Museum
Nuov. Ann. Sci. Natur.	Nuovi Annali delle Scienze naturali
Nuov. Antol. Sci.	Nuova Antologia di Scienze, Lettere (Lettere, Scienze) ed Arti
Nuov. Cimento	Il Nuovo Cimento, Giornale di Fisica, di Chimica, e di Storia Naturale
Nuov. Giorn. Bot. Ital.	Nuovo Giornale Botanico Italiano (e Bullettino della Societa Botanica Italiana)
Nuov. Notarisia	La Nuova Notarisia. Rassegna (trimestrale) consacrata allo Studio delle Alghe (e Corollario alla "Sylloge Algarum Omnium")
Nürnb. Natur. Ges. Abh.	Abhandlungen der Naturhistorischen Gesellschaft zu Nürnberg
Nye Hygaea	Nye Hygaea

Nyt Mag. Naturvid.	Nyt Magazin for Naturvidenskaberne
Nyt Tidsskr. Fys. Kem.	Nyt Tidsskrift for Fysik og Kemi.
Oberhess. Ges. Ber.	Berichte der Oberhessischen Gesellschaft für Naturkunde und Heilkunde in Giessen
Odontol. Soc. Trans.	Transactions of the Odontological Society of Great Britain
Oesterr. Bot. Zts.	Oesterreichische Botanische Zeitschrift
Oesterr. Chem. Ztg.	Oesterreichische Chemiker Zeitung
Oesterr. landw. Wochenbl.	Oesterreichisches landwirtschaftliches Wochenblatt
Oesterr. Med. Jahr.	Medicinisches Jahrbuch des k. k. Oesterreichischen Staates
Oesterr. Med. Wochenschr.	Oesterreichische Medicinische Wochenschrift, als Erganzungsblatt der medicinischen Jahrbücher
Oesterr. Wochenschr.	Oesterreichische Wochenschrift fur Wissenschaft, Kunst, und offentliches Leben
Oesterr. Zts. Berg. Huttenw.	Oesterreichsche Zeitschrift fur Berg- und Huttenwesen
Oesterr.-ung. Zts. Zuckerind.	Oesterreichisch-ungarische Zeitschrift fur Zuckerindustrie und Landwirtschaft
Off. Gaz.	Official Gazette, United States Patent Office
Offenbach. Ver. Naturk. Ber.	Bericht des Offenbacher Vereins fur Naturkunde uber seine Thatigkeit
Oil Colour J.	Oil and Colourman's Trade Journal
Oil, Paint Drug. Rep.	Oil, Paint and Drug Reporter
Oise	See Beauvais
Oise Mem. Soc. Acad.	Memoires de la Société Academique d'Archeologie, Sciences, et Arts du departement de l'Oise
Oken Isis	Isis, oder Encyclopädische Zeitung
Omaha Drug.	Omaha Druggist (The), Omaha
Omodei Ann. Univ.	Annali Universali di Medicina
Ontario Entom. Soc. Rep.	Report of the Entomological Society of Ontario
Oporto	See Porto
Ophthalm. Bibliothek	Ophthalmologische Bibliothek
Ophthalm. Hosp. Reports	Ophthalmic Hospital Reports and Journal of the Royal London Ophthalmic Hospital
Ophthalmic Rev.	The Ophthalmic Review: a Quarterly Journal of Ophthalmic Surgery and Science
Organ Rübenzuckerind.	Organ des Centralvereins fur Rubenzuckerindustrie
Orgelb.	Die Orgelbauzeitung
Orleans Ann.	Annales de la Société Royale des Sciences, Belles-Lettres, et Arts d'Orleans
Orleans, Bull.	Bulletin des Sciences Physiques, Medicales, et d'Agriculture d'Orleans
Ornis	Ornis, oder das Neuste und Wichtigste der Vögelkunde, etc.
Ornith. Jahr.	Ornithologisches Jahrbuch
Ornith. Monatsber.	Ornithologische Monatsberichte
Ornithol.	The Ornithologist
Ornithol. Ool.	The Ornithologist and Oologist
Örsted Tidsskrift	Tidsskrift for Naturvidenskaberne
Orvos-Termesz. Ertes.	Orvos-Termeszettudomanyi Ertesito a Kolozsvari Orvos-Termeszettudomanyi Tarsulat es az Erdelyi Museum-Egylet Termeszettudomanyi Szakosztalyanak az..szakuleseirol..(Medical and Natural History Proceedings of the sections of the Klausenburg Medical and Natural History Society and of the Natural History section of the Museum Association of Transylvania

Osnabrück, Jahr.	Jahresbericht des Naturwissenschaftlichen Vereins zu Osnabrück
Ottawa Field-Natur. Club Trans.	Ottawa Field-Naturalists' Club Transactions
Ottawa Natur.	The Ottawa Naturalist
Ouest France Soc. Sci. Nat. Bull.	See Nantes...
Oversigt K. Danske Vidensk. Selsk. Forh.	Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlinger
Pacific Drug. Rev.	Pacific Drug Review, Portland
Pacific Pharm.	Pacific Pharmacist
Padova, Mem. Acad.	Memorie dell' Accademia di Scienze, Lettere, ed Arti di Padova
Padova, Nuovi Saggi	Nuovi Saggi dell' Accademia di Scienze, Lettere, ed Arti di Padova
Padova, Rivista Period.	Rivista Periodica dei Lavori della I. R. Accademia di Scienze, Lettere, ed Arti di Padova
Padova, Soc. Sci. Atti	Atti della Societa Veneto-Trentina di Scienze naturali
Padova Soc. Sci. Bull.	Bullettino della Societa Veneto-Trentina di Scienze Naturali residente in Padova
Palermo Accad. Atti	Atti della Reale Accademia di Scienze, Lettere e Belle Arti di Palermo
Palermo Circ. Mat. Rend.	Rendiconti del Circolo Matematico di Palermo
Palermo, Effemeridi	Effermeridi scientifiche e letterarie per la Sicilia; coi Lavori del R. Instituto d'Incorraggiamento per la Sicilia
Palermo, Giorn. Sci. Natur.	Giornale di Scienze naturali ed economiche, pubblicato per Cura della Socïeta di Scienze naturali ed economiche di Palermo
Palermo, Mem. Spettrosc. Ital.	Memorie della Societa degli Spettroscopisti Italiani
Palermo Oss. Bull. Meteorol.	Bullettino Meteorologico del Reale Osservatorio di Palermo
Palermo Oss. Ossvz. Meteorol.	R. Osservatorio di Palermo. Stazioni di Valverde Osservazioni meteorologiche
Palomba, Raccolta	Raccolta di Lettere, etc., intonno alla Fisica ed alle Mathematiche
Palyamunkak	Palyamunkak. Termerzetlud (Prize Essays of the Hungarian Academy)
Pander, Beitr. Naturk.	Beiträge zur Naturkunde aus den Ostseeprovinzen Russlands
Paper	Paper
Paper-Maker Brit. Trade J.	Paper Maker and British Trade Journal
Paper Makers' Monthly J.	Paper Makers' Monthly Journal
Paper Making	Paper Making
Paper Mill	Paper Mill and Woodpulp News
Papers Naval Archit.	Papers on Naval Architecture and other subjects connected with naval science
Paper Trade J.	Paper Trade Journal
Papier-Fabr.	Papier-Fabrikant, Der
Papier Ztg.	Papier Zeitung
Papierhandel	Der Papierhandel
Papilio	Papilio
Papir J.	Papir Journalen
Par. P.	Paraguay Patent
Para, Mus Hist. Natur. Bol.	Boletim do Museu Paraense de Historia Natural e Ethnographia
Paris, Acad. Med. Bull.	Bulletin de l'Academie de Medecine

Paris, Acad. Med. Mem.	Memoires de l'Academie de Medecine
Paris, Acad. Sci. Compt. rend.	Comptes Rendus hebdomadaires des Seances de l'Academie des Sciences
Paris, Acad. Sci. Mem.	Memoires de l'Academie des Sciences de l'Institut de France
Paris, Ann. Cerc. Med.	Annales du Cercle Medicale
Paris, Ann. Conserv.	Annales du Conservatoire des Arts et Metiers
Paris, Ann. Ecole Norm.	Annales scientifiques de l'Ecole Normale Superieure
Paris, Ann. Ponts Chauss.	Annales des Ponts et Chaussees. Memoires et documents relatifs a l'Art des Constructions et au Service de l'Ingenieur
Paris, Ann. Soc. Entom.	Annales de la Société Entomologique de France
Paris, Annaes Sci.	Annaes das Sciencias, etc, por huma Sociedade de Portuguezes residentes em Paris
Paris, Annu. Med. Chir. Hosp.	Annuaire medico chirurgical des Hopitaux, etc., de Paris
Paris, Annu. Soc. Met.	Annuaire de la Société Meteorologique de France
Paris, Anthropol. Soc. Bull.	Bulletin de la Société d'Anthropologie de Paris
Paris, Anthropol. Soc. Mem.	Memoires de la Société d'Anthropologie de Paris
Paris, Bull. Fac. Med.	Bulletins de la Faculte de Medecine de Paris et de la Société etablie dans son sein
Paris, Bull. Soc. Aerost.	Bulletin de la Société Aerostatique et Meteorologique de France
Paris, Bull. Soc. Sci. Natur.	Bulletin de la Société des Sciences Naturelles de France
Paris, Bur. Long. Annu.	Annuaire pour l'An...publie par le Bureau des Longitudes
Paris, Caus. Sci.	Causeries Scientifiques de la Société Zoologique de France
Paris, Club Alpin Franc. Annu.	Annuaire du Club Alpin Francais
Paris, Com. Intl. Carte Ciel Bull.	Institut de France. Academie des Sciences. Bulletin du Comite International Permanent pour l'Execution Photographique de la Carte du Ciel
Paris Congr. Bot. Act.	Actes du Congres International de Botanique tenu a Paris in aout 1867
Paris Congr. Bot. Compt. rend.	...Comptes Rendus...Congres International de Botanique et d'Horticulture
Paris, Congr. Med. Intl.	Congres Medical International de Paris, 1867
Paris, Ecole Norm. Ann.	Annales Scientifiques de l'Ecole Normale Superieure, publies sous les auspices du Ministre de l'Instruction Publique
Paris, Ecole Poly. Corresp.	Correspondance sur l'Ecole Polytechnique, a l'usage des Eleves de cette Ecole
Paris, Ecole Poly. J.	Journal de l'Ecole Polytechnique publie par le Conseil d'Instruction de cet Etablissement
Paris, Ethnog. Soc. Compt. rend.	Comptes Rendus des Seances de la Société d'Ethnographie Americaine et Orientale
Paris, Hautes Etudes Bibl.	Bibliotheque de l'Ecole des Hautes Etudes...Section des Sciences Naturelles
Paris, Ingen. Civ. Mem.	Memoires et Compte Rendu des Travaux de la Socéité des Ingenieurs Civils (de France)
Paris, J. Bot.	Journal de Botanique, par une Société de Botanistes
Paris, J. Chir.	Journal de Chirurgie
Paris, Lab. Histol. Trav.	Ecole Pratique des Hautes Etudes. Laboratoire d'Histologie du College de France. Travaux
Paris, Mem. Acad. Med.	Memoires de l'Academie (Royale) de Medecine
Paris, Mem. Acad. Sci.	Memoires de l'Academie des Sciences
Paris, Mem. Inst.	Memoires de la Classe des Sciences mathematiques et physiques de l'Institut

Paris, Mem. Soc. Savants	Memoires des Sociétés Savants et Litteraires de la Republique Francaise
Paris, Mem. Savants Etrang.	Memoires presentes par divers Savants a l'Academie des Sciences de l'Institut de France
Paris, Mem. Soc. Ethnol.	Memoires de la Société Ethnologique
Paris, Mem. Soc. Fac. Med.	Memoires de la Société de la Faculte de Medecine
Paris, Mem. Soc. Linn.	Memoires de la Société Linneenne de Paris
Paris, Mem. Soc. Med.	Memoires de la Société de Medecine
Paris, Mem. Soc. Med. Observ.	Memoires de la Société Medicale d'Observation
Paris, Mus. Hist. Natur. Ann.	Annales du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Archiv.	Archives du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Bull.	Bulletin du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Cent.	Centenaire de la Fondation du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Mem.	Memoires du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Nouv. Ann.	Nouvelles Annales du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Nouv. Archiv.	Nouvelles Archives du Museum d'Histoire Naturelle
Paris Obs. Ann.	Annales de l'Observatoire de Paris
Paris, Obs. Montsouris Annu.	(Ville de Paris.) Annuaire de l'Observatoire (municipal de Paris, dit Observatoire) de Montsouris...
Paris, Poids Mes. Proc.-Verb.	Comite International des Poids et Mesures. Proces-Verbaux des Seances
Paris, Poids Mes. Trav. Mem.	Travaux et Memoires du Bureau International des Poids et Mesures
Paris, Recueil Soc. Med. Observ.	Recueil des travaux de la Société Medicale d'Observation de Paris
Paris, Recueil. Trav. Soc. Med. Allemande	Recueil des Travaux lus a la Société Medicale Allemande de Paris
Paris, Soc. Acclim. Bull.	Bulletin de la Société Zoologique d'Acclimatation
Paris, Soc. Anat. Bull.	Bulletin de la Société Anatomique de Paris
Paris, Soc. Anthrop. Bull.	Bulletins de la Société d'Anthropologie de Paris
Paris, Soc. Anthrop. Mem.	Memoires de la Société d'Anthropologie de Paris
Paris, Soc. Biol. Mem.	Comptes Rendus des Seances et Memoires de la Société de Biologie
Paris, Soc. Chir. Bull.	Bulletin de la Société de Chirurgie de Paris
Paris, Soc. Chir. Mem	Memoires de la Société de Chirurgie de Paris
Paris, Soc. Entom. Ann.	Annales de la Société Entomologique de France
Paris, Soc. Entom. Bull.	Bulletin de la Société Entomologique de France
Paris, Soc. Geogr. Bull.	Bulletin de la Société de Geographie
Paris, Soc. Geogr. Compt. rend.	Compte Rendu des Seances de la Société de Geographie et de la Commission Centrale
Paris, Soc. Hist. Natur. Mem.	Memoires de la Société d'Histoire Naturelle de Paris
Paris, Soc. Ing. Civ. Mem.	Memoires et Comptes Rendus des Travaux de la Société des Ingenieurs Civils
Paris Soc. Linn. Bull.	Bulletin mensuel de la Société Linneenne de Paris
Paris, Soc. Math. Bull.	Bulletin de la Société Mathematique de France
Paris, Soc. Med. Emul. Bull.	Bulletins de la Société Medicale d'Émulation
Paris, Soc. Med. Emul. Mem.	Memoires de la Société Medicale d'Émulation
Paris, Soc. Philom. Bull.	Bulletin des Sciences de la Société Philomathique de Paris

Paris, Soc. Philom. Mem. Cent.	Memoires publies par la Société Philomathique a l'occasion du Centenaire de sa Fondation, 1788–1888
Paris, Soc. Philom. Nouv. Bull.	Nouveau Bulletin des Sciences de la Société Philomatique de Paris
Paris, Soc. Philom. Proc. Verb.	Extraits des Proces-Verbaux des Seances de la Société Philomatique
Paris, Soc. Phys. Seances	Seances de la Société Francaise de Physique
Paris, Soc. Speleol. Mem.	Memoires de la Société de Speleologie
Paris Tow. Nauk Scisl. Pam.	Pamietnik Towarzystwa Nauk Scislych w Paryzu
Paris, Trav. Soc. Amat.	Notice des Travaux de la Société des Amatuers des Sciences physiques et naturelles de Paris
Parlatore, Giorn. Bot.	Giornale Botanico Italiano
Parma, Giorn. Soc. Med. Chir.	Giornale della Societa Medico-Chirurgica di Parma
Passau Ber. Nat. Ver.	...Bericht des Naturhistoischen Vereins in Passau fur...
Passau, Jahr. Naturhist. Ver.	Jahresbericht des Naturhistorischen Vereins
Pathol. Soc. Trans.	Transactions of the Pathological Society of London
Pavia Ist. Bot. Atti	Atti dell' Istituto Botanico dell' Universita di Pavia. Seguito dell' Archivio Triennale del Laboratorio di Botanica Crittogamica
Pavia Lab. Crittog. Archiv.	Archivio del Laboratorio di Botanica Crittogamica presso la R. Universita di Pavia
Peabody Acad. Mem.	Memoirs of the Peabody Academy of Science
Peabody Acad. Report	Sixth Annual Report of the Trustees of the Peabody Academy of Science.
Penn. Univ. Publ.	Publications of the University of Pennsylvania
Penzance Soc. Trans.	Transactions of the Natural History and Antiquarian Society of Penzance
Perf. Essent. Oil Rec.	Perfumery and Essential Oil Record
Perthsh. Soc. Sci. Trans. & Proc.	Transactions and Proceedings of the Perthshire Society of Natural Science
Peru P.	Peruvian Patent
Pet. Nouv. Entom.	Petites Nouvelles Entomologiques
Petermann, Mitth.	Dr. A. Petermann's Mittheilungen aus Justus Perthes' Geographischer Anstalt
Peters, Zts.	Zeitschrift fur populare Mittheilungen aus dem Gebiete der Medicin, Chirurgie, und Pharmacie; in Verbindung mit einem Vereine von Aerzten und Pharmaceuten der Herzogthümer Schleswig und Holstein
Petroleum	Petroleum
Petroleum Gaz.	Petroleum Gazette
Petroleu m Rev.	Petroleum Review
Pfluger, Archiv. Physiol	Archiv. für die gesammte Physiologie des Menschen und der Thiere
Pharm.	Pharmakologie
Pharm.-Ber. Deut.-Arzbuch.	Pharmakopoe-Bericht. Die vegetablischen Drogen des Deutschen Arzneibuches, 5te. Ausgabe, Caesar & Loretz, Halle
Pharm. Centr.	Pharmaceutisches Central-Blatt
Pharm. Centralh.	Pharmaceutische Centralhalle fur Deutschland
Pharm. Era	Pharmaceutical Era
Pharm. J.	The Pharmaceutical Journal (and Transactions)
Pharm. Post	Pharmazeutische Post
Pharm. Weekblad	Pharmazeutische Weekblad
Pharm. Ztg.	Pharmazeutische Zeitung

Pharm. Zts.	Pharmazeutische Zeitschrift
Pharm. Zts. Russland	Pharmaceutische Zeitschrift für Russland
Phil. Mag.	Philosophical Magazine
Phil. Stud.	Philosophische Studien
Phil. Trans.	Philosophical Transactions of the Royal Society of London
Phila. Acad. Natur. Sci. J.	Journal of the Academy of Natural Sciences of Philadelphia
Phila., Acad. Natur. Sci. Proc.	Proceedings of the Academy of Natural Sciences of Philadelphia
Phila. Amer. Entom. Soc.	See Amer. Entom. Soc.
Phila. Coll. Pharm. Journ.	Journal of the Philadelphia College of Pharmacy
Phila. Eng. Club	Proceedings of the Engineers' Club of Philadelphia
Phila. Entom. News	Entomological News (and Proceedings of the Entomological Section of the Academy of Natural Sciences of Philadelphia)
Phila. Entom. Soc. Proc.	Proceedings of the Entomological Society of Philadelphia
Phila. Med. Mus.	Philadelphia Medical Museum
Phila. Med. Phys. J.	The Philadelphia Medical and Physical Journal
Phila. Phot.	The Philadelphia Photographer
Philippine J. Sci.	Philippine Journal of Science
Phot. Archiv	Photographisches Archiv
Phot. Bull.	Anthony's Photographic Bulletin
Phot. Chronik.	Photographische Chronik und allgemeine Photographen-Zeitung
Phot. J.	Wilhelm Horn's Photographische Journal
Phot. Corr. (Korr.)	Photographische Korrespondenz
Phot. Mag.	Photographisches Magazine
Phot. Mitth.	Photographische Mittheilungen
Phot. Monats.	Photographische Monatshefte
Phot. News	Photographic News
Phot. Rundsch.	Photographische Rundschau und Photographisches Centralblatt
Phot. Soc. J.	Journal of the Photographic Society of London
Phot. Soc. Trans.	Trans. of the Photographic Society of London
Phot. Times	The Photographic Times
Phot. Wochenbl.	Photographisches Wochenblatt
Phot. World	The Photographic World
Phot. Centr.	Photographisches Centralblatt
Phot. Ztg.	Deutsche Photographen-Zeitung
Phys. Rev.	Physical Review
Physikal.-Chem. Zentr.	Physikalisch-chemisches Zentralblatt
Physikal. Meddel.	Physikalske Meddelelser
Physikal. Zts.	Physikalische Zeitschrift
Physiol. Russe	Le Physiologiste Russe
Physiol. Soc. Proc.	See J. Physiol.
Phytologist	The Phytologist: a popular Botanical Miscellany
Pisa, Ann. Scuola Norm.	Annali della R. Scuola Normale Superiore di Pisa. Scienze Fisiche e Matematiche
Pisa, Ann. Univ. Tosc. Sci. Cosm.	Annali della Universita Toscana. Scienze Cosmologiche
Pisa, Miscell. Med. Chir.	Miscellanea medico-chirurgico-farmaceutiche raccolte in Pisa
Pisa, Nuov. Giorn.	Nuovo Giornale de' Letterati
Pisa Soc. Sci. Proc.	Atti della Société Toscana di Scienze Naturali residente in Pisa

Pisa Soc. Tosc. Atti (Mem.)	Atti della Societa Toscana di Scienze Naturali residente in Pisa. Memorie
Pisa Soc. Tosc. Atti (Proc. Verb.)	Arti della Societa Toscana di Scienze Naturali residente in Pisa. Processi Verbali
Pistoja, Atti Accad.	Atti della R. Accademia Pistojese di Scienze, Lettere, ed Arti; Memorie di Matematica e Fisca
Plant World	Plant World, The
Plata Mus. Anales	Anales del Museo de La Plata. Materiales para la Historia fisica y moral del Continente Sud-Americano
Plata Mus. Revista	Revista del Museo de La Plata
Plon Biol. Sta. Forschungsber.	Forschungsberichte aus der Biologischen Station zu Plon
Plymouth Inst. Trans.	Annual Reports and Transactions of the Plymouth Institution and Devon and Cornwall Natural History Society
Pogg. Ann.	Poggendorff's Annalen der Physik und Chemie
Pogg. Ann. Beibl.	Poggendorff's Annalen der Physik und Chemie Beiblatter
Poligrafo	Il Poligrafo: Giornale di Science, Lettere, ed Arti
Polit.	Il Politecnico
Pollichia, Jahr.	Jahresbericht der Pollichia, eines naturwissenschaftlichen Vereins der Baierischen Pfalz (der Rheinpfalz)
Polsk. Tow. Przyrod. Kopernika	See Kosmos (Lwow)
Poly. Centr.	Polytechnisches Centralblatt
Poly. Centralh.	Polytechnische Centralhalle
Poly. Mitth.	Polytechnische Mittheilungen
Poly. Notiz.	Polytechnisches Notizblatt
Polygraph. Centr.	Polygraphisches Centralblatt
Pommer, Zts.	Schweizerische Zeitschrift fur Natur- und Heilkunde
Pop. Mag. Anthropol.	The Popular Magazine of Anthropology
Pop. Sci. Mon.	Popular Science Monthly
Popular Sci. Rev.	The Popular Science Review: a Quarterly Miscellany of entertaining and instructive articles on Scientific subjects
Pontif. Univ. Gregor.	Pontificia Universita Gregoriana. Continuazione del Bullettino Meteorologico dell' Observatorio del Cellegio Romano
Port. P.	Portuguese Patent
Portland, Soc. Natur. Hist. Proc.	Proceedings of the Portland Society of Natural History
Porto, Ann. Soc. Lit.	Annaes da Sociedade Lit. Portuense
Porto Soc. Instruc. Rev.	Revista da Sociedade de Instruccao do Porto
Potsdam Astrophys. Obs. Publ.	Publicationen des Astrophysikalischen Observatoriums zu Potsdam
Pottery Gaz.	Pottery Gazette
Pottery and Glass	Pottery and Glass
Power	Power
Prace Mat.-Fiz.	Prace Matematyczno-Fizyczne. (Mathematical and Physical Papers)
Pract. Drug.	Practical Druggist and Pharmaceutical Review of Reviews, New York
Pract. Mag.	The Practical Magazine (London)
Pract. Mechan. J	The Practical Mechanics Journal
Practitioner	The Practitioner
Prag, Abh.	Pojednani Kral. Ceske Spolecnosti Nauk. Abhandlungen der Königl. Böhmischen Gesellschaft der Wissenschaften

Prag, Ceske Ak. Fr. Jos. Pam.	Pomatnik na oslavu padesaitketeho panovnickeho Jubilea jeho Velicenstva Cisare a Krale Frantiska Josefa I. Vydala Ceska Akademie Cisare Frantisks Josefa pro Vedy, Slovesnost a Umeni. (Memoira in celebration of the fifty years Jubilee of the reign of H. I. & R. M. Francis Joseph I. Published by the Bohemian Imperial Francis Joseph Academy of Science, Literature and Art)
Prag, Ceske Akad. Fr. Jos Rozpr. (Trida 2)	Rozpravy Ceske Akademie Cisare Frantiska Josefa pro Vedy, Slovesnost a Umeni v Praze. (Trida II.) (Transactions of the Bohemian Imperial Francis Joseph Academy of Science, Literature and Art in Prague. Class II)
Prag. Fr. Jos. Acad. Sci. Bull.	Academie des Sciences de l'Empereur Francois Joseph I. Bulletin International
Prag, Jahr. Böhm. Mus.	Jahrbucher des Bohmischen Museums für Natur- und Landerkunde
Prag, Jahr. Realschule	Jahresbericht der k. k. Bohmischen Ober-Realschule zu Prag
Prag, Lotos Abh.	Abhandlungen des Deutschen Naturwissenschaftlich-Medicinischen Vereines fur Böhmen "Lotos"
Prag, Monatschr. Mus.	Monatsschrift der Gessellschaft des vaterländischen Museums in Bohmen
Prag, Sitzber.	Zpravy o Zasedani (Vestnik) Kralovske Ceske Spolecnosti Nauk. Trida. Mathematicko-Prirodove-decka. Sitzungsberichte der Konigl. Bohmischen Gesellschaft der Wissenschaften. Mathematisch-Naturwissenschaftliche Classe
Prag Sternw. Magn. Mereorol. Beob.	Magnetische und Meteorologische Beobachtungen an der K. K. Sternwarte zu Prag
Prag, Verh.	Verhandlungen der Gesellschaft des vaterländisches Museums in Bohmen
Prag, Vierteljahrschr.	Vierteljahrschrift fur die praktische Heilkunde
Pressburg, Corresp. Blatt.	Correspondenzblatt des Vereins für Naturkunde zu Pressburg
Pressburg, Verh.	Verhandlungen des Vereins für Naturkunde zu Pressburg
Presse Sci.	Presse Scientifique des Deux Mondes
Preuss. Bot. Ver. Sitzber.	See Konigsberg Schriften
Preuss. Geod. Inst. Publ.	Publication des Konigl Preuss. Geodätischen Instituts
Preuss. Geod. Inst. Veroff.	Veroffentlichung des Konigl. Preussischen Geodatischen Instituts
Preuss. Landes-Oekon -Kolleg. Archiv.	See Landw. Jbuch.
Pribram Bergakad	See Wien, Berg- u. Huttenm. Jbuch.
Princeton Mus. Contr.	Contributions from the (E. M.) Museum of Geology and Archaeology of Princeton College
Pringsheim, Jahr. Wiss. Bot.	Jahrbucher fur Wissenschaftliche Botanik
Print. Reg.	Printers' Register
Prog. agric. viti.	Progres agricole et viticole
Proc. Amer. Acad.	Proceedings of the American Academy of Arts Sciences
Proc. Amer. Inst. Elec. Eng.	Proceedings of the American Institute of Electrical Engineers
Proc. Amer. Micro. Soc.	Proceedings of the American Microscopical Society
Proc. Amer. Pharm. Assoc.	Proceedings of the American Pharmaceutical Association
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society

Proc. Amer. Soc. Civil Eng.	Proceedings of the American Society of Civil Engineers
Proc. Amer. Soc. Micro.	Proceedings of the American Society of Microscopists
Proc Amer. Soc. Test. Mat.	Proceedings of the American Society for Testing Materials
Proc. Amer. Water Works Assoc.	Proceedings of American Water Works Association
Proc. Assoc. Off. Agric. Chem.	Proceedings of the Association of Official Agricultural Chemists, Washington
Proc. Austral. Inst. Min. Eng.	Proceedings Australian Institute of Mining Engineers
Proc. Cambr. Phil. Soc.	Proceedings of the Cambridge Philosophical Society
Proc. Chem. Soc.	Proceedings of the Chemical Society (London)
Proc. Eng. Soc. Western Penn.	Proceedings of the Engineers' Society of Western Pennsylvania
Proc. Inst. Civil Eng.	Proceedings of the Institution of Civil Engineers
Proc. Inst. Mech. Eng.	Proceedings of the Institution of Mechanical Engineers
Proc. Natl. Wholesale Drug. Assoc.	Proceedings of the National Wholesale Druggists' Association
Proc. Physiol. Soc.	Proceedings of the Physiological Society
Proc. Roy. Soc. Edinb.	Proceedings of the Royal Society of Edinburgh
Proc. Roy. Soc. London	Proceedings of the Royal Society of London
Proc. Roy. Soc. Med.	Proceedings of the Royal Society of Medicine
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine
Proc. U. S. Naval Inst.	Proceedings of U. S. Naval Institute
Progres Med.	Le Progres Medical. Journal de Medecine, de Chirurgie et de Pharmacie
Progressive Age	Progressive Age
Propogation ind.	La Propogation industrielle. Revue mensuelle illustre des inventions, machines, appareils et procedes de la France, etc.
Prov. Med. Assoc. J.	Journal of the Provincial Medical Association
Prov. Med. Surg. Assoc. Trans.	Transactions of the Provincial Medical and Surgical Association
Psyche	Psyche. Organ of the Cambridge Entomological Club
Psychol. Med. J.	Journal of Psychological Medicine
Publ. Carnegie Inst.	Publications of the Carnegie Institution of Washington
Publ. ind.	Publication industrielle des machines par Armengaud
Public Analysts Proc.	Proceedings of the Society of Public Analysts
Public Health	Public Health
Pulp Paper Mag. Can.	Pulp and Paper Magazine of Canada
Pure Products	Pure Products. Scientific Station for Pure Products, New York
Puy, Soc. Agric. Ann.	Annales de la Société d'Agriculture, Sciences, etc., du Puy
Quart. J. Chem. Soc.	Quarterly Journal of the Chemical Society
Quart. J. Dent. Sci.	Quarterly Journal of Dental Science.
Quart. J. exp. Physiol.	Quarterly Journal of experimental Physiology
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society
Quart. J. Math.	The Quarterly Journal of Pure and Applied Mathematics
Quart. J. Micro. Sci.	Quarterly Journal of Microscopical Science
Quart. J. Micro. Soc.	Quarterly Journal of the Microscopical Society
Quart. J. Sci.	The Journal of Science and the Arts Continued as the Quarterly Journal of Science, Literature, and Arts

Quebec, Lit. Hist. Soc. Trans.	Transactions of the Literary and Historical Society of Quebec
Queensl. P.	Queensland Patent
Queensl. Annu. Rep. Brit. N. Guinea	Annual Report on British New Guinea
Queensl. Natur. Hist. Soc. Trans.	Transactions of the Natural History Society of Queensland
Queensl. Mus. Ann.	Annals of the Queensland Museum
Queensl. Roy. Soc. Proc.	The Proceedings of the Royal Society of Queensland
Quekett Micro. Club J.	Journal of the Quekett Microscopical Club
Quetelet, Corresp. Math.	Correspondance Mathematique et Physique
Radium	Radium, Le
Railroad Eng. J.	The Railroad and Engineering Journal. The American Railroad Journal and Van Nostrand's Engineering Magazine have been consolidated in this publication
Ranuzzi, Annuario Geogr.	Annuario geographico Italiano
Rass. minerar.	Rassegna mineraria metallurgica e chimica
Rauch Staub	Rauch und Staub
Rayer, Archiv.	Archives de Medecine comparee
Reclam, Kosmos	Kosmos: Zeitschrift fur angewandte Naturwissenschaften
Records Min.	Records of Mining
Recueil Math. (Moscou)	Recueil Mathematique. Publie par la Société Mathematique de Moscou
Rec. Trav. Chim. Pays-Bas	Recueil des Travaux Chimiques des Pays-Bas (et de la Belgique)
Rec. Zool. Suisse	Recueil Zoologique Suisse, comprenant l'Embryologie, l'Anatomie et l'Histologie comparees, la Physiologie, l'Ethologie, la Classification des Animaux vivants et fossiles
Regensburg Bot. Ges.	See Flora
Regensburg Bot. Ges. Denkschr.	Denkschriften der Königlich (Bayerischen) Botanischen Gesellschaft zu Regensburg
Regensburg, Bot. Ztg.	Botanische Zeitung; herausg. von der k. Baier. Botanischen Gesellschaft zu Regensburg
Regensburg, Korresp. Blatt.	Korrespondenz-Blatt des Zoologischmineralogischen Vereins in Regensburg
Reichert, Archiv.	Archiv für Anatomie, Physiologie, und wissenschaftliche Medicin
Reil, Archiv.	Archiv. für die Physiologie
Reimann's Ztg.	Reimann's Farberzeitung
Reims, Seances Acad.	Seances et Travaux de l'Academie de Reims
Rend. soc. chim. ital.	Rendiconti della societa chimica italiana
Rep.	Repertorium, Repertoire Repertory
Rep. Anal. Chem.	Repertorium der analytischen Chemie...Organ des Vereins Analytischer Chemiker
Rep. Anat. Physiol.	Repertoire generale d'Anatomie et de Physiologie pathologiques et de Clinique chirurgicale
Rep. Chim.	Repertoire generale de Chimie (1901–), G. Jaubert
Rep. Chim. pure (appl.)	Repertoire de Chimie pure (et appliquée) (Societe Chimique de Paris, 1859–1864)
Rep. Pat. Inv.	The Repertory of Patent Inventions and other discoveries and improvements in arts, manufactures and agriculture
Rep. Math.	Repertorium der literarischen Arbeiten aus dem Gebiéte der reinen und angewandten Mathematik

Rep. Meteorol.	Repertorium für Meteorologie, herausgegeben von der Kaiserlichen Akademie der Wissenschaften
Rep. Pharm.	Repertorium für die Pharmacie
Rep. Phys.	Repertorium der Physik
Rep. Phys.-Tech.	See Carl
Rep. Chem. Lab. Amer. Med. Ass.	Reports of the Chemical Laboratory of the American Medical Association, Chicago
Rep. Council Pharm. Chem.	Reports of the Council of Pharmacy and Chemistry, American Medical Association, Chicago
Rep. H. M. Insp. Expl.	Report of His Majesty's Inspectors of Explosives
Rep. N. Y. Bd. Pharm.	Report of the New York State Board of Pharmacy
Rev. Anthrop.	Revue d'Anthropologie
Rev. Artill.	Revue d'Artillerie
Rev. Biol. Nord France	Revue Biologique du Nord de la France
Rev. Bot.	Rev. de Botanique. Bulletin mensuel de la Société Francaise de Botanique
Rev. Bryol.	Revue Bryologique. Bulletin bimestriel consacre a l'Etude des Mousses et des Hepatiques
Rev. chim. ind.	Revue de chimie industrielle et La revue de physique et de chimie
Rev. Cours. Sci.	Revue des Cours Scientifiques de la France et de l'Etranger
Rev. deux Mondes	Revue des deux Mondes (Paris)
Rev. Entom.	Revue d'Entomologie publiee par la Société Francaise d'Entomologie
Rev. gen. Bot.	Revue generale de Botanique
Rev. gen. chim.	Revue generale de chimie pure et appliquee (G. Jaubert)
Rev. gen. lait	Revue generale du lait
Rev. gen. mat. color.	Revue generale de matieres colorantes et de leurs applications aux textiles
Rev. gen. sci.	Revue generale des sciences pure et appliquee
Rev. Hortic.	Revue Horticole, Journal d'Horticulture pratique
Rev. hyg. pol. sanitaire	Revue d'hygiene et de police sanitaire
Rev. Ind.	Revue Industrielle
Rev. Ind. Chim.	Revue des industries chimiques et agricoles
Rev. Mag. Zool.	Revue et Magazin de Zoologie, pure et appliquee
Rev. Maritime Colon.	Revue Maritime (et Coloniale)
Rev. Med. Chir.	Revue Medico-Chirurgicale de Paris
Rev. Med. Franc. Etrang.	Revue Medicale Francaise et Etrangere
Rev. Met.	Revue de Metallurgie
Rev. Mycol.	Revue Mycologique. Recueil trimestriel illustre consacre a l'Etude des Champignons
Rev. phot.	Revue de photographie
Rev. Quest. Sci.	Revue des Questions scientifiques publiee par la Société Scientifique de Bruxelles
Rev. Sci.	(la) Revue Scientifique (de la France et de l'Etranger. Revue des Cours Scientifiques)
Rev. Sci. Natur.	Revue des Sciences Naturelles
Rev. Soc. Hyg. Aliment.	Revue de la société scientifique d'Hygiene alimentaire et de l'alimentation rationelle de l'homme
Rev. Suisse Zool.	Revue Suisse de Zoologie (et) Annales (de la Société Zoologique Suisse et) du Musee d'Histoire Naturelle de Geneve
Rev. Univ. Mines	Revue universelle des Mines, de la Metallurgie, des Travaux Publics, des Sciences et des Arts Appliquee a l'Industrie. Annuaire de l'Association des Ingenieurs sortis de l'Ecole de Liege

Rev. Vit.	Revue Viticulture
Rev. Zool.	Revue Zoologique, par la Société Cuvierienne
Revista Brazil.	Revista Brazileira, Journal de Sciencias, Lettras, e Artes
Revista, Chim. pure app.	Revista de chimica pure applicada
Revista ind. agric. Tucuman	Revista industrial y agrocola de Tucuman
Revista Ligure	Revista Ligure, giornale di Lettere, Scienze, etc.
Revista Med. Chile	Revista medica de Chile
Revista Med. Cirug. Habana	Revista de Medicina y Cirugia, Habana
Revista Minera	Revista Minera, periodico cientifico e industrial
Revista real acad. cien. Madrid	Revista de la real academia de ciencias de Madrid
Revista Telegr.	Revista de Telegrafos
Revista Trim. Microgr.	Revista Trimestral Micrografica. Organo del Laboratorio Histologico de la Facultad de Medicina de Madrid
Rhea	Rhea, Zeitschrift fur die gesammte Ornithologie
Rheinische Monatsschr.	Rheinische Monatsschrift fur praktische Aerzte
Rheinl. Westphal.	See Bonn.
Rheinl. Westphal. Corresp.	Correspondenzblatt des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Rheinl. Westphal. Verh.	Verhandlungen des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Rheinl. Westphal. Sitzber.	Sitzungsbericht des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Rheinpfalz Pollichia Festschr.	Festschrift zur Funfzigjahrigen Stiftungsfeier der Pollichia, Naturwissenschaftlichen Vereines der Rheinpfalz
Rheinpfalz Pollichia Jahr.	Jahresbericht der Pollichia, eines Naturwissenschaftlichen Vereins der Rheinpfalz
Rheinpfalz Pollichia Mitth.	Mittheilungen der Pollichia, eines Naturwissenschaftlichen Vereins der Rheinpfalz
Rheinpfalz Pollichia Sep. Ausg.	...Separat-Ausgabe der Pollichia, des Naturwissenschaftlichen Vereines der Pfalz
Rhodora	Rhodora. Journal of the New England Botanical Club
Riga, Arb. Naturf. Vei.	Arbeiten des Naturforschenden Vereins in Riga
Riga, Corresp. Blatt. Naturf. Ver.	Correspondenz-Blatt des Naturforschenden Vereins in Riga
Rio de Janeiro Archiv. Palestr.	Archivos da Palestra Scientifica do Rio de Janeiro
Rio de Janeiro Mus. Nac. Archiv.	Archivos do Museu Nacional do Rio de Janeiro
Rio de Janeiro Mus. Nac. Revista	Revista do Museu Nacional do Rio de Janeiro... (Seguimento aos Archivos do Museu Nacional)
Rio de Janeiro Obs. Annaes	(Annaes do Imperial Observatorio do Rio de Janeiro)
Rio de Janeiro Obs. Bol.	Boletim mensal do Observatorio do Rio de Janeiro
Rio de Janeiro Obs Revista	Revista do Observatorio. Publicacao mensal do Imperial Observatorio do Rio de Janeiro
Rio, Revista	Revista tri mensal de Historia e Geographis: Journal do Instituto Historico e Geographico Brasileiro
Rio, Soc. Vell. Trabal	Trabalhos da Sociedade Vellosiana (Bibliotheca Guanabarense)
Riv.	Rivista
Riv. Bolognese	Rivista Bolognese di Scienze e Lettere
Riv. Geogr. Ital.	Rivista Geografica Italiana (e Bolletino della Societa di Studi Geografici e Coloniali in Firenze)

Riv. Ital. Sci. Natur. Napoli	Rivista Italiana di Scienze Naturali e loro Applicazioni pubblicata per cura degli Aspiranti Naturalisti
Riv. Ital. Sci. Natur. Siena	Rivista Italiana di Scienze Naturali e Bollettino del Naturalista Collettore, Allevatore, Coltivatore
Riv. Mat.	Rivista di Matematica
Riv. Mineral. Crist.	Rivista di Mineralogia e Cristallografia Italiana
Riv. Patol. Veg.	Rivista di Patologia Vegetale
Riv. Sci.-Ind.	Rivista Scientifico-Industriale delle principali Scoperte ed Invenzioni fatte nelle Scienze e nelle Industrie
Riv. Sper. di Freniatria	Rivista Sperimentale di Freniatria e di Medicina legale...
Riv. Vit. Ital.	Rivista di Viticoltura ed Enologia Italiana...
Robin, J. Anat.	Journal de l'Anatomie et de la Physiologie normales et pathologiques de l'homme et des animaux
Rochelle	See under Charente-Inf.
Rochester Acad. Sci. Proc.	Proceedings of the Rochester New York Academy of Science
Rochester Trans. Elec. Med. Assoc.	Transactions of the National Electic Medical Association at its Third Meeting, at Rochester, U. S.
Rock Products	Rock Products
Röhr, Notizen	Notizen aus dem Gebiete der practischen Pharmacie
Rollett	See Graz.
Roma	See Congr. Med. Int. Atti, 1894
Roma, Atti Nuovi Lincei	Atti dell' Accademia Pontificia de' Nuovi Lincei
Roma, Atti Reale Accad.	Atti della Reale Accademia dei Lincei
Roma, Corrisp. Sci.	Corrispondenza Scientifica in Roma per le avanzamento delle Scienze, etc.
Roma Ist. Bot. Annuario	Annuario del R. Istituto Botanico di Roma
Roma Lab. Anat. Norm. Ric.	Ricerche fatte nel Laboratorio di Anatomia Normale della R. Universita di Roma
Roma, Nuovi Lincei Mem.	Memorie della Pontificia Accademia dei Nouvi Lincei
Roma, Oss. Coll. Rom. Mem.	Memorie del R. Osservatorio del Collegio Romano
Roma, R. Accad. Lincei	Atti della R. Accademia dei Lincei
(Roma), Soc. Ital. Mem.	Memorie di Mathematica e di Fisica della Societa Italiana delle Scienze
Roma, Soc. Studi Zool. Boll.	Bolletino della Societa Romana per gli Studi Zoologici
Roma, Specola Vaticana Pubbl.	Pubblicazioni della Specola Vaticana
Roma, Uff. Centr. Meterol. Ann.	Annali dell' Ufficio Centrale di Meterologia Italiana
Römer, Archiv Bot.	Archiv fur die Botanik
Roser Wunderlich, Archiv	Archiv fur physiologische Heilkunde. Continued as the Archiv. d. Heilk.
Rotterdam Nieuwe Verh.	Nieuwe Verhandelingen van het Bataafsch Genootschap der Proefondervindelijke Wijsbegeerte Rotterdam
Rouen, Bull. Soc. Emul.	Bulletins (des travaux) de la Société Libre d'Émulation de Rouen
Rouen, Soc. Sci. Bull.	Bulletin de la Société des Amis des Sciences Naturelles de Rouen
Rouen, Trav. Acad.	Precis analytique des Travaux de l' Academie des Sciences, Belles-Lettres, et Arts de Rouen
Roumanie Inst. Meteorol. Ann.	Annales de l'Institut Meteorologique de Roumanie Annalele Institutului Meteorologio al Romaniei
Roy. Engin. Papers	Papers on subjects connected with the duties of the Corps of Royal Engineers
Roy. Inst. J.	Journal of the Royal Institution of Great Britain

Roy. Inst. Proc.	Notices of the Proceedings at the Meetings of the Members of the Royal Institution of Great Britain, with Abstracts of the Discourses delivered at the Evening Meetings
Roy. School Naval Archit. Ann.	The annual of the Royal School of Naval Architecture and Marine Engineering
Roy. Soc. Proc.	Abstracts of the Papers printed in the Philosophical Transactions of the Royal Society of London, from 1800 to 1854 inclusive. Continued as the Proceedings of the Royal Society of London
Rugby, Natur. Hist. Soc. Reports	Reports of the Rugby School Natural History Society
Russ. Annu. Geol. Mineral.	Russian Annual of Geology and Mineralogy
Russ. Annuaire Mines	Annuaire du Journal des Mines de Russie
Russ. Chem. Soc. J.	Journal of the Russian Chemical Society
Russ. Geogr. Ges. Denkschr.	Denkschriften der Russischen Geographischen Gesellschaft zu St. Petersburg
Russ. J. exp. Landw.	Russiches Journal für experimentelle Landwirtschaft
Russ. Jahr. Pharm.	Russisches Jahrbuch der Pharmacie
Russ. P.	Russian Patent
Russ. Pharm. Zts.	Pharmaceutische Zeitschrift für Russland
Russ. Phys.-Chem. Soc. J.	Journal of the Russian Physico-Chemical Society of the Imperial University of St. Petersburg
Rust, Mag.	Magazin fur die gesammte Heilkunde, etc.
S. Africa Chem. Metall. Soc.	The Journal of the Chemical and Metallurgical Society of South Africa
S. Africa Chem. Metall. Soc. Proc.	The Proceedings of the Chemical and Metallurgical Society of South Africa
S. Africa. Mus. Ann.	Annals of the South African Museum
S. Africa. Phil. Soc. Trans.	The Transactions of the South African Philosophical Society
S. Austral. P.	South Australian Patent
S. Austral. Roy. Soc. Mem.	Memoirs of the Royal Society of South Australia
S. Austral. Roy. Soc. Trans.	Transactions and Proceedings and Report of the Royal Society of South Australia
S. C. Med. Assoc. Trans.	Transactions of the South Carolina Medical Association
S. London Entom. Natur. Hist. Soc. Proc.	(Abstract of) Proceedings of the South London Entomological and Natural History Society
S. Wales Inst. Civ. Engin. Proc.	Proceedings of the South Wales Institute of Civil Engineers
S. Wales Roy. Inst. Report	The annual report of the Council of the Royal Institution of South Wales, with Appendix of Original Papers on Scientific Subjects
Sächs. Ingen Ver. Mitth.	Mittheilungen des Sächsischen Ingenieur-Vereins; herausg. v. d. Verwaltungsrathe des Vereins
Sächs. Meteorol. Inst. Abh.	Abhandlungen des Königl. Sächs. Meteorologischen Institutes
Sachs. Thüring. Naturwiss. Ver.	See Zts. Naturwiss.
Salem	See Essex Institute
San Fernando Obs. Marina An.	Anales del Instituto y Observatorio de Marina de San Fernando
Sanitary Record	Sanitary Record and Journal of Municipal Engineering, The
Santiago Chile, Univ. Anales	(Republica de Chile.) Anales de la Universidad
Sao Paulo, Rev. Mus. Paulista	Revista do Museu Paulista

Saone-et-Loire Soc. Sci. Bull.	Bulletins de la Société des Sciences Naturelles de Saone-et-Loire
Saone-et-Loire Soc. Sci. Mem.	Memoires de la Société des Sciences Naturelle de Saone-et-Loire
Sarthe, Bull. Soc. Agric.	Bulletin de la Société d'Agriculture, Sciences, etc., de la Sarthe
Savoie Acad. Mem.	Memoires de l'Academie des Sciences, Belles-Lettres et Arts de Savoie
Savoie Soc. Hist. Natur. Bull.	Bulletins de la Société d'Histoire Naturelle de Savoie
Savoie Soc. Hist. Natur. (Compt. rend.)	Société d'Histoire Naturelle de Savoie a Chambery
Schaffhausen	See Schweizer. Entom. Gesell.
Scheik. Onderz.	See Utrecht. Scheik. Onderzoek
Schemnitz Bergakad.	See Wien, Berg- u. Hüttenm. Jahr.
Scherer, J. Chem.	Allgemeines Journal der Chemie
Schlesw.-Holst. Naturwiss. Ver. Schr.	Schriften des Naturwissenschaftlichen Vereins für Schleswig-Holstein
Schlömilch, Zts.	Zeitschrift fur Mathematik und Physik
Schneider, Ann. Staatsarzneik.	Annalen der gessammten Staatsarzneikunde
School Mines Quart.	School of Mines, Quarterly, The
School of Mines, Records	Records of the School of Mines
Schrader, J. Bot.	Journal für die Botanik
Schröder, Berig. Zeevaart.	Berigten en Verhandelingen over eenige onderwerpen des Zeevaarts
Schröder, Verh. Zeevaart.	Verhandelingen en Berigten over eenige onderwerpen der Zeevaart-Kunde
Schuh Ind.	Schuh Industrie
Schumacher, Jahr.	Jahrbuch, (H. C. Schumacher, (1836-38))
Schwäb. Ges. Denkschr.	Denkschriften der Schwäbischen Gesellschaft der Aerzte und Naturforscher
Schwalbe	Ornithologische Section der k. k. Zoologisch-Botanischen Gesellschaft in Wien. Die Schwalbe. Berichte des Comites für Ornithologische Beobachtungs-Stationen in Oesterreich
Schweigger, J. (Schw. J.)	Journal für Chemie und Physik
Schweiz. Alpenclub Jahr.	Jahrbuch des Schweizer Alpenclub
Schweiz. Bot. Ges. Ber.	Berichte der Schweizerischen Botanischen Gesellschaft
Schweiz. Entom. Ges. Mitth.	Mittheilungen der Schweizerischen Entomologischen Gesellschaft
Schweiz. Ges. Neue Denkschr.	Neue Denkschriften der allgemeinen Schweizerischen Gesellschaft fúr die gesammten Naturwissenschaften
Schweiz. Ges. Verh.	Verhandlungen der Schweizerischen Gesellschaft für die geasmmten Naturwissenschaften
Schweiz. Monatsschr.	Schweizerische Monatsschrift für praktische Medizin
Schweiz. Naturf. Ges.	See Beitr. Kryptog. Schweiz.
Schweizer. Naturf. Ges. Verh.	Verhandlungen der Schweizerischen Naturforschenden Gesellschaft
Schweiz. Phot.-Ver.	See Wien, Phot. Correspond.
Schweiz. Poly. Zts.	Schweizerische polytechnische Zeitschrift. Unter Mitwirkung des Schweizerischen Polytechnikums, etc.
Schweiz. Wochenschr.	Schweizerisch Wochenschrift für Chemie und Pharmacie
Schweiz. Zts. Heilk.	Schweizerische Zeitschrift für Heilkunde
Sci.	Science
Sci. Abst.	Science Abstracts. Physics and Electrical Engineering
Sci. Amer.	Scientific American

Sci. Amer. Suppl.	Scientific American Supplement
Sci. Can.	Scientific Canadian
Sci. Ind. Bull. Roure-Bertrand Fils	Scientific et Industrial Bulletin Roure-Bertrand Fils
Sci. Proc. Roy. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society
Sci. Rev.	The Scientific Review and Journal of the Inventors Institute
Sci. Trans. Roy. Dublin Soc.	Scientific Transactions of the Royal Dublin Society
Scienz. Ital. Congr.	Nuovo Congresso degli Scienziati Italiani in Venezia; porzione geologica
Sclater, Ibis	The Ibis, a Magazine of General Ornithology
Scott. Arbor. Soc. Trans.	Transactions of the Scottish Arboricultural Society
Scott. Geogr. Mag.	The Scottish Geographical Magazine
Scott. Meteorol. Soc. J.	Journal of the Scottish Meteorological Society
Scott. Micro. Soc. Proc. & Trans.	Proceedings and Transactions of the Scottish Microscopical Society
Scott. Natur.	A Magazine of Scottish Natural History (and Journal of the Perthshire Society of Natural Science)
Scott. Soc. Arts Trans.	Transactions of the Royal Scottish Society of Arts
Seeman, J. Bot.	The Journal of Botany, British and Foreign
Seifenfabr.	Seifenfabrikant, Der
Seifens. Ztg.	Seifensieder Zeitung und Revue über die Harz, Fett und Oelindustrie
Seine (Dep. de la)	See (France) Soc. Agr. Mem.
Seine, Mem. Soc. Agric.	Memoires d'Agriculture par la Société Agricole de la Seine
Seine-et-Oise, Mem.	Memoires de la Société des Sciences Naturelles de Seine et Oise
Seism. J. Japan	Seismological Journal of Japan
Selenka, Archiv Zool.	Nederländisches Archiv für Zoologie
Semi-Ann. Rep. Schimmel & Co.	Semi-Annual Report, Schimmel & Co., Miltitz
Senckenberg. Naturf. Ges. Abh.	Abhandlungen herausg. von der Senckenbergischen Naturforschenden Gesellschaft
Senckenberg, Naturf. Ges. Ber.	Bericht über die Senckenbergische naturforschende Gesellschaft in Frankfurt am Main
Shanghai, J.	Journal of the North-China Branch of the Royal Asiatic Society
Shanghai, J. Lit. Soc.	Journal of the Literary and Scientific Society of Shanghai
Shoe Lea. Reporter	Shoe and Leather Reporter
Shropsh. Soc. Trans.	Transactions of the Shropshire Archaeological and Natural History Society
Sicilia, Atti Soc. Acclim.	Atti della Societa di Acclimazione e di Agricoltura in Sicilia
Sidereal Messenger	The Sidereal Messenger
Siebenb. Karpath. - Ver. Jahr.	Jahrbuch des Siebenbürgischen Karpathen-Vereins
Siebold, J. Geburtshülfe	Journal für die Geburtshülfe, Frauenzimmer, etc., von Elias von Siebold
Siebold Kölliker, Zts.	Zeitschrift für wissenschaftliche Zoologie
Siebold, Lucina	Lucina; eine Zeitschrift zur Vervollkommung der Entbindungskunst
Siena, Atti Accad.	Atti dell' Accademia delle Scienze di Siena detta de' Fisio-critici
Silbermann, Rev. Entom.	Revue Entomologique

Silliman, J.	The American Journal of Science and Arts
Singapore Roy. Asiat. Soc. J.	Journal of the Straits Branch of the Royal Asiatic Society. Singapore
Sitzber. kais. Akad. Wiss. Wien.	Sitzungsberichte der kaiserlichen Akademie der Wissenschaften, Wien (Mathematisch-naturwissenschaftliche Klass) Abteilungen I, IIa, IIb, III
Sitzb. könig Akad. München	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München
Sitzber. könig. Akad. Wiss. Berlin	Sitzungsber der koniglich preussischen Akademie der Wissenschaften zu Berlin
Sitzber. könig. preuss. Akad.	Sitzungsberichte der koniglich preussischen Akademie der Wissenschaften
Skand. Archiv Physiol.	Skandinavisches Archiv für Physiologie
Skand. Naturf. Forh.	Forhandlingar vid det af Skandinaviska Naturforskare och Lakare hallna Möte i Gotheborg
Skand. Naturf. Mod. Forh.	Forhandlingerne ved de Skandinaviske Naturforskeres 11te Mode i Kjobenhavn fra den 3die til den 9de Juli, 1873
Skand. Natur Möt. Forh.	Förhandlingar vid de Skandinaviska Naturforskarnes Tolfte Mote i Stockholm fran den 7 till den 14 Juli, 1880
Skandia	Skandia. Tidskrift för Vetenskap och Konst; utgifven af Svenska Litteratur-Foreningen
Skofitz	See Oesterreich. Botan. Zeitschr.
Skofitz, Bot. Wochenbl.	Oesterreichisches Botanisches Wochenblatt
Skofits, Bot. Zts.	Oesterreichische Botanische Zeitschrift
Smithsonian Contrib	Smithsonian Contributions to Knowledge
Smithsonian Inst. Astrophys. Obs. Ann	Annals of the Astrophysical Observatory of the Smithsonian Institution
Smithsonian Inst. Bur. Ethnol. Report	Annual Report of the Bureau of (American) Ethnology to the Secretary of the Smithsonian Institution
Smithsonian Misc. Coll.	Smithsonian Miscellaneous Collections
Smithsonian Report	Annual Report of the Board of Regents of the Smithsonian Institution, showing the Operations, Expenditures and Condition of the Institution
Snelling's Phot. J.	Snelling's Photographisches Journal
Soc. Bot. Ital Bull.	See Nuovo Giorn. Bot. Ital
Soc. Broteriana	See Coimbra, Soc. Broter. Biol.
Soc. Elvet. Sci. Naturf. Atti	See Schweiz. Naturf. Ges. Verh.
Soc. Entom. Ross. Horae	Horae Societatis Entomologicae Rossicae variis sermonibus in Rossia usitatis editae
Soc. Franc. Bot.	See Rev. Bot.
Soc. Franc. Entom.	See Rev. Ent.
Soc. Freniatr. Ital.	See Riv. Sper. di Freniatria
Soc. Geogr. Finland	See Fennia
Soc. Helvet. Actes.	Actes de la Société Helvetique des Sciences Naturelles
Soc. Helvet. Sci. Naturf Act.	See Schweiz. Natf. Ges. Verh.
Soc. Ital. Antrop.	See Arch. Antropologia
Soc. Ital. Fis.	See Nuovo Cimento
Soc. Ital. Micro. Boll.	See Acireale, Soc. Ital. Micr. Boll.
Soc. Ital. Sci.	See (Roma), Soc. Ital. Mem.
Soc. Ital. Sci. Nat.	See Milano, Soc. Ital.
Soc. Ligust. Sci. Natur Geogr.	See Genova, Soc. Ligust. Atti
Soc. Malacol. France	See Ann. Malacol.

Soc. Malacol. Ital. Bull.	See Bull. Malacol. Ital.
Soc. Meteorol. Ital.	See Moncalieri Oss. Boll.
Soc. Mex. Hist. Natur.	See Naturaleza
Soc. Napoli	Societa reale di Napoli. Rendiconto dell' Academia delle Scienze fisiche e mathematiche
Soc. Nat. Sicil.	See Nat. Sicil.
Soc. Pharm. Anvers	See J. de Pharm.
Soc. Public Analysts	See Analyst
Soc. Speleol.	See Spelunca, Paris
Soc. Telegr.-Engin. Elect.	See Telegr. Eng. J.
Soc. Tosc. Sci. Nat.	See Pisa Soc. Tosc.
Soc. Ven.-Trent. Sci. Nat.	See Padova Soc. Sci.
Soc. Zool. Suisse Ann.	See Rev. Suisse: Zool.
Soc. Zool. Tokyo	See Annot. Zool. Jap.
Somerset. Archaeol. Soc. Proc.	Proceedings of the Somersetshire Archaeological and Natural History Society
Somerset. Sov. Proc.	Somersetshire Archaeological and Natural History Society's Proceedings
Somme (Dep. de la)	See under Amiens
Southern Pharm. J.	Southern Pharmaceutical Journal
Span. P.	Spanish Patent
Spatula	Saptula (The), Boston
Spelunca. Paris	Spelunca. Bulletin de la Société de Speleologie
Sperimentale	Lo Sperimentale. Giornale Italiano di Scienze Meidche
Spettatore Vesuvio	Lo Spettatore del Vesuvio e de' Campi Flegrei
Spettrosc. Ital. Mem.	Memorie della Societa degli Spettroscopisti Italiani
Spongia, Comm.-Med.	Commentarii di Medicina
Sprechsaal	Sprechsaal
Spregnel, Jahr.	Jahrbücher der Gewächskunde
Sprengst. Waffen Mun.	Sprengstoffe, Waffen und Munition
St. Andrew's Med. Grad. Assoc. Trans.	Transactions of the St. Andrew's Medical Graduates Association
St. Barthol. Hosp. Reports	St. Bartholomew's Hospital Reports
St. Etienne, Bull. Soc. Ind. Mineral	Bulletin de la Société de l'Industrie Minerale
St. Gallen, Ber. Naturwiss. Ges.	Berichte über die Thätigkeit der St. Gallischen Naturwissenschaftlichen Gesellschaft
St. Louis, Bot. Gard. Report	Missouri Botanical Garden Report
St. Louis, Trans. Acad. Sci.	The Transactions of the Academy of Science of St. Louis
St. Petersb. Acad. Sci. Bull.	Bulletin scientifique publie par l'Academie Imperiale des Sciences de St. Petersbourg
St. Petersb. Acad. Sci. Compt. rend.	Compte Rendu de l'Academie Imperiale des Sciences de St. Petersbourg
St. Petersb. Acad. Sci. Mem.	Memoires de l'Academie Imperiale des Sciences de St. Petersbourg
St. Petersb. Acad. Sci. Nova Acta.	Nova Acta Academiae Scientiarum Imperialis Petropolitanae
St. Petersb. Acad. Sci. Recueil	Recueil des Actes des Seances Publiques de l'Academie Imperiale des Sciences de St. Petersbourg
St. Petersb. Ann. Mines Russ.	Annuaire du Journal des Mines de Russie
St. Petersb. Archiv. Sci. Biol.	Archives des Sciences Biologiques publiees par l'Institut Imperial de Medecine Experimentale a St. Petersbourg
St. Petersb., Congr. Bot. Bull.	Bulletin du Congres International de Botanique et d'Horticulture de St. Petersbourg le 6/18, le 8/20 et le 10/22 Mai 1869

St. Petersb. Inst. Med. Exper.	See St. Petersb. Arch. Sci. Biol.
St. Petersb. Med. Zts.	St. Petersburger Medicinische Zeitschrift
St. Petersb. Med. Wochenschr.	St. Petersburger Medicinische Wochenschrift
St. Petersb. Mem. Savants Etrang.	Memoires presentes a l' Academie Imperiale des Sciences de St. Petersbourg par divers Savants
St. Petersb. Mineral. Ges. Verh.	Verhandlungen der Russisch-Kaiserlichen Mineralogischen Gesellschaft zu St. Petersbourg
St. Petersb., Russe Geogr. Mem. (Geogr.)	Memoirs de la Société Imperiale Russe de Geographie Section de Geographie generale
St. Petersb., Russ. Geogr. Soc. Bull.	Bulletins of the Imperial Russian Geographical Society
St. Petersb. Schr. Mineral.	Schriften der in St. Petersburg gestifteten Kaiserlich-Russischen Gesellschaft für die gesammte Mineralogie
St. Petersb. Verh. Mineral. Ges.	Verhandlungen der Kaiserlich-Russischen Mineralogischen Gesellschaft zu St. Petersburg
St. Petersb. Verm. Abh.	Vermischte Abhandlungen aus dem Gebiete der Heilkunde von einer Gesellschaft pract. Aerzte zu St. Petersburg. Additional title in 1835, Medizinisch-praktische Abhandlung von Deutschen in Russland lebenden Aerzten. Continued as the Neue Abhandlung St. Petersburg
St. Quentin, Ann.	Annales Agricoles du department de l'Aisne, publiees par la Société des Sciences, Arts, Belles-Lettres, et Agriculture de St. Quentin. Annales Scientifiques, Agricoles, et Industrielles du departement de l'Aisne (Société Academique de Saint Quentin)
St. Quentin, Mem.	Memoires de la Société des Sciences, Arts, Belles-Lettres, et Agriculture de la ville de St. Quentin
St. Quentin, Seances Publ.	Société des Sciences, Arts, Belles-Lettres, et Agriculture de la ville de St. Quentin: Seances publiques.
St. Quentin, Travaux	Société Academique des Sciences, Arts, Belles-Lettres, et Agriculture de St. Quentin (Aisne)
St. Thomas's Hosp. Reports	St. Thomas's Hospital Reports
Stahl Eisen (Zts)	Stahl und Eisen, Zeitschrift für das deutsche Eisenhüttenwesen
Stavanger Mus. Aarsber.	Stavanger Museums Aarsberetning
Staz. sper. agrar. ital.	Stazioni sperimentali agraria italiana, La
Steiermark. Geog. Mont. Ver. Ber.	Bericht des Geognostisch-montanistischen Vereins für Steiermark
Steiermark Mitth.	Mittheilungen des Naturwissenschaftlichen Vereines fur Steiermark
Steiermark. Mont. Lehranst. Jahr.	Die Steiermarkisch standische montanistische Lehranstalt zu Vordernberg
Stein, Ann.	Annalen der Geburtshulfe uberhaupt und der Entbindungsanstalt zu Marburg insbesondere
Stettin, Entom. Ztg.	Entomologische Zeitung; herausg. v. d. Entomologischen Vereine zu Stettin
Steyermärk. Zts.	Steyermärkische Zeitschrift
Stirling Field Club Trans	Stirling Field Club....Transactions
Stirling Soc. Trans.	Stirling Natural History and Archaeological Society. Transactions
Stockholm, Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar
Stockholm, Bihang Akad. Handl.	Bihang till Kongl. Svenska Vetenskaps Akademiens Handlingar
Stockholm Bot. Sällsk.	See Bot. Centrbl.

Stockholm Entom. För.	See Ent. Tidskr.
Stockholm, Horti Bergiani Acta	Acta Horti Bergiani. Meddelanden fran Kongl. Svenska Vetenskaps-Akademiens Trädgard Bergielund utgifna af Bergianska Stiftelser
Stockholm, Öfversigt	Öfversigt af Kongl. Vetenskaps Akademiens Förhandlingar
Stockholm Physiol. Lab. Mitth.	Mittheilungen vom Physiologischen Laboratorium des Carolinischen Medico-Chirurgischen Instituts in Stockholm
Stockholm, Svenska Läk. Sallsk Handl.	Handlingar ved Svenska Läkare-Sällskapet
Stockholm, Vet. Akad. Lefnadsteckn.	Lefnadsteckningar öfver Kongl. Svenska Vetenskaps-Akademiens efter ar 1854 aflidna Ledamoter
Stockholm, Ymer	Ymer. Tidskrift utgifven af Svenska Sallskapet för Antropologi och Geografi
Strasbourg Soc. Hist. Natur. Mem.	Memoires de la Société du Museum d'Histoire Naturelle de Strasbourg
Strasbourg Soc. Sci. Bull.	Bulletin de la Société des Sciences Naturelles de Strasbourg
Strasbourg Soc. Sci. J.	Journal de la Société des Sciences, Agriculture, et Arts, du departement du Bas-Rhin
Strasbourg Soc. Sci. Mem.	Memoires de la Société des Sciences, Agriculture, et Arts, de Strasbourg
Stray Feathers	Stray feathers. A journal of Ornithology for India and its dependencies
Stricker	See Medizin. Jahr.
Sts. Settl. P.	Straits Settlement Patent
Student	The Student and Intellectual Observer of Science, Literature, and Art
Sturgeon, Ann. Elect.	Annals of Electricity, Magnetism, and Chemistry, and Guardian of Experimental Science
Sturgeon, Ann. Phil.	Annals of Philosophical Discovery and Monthly Reporter of the Progress of Practical Science
Sucr.	La sucrerie indigene
Sucr. Belge	Sucrerie Belge, La
Sucr. ind. colon.	Sucrerie indigene et colonaile, La
Suddeut. Apoth. Ztg.	Suddeutsche Apotheker Zeitung
Suisse Soc. Zool. Ann.	See Rev. Suisse Zool.
Surveyor	Surveyor and Municipal and County Engineer, The
Sussex Natur. Hist. Soc. Proc.	See Brighton Nat. Hist. Soc. Proc.
Svea	Svea. Tijdskrift for Vetenskap och Konst
Svensk farm. Tidskr.	Svensk farmaceutisk Tidskrift, Stockholm
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift
Svenska Lak. Sallsk. Forh.	Forhandlingar ved Svenska Läkare-Sallskapets Sammankomster
Svenska Mosskulturför.	Svenska Mosskulturföreningens
Svenska Sällsk. Antrop. & Geogr.	See Stockh., Ymer
Swart, Verh.	Verhandelingen en Berigten betrekkelijk het Zeewezen en de Zeewaartkunde
Swed. P.	Swedish Patent
Swiss P.	Swiss Patent
Sydney	See New South Wales
Sydney Aust. Mus. Mem.	The Australian Museum, Sydney. Memoirs
Sydney, Austral. Mus Records	Records of the Australian Museum
Symons, Meteorol. Mag.	Symon's monthly Meteorological Magazine
Tablettes Zool.	Tablettes Zoologiques

Tagbl. Frankf. Naturf.	Tageblatt Frankfurter Naturforscher
Taprobanian	The Taprobanian, a Dravidian Journal of Oriental Studies in and around Ceylon, in Natural History, Archaeology, Philology, History
Tasmania J. Natur. Sci.	The Tasmanian Journal of Natural Science, Agriculture, Statistics, etc.
Tasmania P.	Tasmanian Patent
Tasmania, Roy. Soc. Monthly Not.	Monthly Notices of Papers and Proceedings of the Royal Society of Tasmania
Tasmania, Roy. Soc. Reports	Reports of the Royal Society of Tasmania
Taylor, Sci. Mem.	Scientific Memoirs, selected from the Transactions of Foreign Academies and Learned Societies and from Foreign Journals
Tech. Blätter	Technische Blätter. Vierteljahrschrift des Deutschen Polytechnischen Vereins in Bohmen
Tech. Chem. Jahr.	Technisch-Chemisches Jahrbuch (Biedermann)
Tech. Gemeindebl.	Technisches Gemeindeblatt
Technikum	Technikum des Ledermarkts
Technol.	Le Technologiste (F. Malepeyre)
Technol. Quart.	Technology Quarterly
Teign Field Club Proc.	Reports of the Proceedings of the Teign Naturalists' Field Club
Tekn. Tidskr.	Teknisk Tidskrift
Telegr. Eng. J.	Journal of the Society of Telegraph-Engineers and Electricians
Telegr. J.	The Telegraphic Journal and Electrical Review
Telegr. Ver. Zts.	Zeitschrift des Deutsch-osterreichischen Telegraphen-Vereins
Temminck, Verh.	Verhandelingen over de natuurlijke Geschiedenis der Nederlandsche overzeesche bezittingen, door de leden der Natuurkundige Commissie in Oost-Indie en andere schrijvers
Termr. Füz.	Termeszetrajzi Fuzetek...Kiadja a Magyar Nemzeti Muzeum. (Natural History Magazine...published by the Hungarian National Museum)
Termt. Közlön.	Termeszettudomanyi Kozlony...Kiadja a K. M. Termeszettudomanyi Tarsulat. (Natural Science Papers...Published by the Royal Hungarian Natural Science Society)
Terrestrial Magn.	Terrestrial Magnetism (and Atmospheric Electricity). An International Quarterly Journal
Texas Acad. Sci. Trans.	Transactions of the Texas Academy of Science
Text. Amer.	Textile American
Text. Col.	The Textile Colorist
Text. Färb. Ztg.	Textil und Farberei-Zeitung
Text. Mfr.	The Textile Manufacturer
Text. Rec.	The Textile Record
Text. World Rec.	Textile World Record
Text. Ztg.	Textil Zeitung
Textilfreund	Der Textilfreund
Teyler's Verh.	Geologische Verhandel af Antwoord af de in 1828 uitgeschrevene en in 1830 herhaalde Prysvraag: Wat men van Geologie, etc.
Therap. Gaz.	The Therapeutic Gazette
Therap. Monats.	Therapeutische Monatshefte
Therap. Neuheit	Therapeutischen Neuheiten, Leipzig
Therapist	Therapist (The) London

Thomson, Ann. Phil.	Annals of Philosophy, or Magazine of Chemistry, Mineralogy, Mechanics, and the Arts
Thomson, Archiv. Entom.	Archives Entomologiques
Thomson, Rec.	Records of General Science
Thonind. Ztg.	Thonindustrie-Zeitung
Throndhjem, Skrifter	Der Kongelige Norske Videnskabers-Selskabs Skrifter i det 19 de Aarhundrede
Tidskr. Kemi. Farm. Terapi	Tidskrfit for Kemi Farmaci Terapi
Tidskr. Mat.	Tidsskrift for Matematik
Tidskr. Mat. Fys.	Tidskrift for Matematik och Fysik, tillegnad den Svenska Elementar-Undervisningen
Tidskr. Phys. Chem.	Tidskrift for Physik og Chemi samt disse Videnskabers Anvendelse
Tiedemann, Zts.	Zeitschrift fur Physiologie
Tijdschr. Entom.	Tijdschrift voor Entomologie; uitgegeven door de Nederlandsche Entomologische Vereeniging
Tijschr. Genootsch. Vis. Unita	Tijdschrift voor Genees-, Heel-, Verlos-, en Scheikundige Wetenschappen, van Wege et Genootschap: "Vis Unita Fortior," te Hoorn.
Tijdschr. Ing.	Tijdschrift van het Koninklijk Instituut van Ingenieurs
Tijdschr. nijv.	Tijdschrift ter befordering van nijverhed
Tijdstroom.	De Tijdstroom; Maandschrift gewijd van Wetenschap, etc.
Tilesius, Jahr.	Jahrbuch der Naturgeschichte zur Anzeige und Prüfung
Timehri	Timehri being the Journal of the Royal Agricultural and Commercial Society of British Guiana
Tirol, Ber. Ver. Durchf.	Bericht über die General-Versammlung des Vereins zur geogr. montan. Durchforschung des Landes Tirol, etc.
Tischl. Ztg.	Deutsche Tischlerzeitung
Tokio Univ. Mem.	Memoirs of the Science Department, University of Tokio, Japan
Tokyo Bot. Soc.	See Bot. Mag., Tokyo
Tokyo, Coll. Sci. J.	The Journal of the College of Science, Imperial University, Japan
Tokyo Geogr. Soc. J.	Journal of the Tokio Geographical Society
Tonind. Ztg.	Tonindustrie Zeitung
Töpfer Ztg.	Deutsche Töpfer und Ziegler Zeitung
Torino, Accad. Sci. Atti	Atti della R. Accademia delle Scienze di Torino
Torino, Accad. Sci. Mem.	Memoire della R. Accademia delle Scienze di Torino
Torino, Ann. Clin.	Annali Clinici
Torino, Lavori Sci. Fis. Mat.	Notizia storica dei lavori fatti dalla Classe di Scienze Fisiche e Mathematiche della R. Accademia delle Scienze negli anni 1864–65
Torino Mus. Boll.	Bollettino dei Musei di Zoologia ed Anatomia comparata della R. Universita di Torino
Torrey Bot. Club Bull.	Bulletin of the Torrey Botanical Club
Torrey Bot. Club Mem.	Memoirs of the Torrey Botanical Club
Tortolini, Ann.	Annali di Scienze, Matematiche, e Fisiche
Toulouse Acad. Sci. Bull.	Bulletin de l'Academie des Sciences, Inscriptions et Belles-Lettres de Toulouse
Toulouse, Acad. Sci. Mem.	Memoires de l'Academie des Sciences, Inscriptions et Belles-Lettres de Toulouse
Toulouse Fac. Sci. Ann.	Annales de la Faculte des Sciences de Toulouse, pour les Sciences Mathematiques et les Sciences Physiques
Toulouse Obs. Ann.	Annales de l'Observatoire Astronomique, Magnetique et Meteorologique de Toulouse.

Toulouse Soc. Hist. Natur. Bull.	Bulletin de la Société d'Histoire Naturelle de Toulouse
Toulouse Soc. Sci. Bull.	Bulletin de la Société des Sciences Physiques et Naturelles de Toulouse
Trans. Acad. Sci. St. Louis	Transactions of the Academy of Sciences of St. Louis
Trans. Amer. Ceram. Soc.	Transactions of the American Ceramic Society
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers
Trans. Amer. Inst. Homoeop.	Transactions of the American Institute of Homoeopathy, Philadelphia
Trans. Amer. Inst. Min. Eng	Transactions of the American Institute of Mining Engineers
Trans. Amer. Med. Assoc. Sec. Pharm. Therap.	Transactions of the Section on Pharmacology and Therapeutics of the American Medical Association
Trans. Amer. Micro. Soc.	Transactions of the American Microscopical Society
Trans. Amer. Soc. Civ. Eng.	Transactions of the American Society of Civil Engineers
Trans. Cambr. Phil. Soc.	Transactions of the Cambridge Philosophical Society
Trans. Can. Inst.	Transactions of the Canadian Institute
Trans. Engl. Ceram. Soc.	Transactions of the English Ceramic Society
Trans. Faraday Soc.	Transactions of the Faraday Society
Trans. Geol. Soc. S. Africa	Transactions of the Geological Society of South Africa
Trans. Illum. Eng. Soc.	Transactions of the Illuminating Engineering Society
Trans. Inst. Brew.	Transactions of the Institute of Brewing
Trans. Jenner Inst. Prev. Med.	Transactions of the Jenner Institute of Preventive Medicine
Trans. Kansas Acad. Sci.	Transactions of the Kansas Academy of Science
Trans. Med.	Transactions Medicales; Journal de Medecine pratique
Trans. Min. Geol. Inst. India	Transactions of the Mining and Geological Institute of India
Trans. Natl. Eclec. Med. Assoc.	Transactions National Eclectic Medical Association Indianapolis
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science
Transv. P.	Transvaal Patent
Trans. Path. Soc.	Transactions of the Pathological Society
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy
Trans. Roy. Soc. Can.	Transactions of the Royal Society of Canada
Trans. Roy. Soc. Edinb.	Transactions of the Royal Society of Edinburgh
Trans. Roy. Soc. London	Transactions of the Royal Society of London
Trans. Soc. Engin	Society of Engineers, Transactions
Trav. Com. Hyg. Publ.	Recueil des Travaux du Comite consultatif d'Hygiene Publique de France et des Actes Officiels de l'Administration Sanitaire
Trenton Natur. Hist. Soc. J.	Journal of the Trenton, New Jersey, Natural History Society
Treviso, Mem. Ateneo	Memorie Scientifiche e Litterarie dell' Ateneo di Treviso
Trier, Jahr.	Jahresbericht der Gesellschaft für nützliche Forschungen zu Trier
Triest Zool. Sta. Arb.	See Wien. Zool. Inst. Arb.
Trieste, Boll.	Bollettino della Societa Adriatica di Scienze Naturali in Trieste
Trieste Mus. Civ. Atti	Atti del Museo Civico di Storia Naturale di Trieste
Trieste, Program. Civ. Scuola	Programma della Civica Scuola Reale autonoma in Trieste

Trinidad Field Natur. Club J.	Journal of the Trinidad Field Nauralists' Club
Trinidad P.	Trinidad Patent
Trinidad, Proc. Sci. Assoc.	Proceedings of the Scientific Association of Trinidad
Trinidad, Sci. Assoc. Proc.	Proceedings of the Scientific Association of Trinidad
Trommsdorff, J. Pharm.	Journal der Pharmacie für Aerzte und Apotheker, und Chemiker
Tromso. Mus. Aarsh.	Tromso Museums Aarshefter
Tropenpflanzer	Tropenpflanzer (Der), Berlin
Tsch. Mineral. Mitth.	Tschermak's Mineralogische Mitteilungen
Tuberculosis	Tuberculosis. The Journal of the National Association for the Prevention of Consumption and other forms of Tuberculosis
Tübinger Blätter	Tübinger Blätter für Naturwissenschaften und Arzneikunde
Tübingen Bot. Inst. Unters.	Untersuchungen aus dem Botanischen Institut zu Tubingen
Tunis P.	Tunis Patent
Turin, Mem. Acad.	Memoires de l'Academie Royale des Sciences de Turin
Tyneside Natur. Field Club Trans.	Transactions of the Tyneside Naturalist's Field Club
U. K. Mar. Biol. Assoc. J.	Journal of the Marine Biological Association of the United Kingdom
U. S. Bur. Anim. Ind. Bull.	U. S. Department of Agriculture. Bureau of Animal Industry
U. S. Bur. Anim. Ind. Report	Annual Report of the Bureau of Animal Industry
U. S. Chief Signal Off. Ann. Report	Annual Report of the Chief Signal Officer (of the Army) to the Secretary of War
U. S. Coast Geod. Surv. Bull.	United States Coast and Geodetic Survey. Bulletin
U. S. Comm. Agric. Report	Report of the Commissioner of Agriculture
U. S. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U. S.
U. S. Dept. Agric. Report	Reports of the Department of Agriculture, U. S.
U. S. Dept. Agric. Yearb.	Yearbook of the United States Department of Agriculture
U. S. Disp.	United States Dispensatory
U. S. Div. Biol. Surv. Bull.	U. S. Department of Agriculture. Division of Biological Survey. Bulletin
U. S. Div. Chem. Bull.	U. S. Department of Agriculture. Division of Chemistry. Bulletin
U. S. Div. Entom. Bull.	U. S. Department of Agriculture. Division of Entomology
U. S. Div. Entom. Insect Life	U. S. Department of Agriculture. Division of Entomology. (Periodical Bulletin.) Insect Life
U. S. Div. Entom. Tech. Ser.	U. S. Department of Agriculture. Division of Entomology. Technical Series
U. S. Div. Ornith. Mamm. Bull.	U. S. Department of Agriculture. Division of Economic Ornithology and Mammalogy. Bulletin
U. S. Div. Soils Bull.	U. S. Department of Agriculture. Division of (Agricultural) Soils. Bulletin
U. S. Entom. Comm. Bull.	Department of the Interior...Bulletin of the United States Entomological Commission
U. S. Entom. Comm. Report	(U. S.) Department of the Interior (Agriculture)... Report of the United States Entomological Commission
U. S. Fish Comm. Bull.	Bulletin of the United States Fish Commission
U. S. Fish Comm. Report	United States Commission of Fish and Fisheries. Report of the Commissioner

U. S. Geol. Surv.	United States Geological Survey
U. S. Monthly Weath. Rev.	(United States) Monthly Weather Review
U. S. Mus. Bull.	Department of the Interior...Bulletin of the United States National Museum
U. S. Mus. Proc.	Department of the Interior...Proceedings of the United States National Museum
U. S. Mus. Report	See Smithsonian Rep.
U. S. Mus. Spec. Bull.	Smithsonian Institution. United States National Museum. Special Bulletin
U. S. Naval Inst. Proc.	United States Naval Institute Proceedings
U. S. Naval Med. Bull.	United States Naval Medical Bulletin
U. S. Naval Obs. Publ.	Publications of the United States Naval Observatory
U. S. N. Amer. Fauna	U. S. Department of Agriculture. Division of Ornithology and Mammalogy. North American Fauna
U. S. P.	United States Patent
U. S. Ph.	United States Pharmacopoeia
U. S. Secty. Agric. Report	Report of the secretary of agriculture
U. S. Signal Serv. Notes	United States of America: War Department. Signal Service Notes
U. S. Signal Serv. Pap.	United States of America, War Department. Professional Papers of the Signal Service
U. S. Surv. Terr. Reports	...Annual Report of the United States Geological (and Geographical) Survey of the Territories
U. S. Weath. Bur. Bull.	U. S. Department of Agriculture. Weather Bureau. Bulletin
U. S. Weath. Bur. Report	U. S. Department of Agriculture. Weather Bureau. Report of the Chief of the Weather Bureau
U. Serv. Inst. J.	Journal of the royal United Service Institution, Whitehall Yard
Udine, Relazioni	Relazioni intorno agli Atti dell' Accademia di Udine
Uhland's Tech. Rund.	Uhland's Technische Rundschau
Umschau	Umschau, Die
Ung. Naturwiss. Ver. Jahr.	Abhandlungen aus dem dritten Bande der Jahrbücher des Ungarischen naturwissenschaftlichen Vereins zu Pest, in Deutscher Uebersetzung Red. von J. Szabo
Univ. Ill. Bull.	University of Illinois Bulletin
Unters. Naturlehre	Untersuchungen zur Naturlehre des Menschen und der Thiere
Upsala, Arsskrift	Universitets Arsskrift utgifven af Kongl. Vetenskaps-Societeten i Upsala
Upsala Bot. För.	See Bot. Notiser
Upsala, Diss. Acad.	Dissertationes Academicae Upsaliae habitae
Upsala, Frey Tidskr.	Frey Tidskrift for Vetenskap och Konst
Upsala Läkaref̈or. Förh.	Upsala Läkareforenings Forhandlingar
Upsala Naturvet. Studentsällsk.	See Bot. Centrbl.
Upsala, Soc. Sci. Nova Acta	Nova Acta Regiae Societatis Scientiarum Upsaliensis
Urug. P.	Uruguay Patent
Utrecht, Aanteek. Prov. Genoots.	Aanteekeningen van het Verhandelde in de Sectie-Vergaderingen van het Provinciaal Utrechtsch Genootschap van Kunsten en Wetenschappen
Utrecht, Ann. Acad.	Annales Academiae Rheno-Trajectinae
Utrecht, Kliniek	Kliniek: Tijdschrift voor Wetenschappenlijke Geneeskunde
Utrecht, Nieuwe Verh. Prov. Genootsch.	Nieuwe Verhandelingen van het Provinciaal Utrechsch Genootschap van Kunsten en Wetenschappen

Utrecht, Onderzoek.	Onderzoekingen gedaan in het Physiologisch Laboratorium der Utrechtsche Hoogeschool
Utrecht, Scheik. Onderzoek.	Scheikundige Onderzoekingen, gedaan in het Laboratorium der Utrechtsche Hoogeschool
Utrecht, Verh. Prov. Genootsch.	Verhandelingen van het Provinciaal Utregtsch Genootschap van Kunsten en Wetenschappen
Valais Soc. Murith.	See Bull. Murith.
Valencia, Act. Med.	Actas del Instituto Medico Valenciano
Valenciennes, Mem. Soc. Agric.	Memoires de la Société d'Agriculture, des Sciences, et des Arts, de l'Arrondissement de Valenciennes
Valentin, Rep.	Repertorium für Anatomie und Physiologie
Van Diemen's Land, Roy. Soc. Papers	Papers and Proceedings of the Royal Society of Van Diemen's Land
Van Diemen's Land, Roy. Soc. Reports	Reports of the Royal Society of Van Diemen's Land (For Horticulture, Botany, and the Advance of Science)
Van Nostrand's Mag.	Van Nostrand's Engineering Magazine
Vargasia	Vargasia: Boletin de la Sociedad de Ciencias fisicas y naturales de Caracas
Varsovie Soc. Natur. Trav.	Comptes Rendus et Memoires de la Société des Naturlistes (a l'Universite Imperiale) de Varsovie
Varsovie Soc. Natur. Trav. (Mem.)	Travaux de la Société des Naturalistes de l'Univsite Imperiale de Varsovie
Vaucluse Acad. Mem.	Memoires de l'Academie de Vaucluse
Venez. P.	Venezuela Patent
Venezia, Ateneo	L'Ateneo Veneto: Rivista mensile di Science, Lettere ed Arti
Venezia, Ateneo Esercit.	Esercitazioni Scientifiche e Letterarie dell' Ateneo di Venerzia
Venezia, Atti	Atti delle Adunanze dell' I. R. Istituto Veneto di Scienze, Lettere, ed Arti
Venezia, Atti Ateneo	Atti dell' Ateneo Veneto
Venezia, Iat. Atti	Atti del Reale Istituto Veneto di Scienze, Lettere ed Arti
Venezia, Ist Mem.	Memorie del Reale Istituto Veneto di Scienze, Lettere ed Arti
Venezia, Mem. Ist Beneto	Memorie dell' I. R. Istituto Veneto di Scienze, Lettere, ed Arti
Ver. Anal. Chem.	See Repert. Anal. Chem.
Verh. Genootsch. Occ. Qui Non.	Verhandelingen van het Genootschap: "Occidir qui qui non servat."
Verh. Ges. deut. Naturf. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte
Verh. poly. Ges.	Verhandlungen der poltechnischen Gesellschaft
Verh. Ver. Gewerbefleis.	Verhandlungen des Vereins zur Beforderung des Gewerbefleisses in Preussen
Veröffent. kais. Gesundh.	Veröffentlichungen des kaiserlichen Gesundheitsamts
Verona, Soc. Ital. Mem.	Memorie di Matematica e Fisica della Societa Italiana della Scienze
Vet. J. London	Veterinary Journal, London
Vet. Med. Assoc. Trans.	Transactions of the Veterinary Medical Association
Veterinarian	The Veterinarian
Victoria Dept. Mines Spec. Reports	Victoria. Department of Mines. Special Reports
Victoria Field Natur. Club	See Victorian Natlist.
Victoria Inst. J.	Journal of the Transactions of the Victoria Institute or Philosophical Society of Great Britain
Victoria Natur.	The Victorian Naturalist. The Journal and Magazine of the Field Naturalists' Club of Victoria

Victoria P.	Victoria Patent
Victoria Pharm. Soc. J.	Quarterly Journal and Transactions of the Pharmaceutical Society of Victoria
Victoria Proc. Roy. Soc.	Proceedings of the Royal Society of Victoria
Victoria Trans. Phil. Inst.	Transactions of the Philosophical Institute (afterwards Royal Society) of Victoria
Victoria Trans. Roy. Soc.	Transactions of the Royal Society of Victoria
Victoria Zool. Soc. Proc.	Proceedings of the Zoological and Acclimatisation Society of Victoria
Vierteljahrschr. ärzt. poly.	Vierteljahrschrift der ärztlichen Polytechnik
Vierteljahrschr. gericht. Med.	Vierteljahrschrift für gerichtliche Medizin und öffentliches Sanitatwesen
Vierteljahrschr. gesundheitspf.	Vierteljahrschrift fur Gesundheitspflege
Vierteljahrschr. Zahnheilk.	Vierteljahrschrift für Zahnheilkunde
Virchow's Archiv path.	Virchows Archiv für pathologie, Anatomie, und Histologie
Viviani, Ann. Bot.	Annali di Botanica
Voget, Notizen	Notizen aus dem Gebeite der practischen Pharmacie
Voigt, Mag.	Magazin fur den neuesten Zustand der Naturkunden, mit Rücksicht auf die dazu gehörigen Hulfswissenschaften
Vosges Soc. Emul. Ann.	Annales de la Société d'Émulation du Department des Vosges
W. Austral. P.	West Australian Patent
Wag. Free Inst. Sci. Trans.	Transactions of the Wagner Free Institute of Science of Philadelphia
Wag. Jahr.	(Wagner's) Jahresbericht über Chemische Technologie
Walker, Elect. Mag.	The Electrical Magazine
Warwick. Field Club Proc.	Proceedings of the Warwickshire Naturalists' and Archaeologists' Field Club
Warwick. Natur. Hist. Soc. Rep.	Annual Reports of the Warwickshire Natural History and Archaeological Society
Washburn Obs. Publ.	Publications of the Washburn Observatory of the University of Wisconsin
Washington	Int. Med. Congr. Trans., 1887
Washington	See also under U. S.
Washington Biol. Soc. Proc.	Proceedings of the Biological Society of Washington
Washington, Mem. Natl. Acad.	Memoirs of the National Academy of Sciences
Washington, Natl. Inst. Bull.	Bulletin of the Proceedings of the National Institution for the Promotion of Science
Washington Phil. Soc. Bull.	Bulletin of the Philosophical Society of Washington
Wasser Abwasser	Wasser und Abwasser
Water Supply Papers	Water Supply Papers
Watford Nat. Hist. Soc. Trans.	Transactions of the Watford Natural History Society and Hertfordshire Field Club
Weale, Quart. Papers	Quarterly Papers on Engineering
Weber, Archiv	Archiv für die systematische Naturgeschichte
Weimer, Zts. Geburtsk.	Gemeinsame Deutsche Zeitschrift für Geburtskunde
Weinlaube	Die Weinlaube
Wernigerode Naturwiss. Ver. Schr.	Schriften des Naturwissenschaftlichen Vereins des Harzes in Wernigerode
West. Brewer	Western Brewer, The
West. Chem. Met.	Western Chemist and Metallurgist
West. Drug.	Western Druggist

Westphäl, Prov. Blätt.	Westphälische Provinciàl-Blätter. Verhandlungen der Gesellschaft zur Beforderung der vaterländischen Cultur in Minden
Westphäl, Ver. Jahr.	Jahres-Bericht des Westfälichen Provinzial-Vereins fur Wissenschaft und Kunst
Wetter	Das Wetter. Meteorologische Montasschrift für Gebildete aller Stände
Wetterau. Ges. Ann.	Annalen der Wetterauischen Gesellschaft für die gesammte Naturkunde
Wetterau. Ges. Festgabe.	Naturhistorische Abhandlungen aus dem Gebiete der Wetterau
Wetterau. Ges. Jahr.	Jahresbericht der Wetterauischen Gesellschaft für die gesammte Naturkunde
Wetterau. Ges. Naturk. Ber.	Bericht der Wetterauischen Gesellschaft für die gesammte Naturkunde zu Hanau
Wiad. Mat.	Wiadomosci Matematyczne
Wieck's Gewerbeztg.	Deutsche Gewerbezeitung (F. Wieck)
Wied. Ann. Phys.	Annalen der Physik und Chemie (Wiedemann's)
Wied. Archiv	Archiv für Zoologie und Zootomie
Wied. Zool. Mag.	Zoologisches Magazin
Wiegmann, Archiv	Archiv für Naturgeschichte
Wien Abh.	Naturwissenschaftliche Abhandlungen
Wien Akad. Ber.	Sitzungsberichte der kaiserlichen Akademie der Wissenschaften; Mathematisch-Naturwissenschaftliche Klasse, II Abthlg. Wien
Wien Akad. Denkschr.	Denkschriften der kaiserlichen Akademie der Wissenschaften. Mathematisch - Naturwissenschaftliche Classe
Wien Akad. Sitzber.	Sitzungsberichte der Mathematisch-Naturwissenschaftlichen Classe der kaiserlichen Akademie der Wissenschaften
Wien Almanach	Almanach der kaiserlichen Akademie der Wissenschaften
Wien Alpen-Verein, Jahr.	Jahrbuch des Oesterreichishcen Alpen-Vereins
Wien Anthrop. Ges. Mitth.	Mittheilungen der Anthropologischen Gesellschaft
Wien Anz.	Anzieger der kaiserlichen Akademie ker Wissenschaften: Math.-Naturwissensch. Classe
Wien Denkschr.	Denkschriften der Kaiselichen Akademie der Wissenschaften: Mathematisch - naturwissenschaftliche Classe
Wien Embryol. Inst. Mitth.	Mittheilungen aus dem Embryologischen Institute der k. k. Universität in Wien
Wien Geogr. Ges. Abh.	Abhandlungen der k. k. Geographischen Gesellschaft in Wien
Wien Geogr. Ges. Festschr.	Festschrift der k. k. Geographischen Gesellschaft 1884–1898
Wien Geogr. Ges. Mitth.	Mittheilungen der k. k. Geographischen Gesellschaft in Wien
Wien Med. Chir. Acad. Abh.	Abhandlungen der k. k. medicinisch-Chirurgischen Josephs-Academie zu Wien
Wien Med. Chir. Acad. Beob.	Beobachtungen der k. k. medicinisch-chirurgischen Josephs-Academie zu Wien
Wien Naturhist. Hofmus. Ann.	Annalen des k. k. Naturhistorischen Hofmuseums
Wien Ornith. Vrr. Mitth.	Mittheilungen des Ornithologischen Vereins in Wien
Wien Phot. Corresp.	Photographische Correspondenz. Organ der Photograph. Gesellsch. in Wien
Wien Schr.	Schriften des Vereines zur Verbreitung naturwissenschaftlicher Kenntnisse

Wien Sitzber.	Sitzungsberichte der Mathematisch-naturwissenschaftlichen Classe der Kaiserlichen Akademie der Wissenschaften
Wien, Sonnblick-Ver. Jahr.	Jahres-Bericht des Sonnblick-Vereines. Wien
Wien. technol. Blätter	Wiener technologishe Blatter
Wien Ver. Naturwiss. Kennt. Schr.	Schriften des Vereins zur Verbreitung Naturwissenschaftlicher Kenntnisse in Wien
Wien, Ver. Ges. Aerzte.	Verhandlungen der k. k. Gesellschaft der Aerzte zu Wien
Wien Verh. Gewerb-Vereins.	Verhandlungen des Neiderösterreichischen Gewerb-Vereins
Wien Wochenbl. Aerzte	Wochenblatt der k. k. Gesellschaft der Aerzte in Wien
Wien Zts. Ges. Aerzte	Zeitschrift der k. k. Gesellschaft der Aerzte zu Wien
Wien, Zool. Bot. Ges. Festschr.	Festschrift zur Feier des fünfundzwanzigjahrigen Bestehens der k. k. Zoologisch-Botanischen Gesellschaft in Wien
Wien, Zool. Bot. Verh.	Verhandlungen der k. k. Zoologisch-Botanischen Gesellschaft in Wien
Wien, Zool. Inst. Arb.	Arbeiten aus dem Zoologischen Institute der Universitat Wien ind der Zoologischen Station in Triest
Wiener Entom. Monatschr.	Wiener Entomologische Monatschrift
Wiener Entom. Ver. Jahr.	Jahresbericht des Wiener Entomologischen Vereins
Wiener Entom. Ztg.	Wiener Entomologische Zeitung
Wiener klin. Wochenschr.	Wiener klinische Wochenschrift
Wiener landw. Ztg.	Wiener landwirtschaftliche Zeitung
Wiener Med. Wochenschr.	Wiener medicinische Wochenschrift
Wiener Mitth. Phot.	Wiener Mitteilungen (Photographischen Inhalts)
Wiener Mus. Ann.	Annalen des Wiener Museums der Naturgeschichte
Wiener Poly. J.	Allgemeines Wiener polytechnisches Journal
Wiener Ztg.	Wiener Zeitung
Wiener Zts. Physik.	Zeitschrift fur Physik, Chemie, und Mineralogie
Wild, Rep. Meteorol.	Repertorium fur Meteorologie, herausg. von der kaiserlichen Akad. der Wissenschaften
Wilna, Collect. Med. Chir.	Collectanea medico-chirurgica Caesarea Academiae Medico-Chirurgicae cura edita
Wilts, Archaeol. Natur. Hist. Mag.	Magazine of the Archaeological and Natural History Society of Wiltshire
Wimereux Lab. (Stat.) Zool.	See Lille Inst. Zool. Trav.
Winchester, J. Sci. Soc.	Journal of Proceedings and Annual Reports of the Winchester and Hampshire Scientific and Literary Society
Wisconsin Acad. Trans.	Transactions of the Wisconsin Academy of Sciences, Arts, & Letters
Wisconsin Natur. Hist. Soc Bull.	Bulletin of the Wisconsin Natural History Society
Wisconsin Natur. Hist. Soc. Pap.	Occasional Papers of the Natural History Society of Wisconsin
Wisconsin Natur. Hist. Soc. Proc.	Proceedings of the Natural History Society of Wisconsin
Wisconsin Univ. Bull. Sci.	Bulletin of the University of Wisconsin. Science Series
Wiss. Abh. Phys.-Tech. Reichsanstalt	Wissenschaftliche Abhandlungen der Physikalish-Technischen Reichsanstalt
Wiss. Meeresuntersuch.	Wissenschaftliche Meeresuntesuchungen herausgegeben von der Kommission zur wissenschaftlichen Untersuchung der deutschen Meere in Kiel und der biologischen Anstalt auf Helgoland

Wochenbl. Archit. Ver.	Wochenblatt, herausgegeben von mitgliedern des Architekten-Vereins zu Berlin
Wochenbl. Papierfabr.	Wochenblatt der Papierfabriken
Wochensch. Brau.	Wochenschrift für Brauerei
Wochenschr. Centr.-Ver. Rubezuker-ind.	Wochenschrift des Central-Vereins für Rubenzuker-industrie in der Oesterr-Ung-Monarchie
Wochenschr. österr. Ing. Ver.	Wochenschrift des österreichischen Ingenieur und Architekten Vereins
Wochenschr. Ver. deut. Ing.	Wochenschrift des Vereins deutscher Ingenieure
Wollen-Gewerbe	Das Deutsche Wollen-Gewerbe
Wollen Ztg.	Wollen Zeitung
Wombat	The Wombat. The Journal of the Geelong Field Naturalists' Club, and the Gordon College Amateur Photographic Association
Woods Holl Mar. Biol. Lab. Bull.	Biological Bulletin. Edited by the Director and Members of the Staff, of the Marine Biological Laboratory, Woods Holl, Mass.
Woods Holl Mar. Biol. Lab. Lect.	Biological Lextures delivered at (from) the Marine Biological Laboratory (of) Woods Holl (Mass.)
Woolhope Field Club Trans.	Transactions of the Woolhope Naturalists' Field Club
Woolwich, Proc.	Minutes of Proceedings of the Royal Artillery Institution
World's Paper Trade Rev.	World's Paper Trade Review
Wunderlich, Archiv. Heilk.	See Roser und Wunderlich
Wurttemberg. Aerzt. Ver. Mitth.	Mittheilungen des Wurttembergischen Aerztlichen Vereins
Wurttemberg, Jahresh.	Jahreshefte des Vereins für vaterländische Naturkunde in Wurttemberg
Wurzburg, Arb. Bot. Inst.	Arbeiten des Botanischen Instituts in Würzburg
Würzburg, Arb. Phys. Lab.	Arbeiten aus dem Physiologischen Laboratorium der Würzburger Hochschule
Wurzburg. Med. Zts.	Wurzburger medicinische Zeitschrift
Wurzburg. Naturwiss. Zts.	Wurzburger Naturwissenschaftliche Zeitschrift; Herausgegeben von der Physikalisch-Medicinischen Gesellschaft
Würzburg Phys. Med. Festschr.	Festschrift zur Feier ihres fünfzigjahreign Bestehens herausgegeben von der Physikalisch-Medizinischen Gesellschaft zu Würzburg
Würzburg, Phys. Med. Sitzber.	Sitzungsberichte der Physikalisch-Medicinischen Gesellschaft zu Würzburg
Würzburg, Phys. Med. Verh.	Verhandlungen der Physikalisch-Medicinischen Gesellschaft
Würzburg, Zool Inst. Arb.	Arbeiten aus dem Zoologisch-Zootomischen Institut in Wurzburg
Year Book Pharm.	See Brit. Pharm. Confer. Proc.
Year-book of Pharm.	Year-book of Pharmacy
Yn Lioar Manninagh	Yn Lioar Manninagh. The Journal of the Isle of Man Natural History and Antiquarian Society
Yokohama, Mitth. Deut. Ges.	Mittheilungen der Deutschen Gesellschaft für Natur und Völkerkunde Ostasiens
Yonne	See Auxere
Yonne, Bull.	Bulletin de la Société des Sciences Historiques et Naturelles de l'Yonne
Yorksh. Natur. Union Trans.	The Transactions of the Yorkshire Naturalists' Union
Yorksh. Phil. Soc. Report	Annual Report of the Council of the Yorkshire Philosophical Society

Yorksh. Proc. Phil. Soc.	Proceedings of the Yorkshire Philosophical Society
Zach, Corresp.	Correspondence Astronomique, Geographique, Hydrographique, et Statistique
Zach, Monat. Corresp.	Monatliche Correspondenz zur Beförderung der Erd- und Himmels-Kunde
Zahntech.	Die Zahntechnische Reform
Zantedeschi, Ann. Fis.	Annali di Fisica
Zeeuwsch Genootsch. Nieuwe Verh.	Nieuwe Verhandelingen van het Zeeuwsch Genootschap der Wetenschappen
Zeeuwsch Genootsch. Wet. Archief	Archief Vroegere en Latere Mededeelingen voornamelijk in Betrekking tot Zeeland, uitgegeven door het Zeeuwsch Genootschap der Wetenschappen
Zentr. Biochem. Biophys.	Zentralblatt für Biochemie und Biophysik
Zentr. exp. Med.	Zentralblatt der experimentellen Medizin (former name Zentralblatt für die gesamte Physiologie und Pathologie des Stoffwechsels)
Zentr. inn. Med.	Zentralblatt für innere Medizin
Zentr. oesterr - ungar Papierind.	Zentralblatt für die oesterr-ungar Papierindustrie
Zentr. Physiol.	Zentralblatt für Physiologie
Zentr. Physiol. Path. Stoffwech.	Zentralblatt für die gesammte Physiologie und Pathologie des Stoffwechsels, Berlin und Wien
Zeuner, Civilingenieur	Der Civilingenieur, Zeitschrift für das Ingenieurwesen
Ziva	Ziva: Casopis prirodnicky
Zool. Anz.	Zoologischer Anzeiger
Zool. Beitr.	Zoologische Beiträge
Zool. Bull.	Zoological Bulletin
Zool. Congr.	See Congr. Int. Zool. C. R. Int. Congr. Zool. Proc.
Zool. Jahr.	Zoologische Jahrbücher. Zeitschrift für Systematik, Geographie und Biologie der Thiere
Zool. J.	The Zoological Journal
Zool. Soc. Proc.	Proceedings of the Scientific Meetings (General Meetings for Scientific Business) of the Zoological Society of London
Zool. Soc. Trans.	Transactions of the Zoological Society of London
Zool. Vortr.	Zoologische Vorträge
Zoologica	Zoologica. Original-Abhandlungen aus dem Gesammtgebeite der Zoologie
Zoologist	The Zoologist; a monthly Journal of Natural History
Ztg. Blechind.	Illustrierte Zeitung für Blechindustrie
Zts. Akklimat.	Zeitschrift für Akklimatisation: Organ des Akklimatisations-Vereins in Berlin
Zts. allg. Erdkunde	Zeitschrift für allgemeine Erdkunde
Zts. allg. österr. Apoth.-Ver.	Zeitschrift des allgemeinen österreichischen Apotheker-Vereins
Zts. allg. Physiol.	Zeitschrift für allgemeine Physiologie
Zts. anal. Chem.	Zeitschrift für analytische Chemie
Zts. Anat.	Zeitschrift für Anatomie und Entwickelungsgeschichte
Zts. ang. Chem.	Zeitschrift für angewandte Chemie, und Zentralblatt für technische Chemie
Zts. ang. Mikr.	Zeitschrift für angewandte Mikroskopie mit besonderer Rücksicht auf die mikroskopischen Untersuchungen von Nahrungs- und Genussmitteln, technischen Produkten, Krankheitsstoffen, etc.
Zts. anorg. Chem.	Zeitschrift für anorganische Chemie
Zts. Bauwesen	Zeitschrift für Bauwesen
Zts. Berg-Hütten Salinenw.	Zeitschrift für das Berg-Hütten und Salinenwesen im Preussichen Staate
Zts. Biol.	Zeitschrift für Biologie

Zts. Bot.	Zeitschrift für Botanik
Zts. Chem.	Zeitschrift für Chemie
Zts. chem. Apparat.	Zeitschrift für chemische · Apparatenkunde (Discontinued)
Zts. Chem. Ind.	Zeitschrift für die Chemische Industrie mit besonderer Berucksichtigung der chemisch-technischen Untersuchungsverfahren 1887; later Zts. ang. Chem.
Zts. chem. Ind. Kolloide	Zeitschrift für Chemie und Industrie der Kolloide
Zts. Chemotherap.	Zeitschrift für Chemotherapie und verwandte Gebiete. (formerly Folia Serologia)
Zts. deut. geol. Ges. Abh.	Zeitschrift der deutschen geologischen Gesellschaft Abhandlungen
Zts. deut. Landw.	Zeitschrift fur deutsche Landwirthe
Zts. Dreschler	Zeitschrift für Dreschsler, Elfenbeingraveure und Holzbildhauer
Zts. Düngerw.	Zeitschrift fur Düngerwesen
Zts. Electrochem.	Zeitschrift für Electrochemie
Zts. Entom. (Breslau)	Zeitschrift für Entomologie im Auftrage des Vereins fur schlesische Insektenkunde zu Breslau
Zts. Ethnol.	Zeitschrift für Ethnologie
Zts. exper. Path. Therap.	Zeitschrift fur experimentelle Pathologie und Therapie, Berlin
Zts. Farben-Ind.	Zeitschrift fur Farben-Industrie
Zts. Feuerwehr.	Illustrirte Zeitschrift fur die deutsche Feuerwehr
Zts. Fischerei	Zeitschrift fur Fischerei
Zts. Fleisch. Milchhyg.	Zeitschrift für Fleisch- und Milchhygiene
Zts. Geburtsh.	Zeitschrift fur Geburtshulfe und Frauenkrankheiten
Zts. Geburtsh. Gynäkol	Zeitshrift für Geburtshulfe und Gynäkologie
Zts. ges. Brauw.	Illustrirte Zeitschrift das gesammte Brauwesen
Zts. ges. Getreidew.	Zeitschrift für das gesamte Getreidewesen
Zts. ges. Naturwiss.	Zeitshrift für die Gesammten Naturwissenschaften
Zts. Ges. Ornith.	Zeitschrift für die gesammte Ornithologie
Zts. ges. Textilind.	Zeitschrift für die gesamte Textilindustrie
Zts. ges. Wasserwirts.	Zeitschrift für die gesamte Wasserwirtschaft
Zts. Heilk.	Zeitschrift für Heilkunde, als Fortsetzung der Prager Vierteljahrsschrift fur praktische Heilkunde
Zts. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten
Zts. Immunit. Abt. I. 13. Abt. Ref.	Zeitschrift für Immunitatsforschung und experimentelle. Therapie. Abteilung I. 13. Abteilung II. or Ref. 1 vol
Zts. Induk. Abst. Vererbungslehre	Zeitschrift fur Induktive Abstammungs- und Vererbungslehre
Zts. Instrumentenk.	Zeitschrift fur Instrumentenkunde
Zts. Klin. Med.	Zeitschrift fur Klinische Medizin
Zts. Krebsforsch.	Zeitschrift fur Krebsforschung
Zts. Kryst. Mineral.	Zeitschrift fur Krystallographie und Mineralogie
Zts. landw. Versuchsw.	Zeitschrift · fur das landwirtschaftliche Versuchswesen in Oesterreich
Zts. Malakozool.	Zeitschrift für Malakozoologie
Zts. Math. Phys.	Zeitschrift fur Mathematik und Physik
Zts. math. Unterr.	Zeitschrift für mathematischen und naturwissenschaftlichen Unterricht
Zts. Mikro. Tek.	Zeitschrift für Mikroscopischen Teknik.
Zts. Morphol. Anthrop.	Zeitschrift für Morphologie und Anthropologie
Zts. Nahr. Genuss. (Z. genuss)	Zeitschrift für Untersuchung der Nahrungs und Genussmittel, sowie der Gebrauchsgegenstände
Zts. Naturwiss.	Zeitschrift für Naturwissenshaften...im Auftrage (Organ) des Naturwissenschaftlichen Vereins für Sachsen und Thüringen

Zts. öffentl. Chem.	Zeitschrift für öffentliche Chemie
Zts. Ohrenheilk.	Zeitschrift für Ohrenheilkunde in deutscher und englischer Sprache
Zts. österr. Ing. Ver.	Zeitschrift des österreichischen Ingenieur und Architekten Vereins
Zts. paraf. Ind.	Zeitschrift fur Parafin Industrie
Zts. Parasit.	Zeitschrift fur Parasitenkunde
Zts. Pflanzenkrankheiten	Zeitschrift für Pflanzenkrankheiten
Zts. physik. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandschaftslehre
Zts. Physik. Chem. Unterr.	Zeitschrift fur dem physikalischen und chemischen Unterricht
Zts. Physiol. Chem.	Zeitschrift für physiologische Chemie (Hoppe-Seylers)
Zts. prakt. Geol.	Zeitschrift fur praktische Geologie
Zts. Psychol.	Zeitschrift fur Psychologie und Physiologie der Sinnesorgane
Zts. ration. Med.	Zeitschrift für rationelle Medicin
Zts. Reprodukt.	Zeitschrift fur Reproduktiontechnik
Zts. Rübenzuckerind.	Neue Zeitschrift für Rübenzuckerindustrie
Zts. Schiess Spreng.	Zeitschrift fur das gesammte Schiess- und Sprengstoffwesen
Zts. Spiritusind.	Zeitschrift fur Spiritusindustrie
Zts. Telegr. Ver.	Zeitschrift des deutsch-osterreichischen Telegraphen-Vereins
Zts. Thiermed.	Zeitschrift für Thiermedicin
Zts. Tuberkulose	Zeitschrift fur Tuberkulose und Heilstättenwesen
Zts. Ver. deut. Ingen.	Zeitschrift des Vereins deutscher Ingenieure
Zts. Ver. Rubenzuckerind.	Zeitschrift des Vereins fur die Rübenzucker-Industrie des deutschen Reichs
Zts. Ver. Zuckerind.	Zeitschrift des Vereins der deutschen Zuckerindustrie
Zts. Wiss. Geogr.	Zeitschrift fur wissenschaftliche Geographie
Zts. wiss. Mikro.	Zeitschrift fui wissenschaftliche Mikroscopie
Zts. wiss. Photochem.	Zeitschirft fur wissenschaftliche Photographie, Photophysik, und Photochemie
Zts. wiss. Zool.	Zeitschrift fur wissenschaftliche Zoologie
Zts. Zuckerind.	Zeitschrift fur Zuckerindustrie
Zts. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Bohmen
Zürich Denkschr. Med. Chir. Ges.	Denkschrift der medizinisch-chirurgischen Gesellschaft des Kantons Zürich
Zürich Mitth.	Mittheilungen der Naturforschenden Gesellschaft in Zürich
Zürich, Monats.	Monatsschrift des wissenschaftlichen Vereins in Zürich
Zürich naturf. Ges.	Vierteljahrschrift der naturforschenden Gesellschaft in Zürich
Zürich Physik. Ges. Jahr.	...Jahresbericht der physikalischen Gesellschaft in Zürich
Zürich, Schweiz. Ges. Neue. Denkschr.	Neue Denkschriften der allgmeinen Schweizerischen Gesellschaft fur die gesammten Naturwissenschaften
Zürich, Soc. Entom.	Societas Entomologica. Organ für den internationalen Entomologenverein. Zurich
Zürich, Unters. Physiol. Lab.	Untersuchungen aus dem Physiologischen Laboratorium der Zuricher Hochschule
Zürich, Verh.	Verhandlungen der Medicinisch-chirurgischen Gesellschaft des Kanton Zürich im Jahr 1826
Zürich, Vierteljahrschr.	Vierteljahrsschrift der Naturforschenden Gesellschaft in Zürich
Zwickau Ver. Naturk. Jahr	Jahresbericht des Vereins für Naturkunde zu Zwickau
Zwolle, Vooruitgang.	De Vooruitgang; Tijdschrift voor Wetenschap

CHAPTER XII

SOLVENTS NON-SOLVENTS PLASTICIZERS

A satisfactory theory embracing solvents, non-solvents, diluents and plasticizing and softening bodies as applied to cellulose derivatives has as yet not been enunciated, the primary reason undoubtedly being that with organophilic colloids as the cellulose ethers and esters we are not dealing with separate and distinct chemical entities, but with groups of compounds individually of unusually high molecular magnitude, each possessing its own solvent idiosyncrasies and propensities, which peculiarities are heightened when two or more liquids are involved, as usually is the case[1].

Likewise, there appears to be no clear-cut or sharp line of demarcation between camphor substitutes, ancillary gelatinizing agents, antacids, stabilizers, gelatinizing accelerators or retardants, high boilers, extensifiers, activators and suppleness-inducing bodies, so that a satisfactory classification seems well-nigh impossible in the light of our present knowledge; for in their deportment towards the

1. For general data on solubility of cellulose derivatives, see: C. van Hoek, Farben-Ztg. 1926, **31**, 2885. Anon., Farbe u. Lack, 1925, 422, 433. Anon., Rev. Prod. Chim. 1925, **28**, 553. E. Kohn, Kunst. 1924, **14**, 101. Anon., Chemicals, 1925, **24**, #25, 11. D. Keyes, Paint, Oil and Chem. Review, 1925, **80**, #21, 8. E. Bainbridge, Amer. Paint J. **9**, 52-B, 18. T. Durrans, Chem. Trade J. 1927, **80**, 251. H. Wolff and C. Dorn, Farben-Ztg. 1922, **28**, 31. D. Keyes, Paint, Oil and Chem. Rev. 1925, **79**, #22, 24. W. Miskella, Paint, Oil and Chem. Rev. 1925, **80**, #6, 16. D. Gillies, Western Paint Rev. 1927, 20. Anon., Farbe. u. Lack, 1927, #22, 297. A. Noll, Farben-Ztg. 1927, **32**, 1553. D. Keyes, Chem. Markets, 1927, **20**, #19, 705. S. Smith, Chemical Age, 1927, **16**, 281. Anon., Rev. Produits Chim. 1925, **28**, 553. H. Garlick, Industrial Chemist, 1926, 437. R. Masterson, Industrial Finishing, 1925, **1**, #3, 30. A. Kohn-Abrest, Kunst. 1924, **14**, 101; Chem. Age, 1924, **32**, 199. H. Willkie, Chem. and Met. Eng. 1921, **25**, 1186. Anon., Chem. Markets, 1927, **21**, #19, 637. H. Gardner, U. S. Paint and Varnish Mfrs. Assoc. Circ. #285; Paint, Oil and Chem. Rev. 1927, **82**, #13, 10. H. Parks and A. van Heuckeroth, U. S. Paint and Varnish Mfrs. Assoc., Circ. #266. J. Simonin, Rev. gen. mat. Plast. 1927, **3**, #10, 603. Anon., Chemist and Druggist, 1926, 105, 667, 730, 804, 866; 1927, 106, 110, 163, 221, 282, 343, 435, 530, 586, 716, 787. A. Noll, Chem. Ztg. 1927, **51**, 546, 566. P. Mowen, Paint, Oil and Chem. Rev. 1928, **85**, #23, 12.

carbohydrate carboxylates and etherified derivatives, their solvent activity is modified, especially attenuated, by the presence of other liquids of dissolving, colloiding or non-solvent power, that accurate generalizations are well nigh impossible.

The solvent capacity of liquids are profoundly modified by temperature, pressure, purity and association with other bodies, and added to this, is the fact that both the cellulose ethers and cellulose esters are far from being chemical entities in their commercial condition as to purity, being rather classes of compounds. For example, an etherified cellulose assaying a percentage of ethoxyl which analytically calculated to a triethylcellulose based on a C_6 cellulose molecule, quite probably contains diethylcellulose, etherified celluloses between diethyl- and the tri-ethyl stage, and also bodies which analytically assay higher than a diethyl-derivative, so that the ultimate analysis indicating precisely a diethylcellulose, is merely the mean of the various ethylated celluloses present, the aggregate ethoxyl of which happens to give a percentage corresponding to a diethyl compound of normal or unaltered cellulose.

Furthermore, we know that the commercial etherification of cellulose is never made on the unchanged or unmodified cellulose but upon the cellulose after it has been more or less profoundly degraded or depolymerized by virtue of treatment with concentrated alkali solutions to form alkalicellulose or soda cellulose, and any determination of alkoxyl is incorrect when calculated as attached to a non-modified cellulose aggregate.

So that determinations of dissolving power as found strewn through the scientific literature are in the majority of instances, especially with the older determinations, practically worthless for accurate generalizations, for the reason that the concentration and temperature is seldom stated, and exact physical constants of the cellulose derivative operated upon are generally lacking in sufficient comprehensiveness. In the deportment of solvents towards the

etherified and esterified carbohydrates, many of the chemicals proposed and products described, in their dissolving function and colloiding eccentricities show an imperceptible blending from one class to another, the effect being often heightened, attenuated or entirely emasculated by the preponderance of one chemical over another, and by the application of pressure, vacuum, heat, or the interposition of the time factor.

Therefore this Chapter should be regarded rather as a synopsis and enumeration of the bodies which have been proposed from time to time and arranged according to a definite chemical classification insofar as feasible, rather than as an attempt at an extended description of each of the over two thousand separate solvents which have been advocated and patented and are to be found within these pages. The cellulose acetate solvent art was largely builded upon information acquired in connection with the development of its predecessor, the nitrocelluloses. Likewise does it appear that advancements in cellulose ether technics will be advanced more rapidly and firmly by having available a resume of those solvent bodies which have heretofore been tried in connection with non-etherified cellulose derivatives, remembering that *the cellulose ethers as a class have a much wider solvent capacity* than either of the older and better known nitrocellulose and acetylcellulose industries, and in the possibility that somewhere in this list lies slumbering a product which will impart to the cellulose ethers the desirable properties conferred upon nitrocellulose by camphor, lies the value of their citation herein, accompanied by 2049 separately numbered bibliographic references indicating more explicit information to be found elsewhere.

The fact that a certain chemical today may be difficult to procure is irrelevant, for it is a truism that rarity in organic chemicals is but a relative term, for the chemical curiosity and museum specimen of today becomes the commercial commodity of tomorrow when the demand arises, helium being a well known example. Bearing in mind the

fact that the cellulose ethers have no technical applications in the dry or undissolved state, and only exhibit their usefulness when or after having passed into solution or colloided, the fact becomes obvious that the role of solvents is of paramount importance, for the primary factor in the expansion of fields of utility with etherified cellulose rests firmly upon the fundamental proposition of the suitability of solvents, and the ability to so manipulate them as to induce results of maximum desirability for specific purposes.

And another central thought is the incontrovertible fact that notable advancement in the cellulose ester art has primarily taken place only when some one discovered new solvents or evolved better methods of utilizing those already known. The psychological moment for the advent of celluloid hinged upon John Wesley Hyatt and the solvency for pyroxylin of camphor in the molten state; the modern cellulose lacquer had its inception in the recognition of amyl acetate as a desirable, non-hygroscopic, high-boiling solvent; the foundation of present artificial leather production rests upon knowledge of combining and blending cellulose esters and oils with solvents of harmonious applicability. Transition from the academic to the utilitarian in all the peaceful arts involving cellulose derivatives has depended upon and awaited disclosures in solvents.

George Audemars could not produce artificial silk in 1855 by nitrating mulberry leaves on which the silkworm feeds, but it remained for Count de Chardonnet nearly thirty years later to lay the corner stone of the rayon industry by an appreciation of solvents as applied to nitrocellulose. Therefore the reason why the subject of "Solvents" (in its broad sense) has been allocated such a comparatively large portion of this work.

As is well known, cellulose ether and ester solutions are not genuine but colloidal solutions, their colloidal character being proven, among other factors, by the varying viscosity of their solutions. The quality and constitution of the solvent or diluent profoundly influences the degree of viscosity

of the resulting solutions, it having been observed that the viscosity usually increases with the molecular weight of homologous solvents. Esters of dibasic acids usually produce more viscous solutions than the corresponding alkyl attached to a monobasic acid both being of substantially the same magnitude of solvent efficiency, i.e., *n*-butyl acetate and *n*-butyl oxalate. The same generalization applies with an aliphatic acid as compared with the hydroxy-acid, both attached to the same alkyl, ethyl propionate and ethyl lactate being illustrative. Comparable viscosity determinations, of course, are only to be obtained at the same temperature and by the maintenance of a definite concentration, the absence of finely divided extraneous matter being assumed.

It is not necessary that a plastifier for the cellulose ethers be a direct solvent for the particular ether, or in fact, that it exert any solvent effect by itself. There are known plastifying bodies which are poor solvents of the etherized celluloses, but which show satisfactory solvent capacity in the presence of a relatively small proportion of a low boiler which is also a direct dissolvant of the cellulose ether and of the plastifier. Such combinations usually require heat and pressure or both, in order to develop the maximum solvent efficiency. And whereas with the nitrocelluloses and cellulose acetate, none of the cyclic or aliphatic hydrocarbons have appreciable dissolving power, many of the cellulose ether types are directly dissolvable, especially when in the presence of a few percent of aliphatic alcohol or acetic ester derived therefrom. And this point becomes of particular significance when it is remembered that *these hydrocarbons are the cheapest available liquids insoluble in water.* Furthermore, with the cellulose ethers, solutions can be attenuated with a larger proportion of hydrocarbon without incipient gelatinization than is possible with the corresponding esters, this tolerance enabling lacquers to be produced comparatively of less expense, based upon the liquid portion.

The cellulose ethers and esters are dissolvable usually by one or more of the following groups of organic liquids, (1) the most important are esters, combinations of one molecule of an organic acid with one or more alcohol molecules with the simultaneous splitting off of water; (2) ketones, combinations of two acid molecules with the formation of a new compound with a CO-group; and (3) ethers, organic oxides, combinations of two univalent alcohols with the elimination of water[1]. Fundamentally these three types of organic liquids dissolve the cellulose ethers direct, usually the avidity of solution diminishing with increase in molecular weight in a homologous series, the more powerful the solvent action, the lower the viscosity of the cellulose ether obtained as the result. In high boilers, colloiding and plastifying agents, the solvent capacity in general, is usually augmented by the presence of a relatively small amount of a lower monohydric aliphatic alcohol or its corresponding acetic ester, and if the plastifiant happens to be soluble in benzene, toluene or xylene, the addition of one or more of these carbocyclic hydrocarbons to the mixture, makes for rapidity of solvent power.

For some time it has been known that there exists a definite relation between the solvent power of a liquid for a cellulose ether or ester and the viscosity of the solution, in general, the best solvents yielding the most mobile solutions[2]. It would be a meritorious scientific undertaking as well as a fruitful one for the industry, if the basic principles underlying this fact could be clarified. E. Mardles[3] has determined the relative solvent powers of single and mixed liquids for various esters, so that it is possible in many instances, to precisely correlate solvent power with viscosity data.

F. Baker[4] found that the observed values for the viscosity of cellulose nitrate solutions were qualitatively in

1. F. Zimmer, Farben-Ztg. 1930, **36**, 70.
2. E. Mardles, J. S. C. I. 1923, **42**, 207-T.
3. J. S. C. I. 1923, **42**, 1277.
4. Chem. Soc. Trans. 1913, **103**, 1653.

agreement with the view that the more active the solvent, the less the viscosity. W. Gibson and R. McCall[1] have measured the viscosity of nitrocellulose solutions in mixtures of alcohol-ether containing small quantities of water, and ascertained that the viscosity reached a minimum value at a definite ratio, which was affected by the origin and treatment of the cellulose ester and its percentage composition. This close correlation of solvent power of a liquid or liquid mixture for cellulose derivatives is apart from its theoretical interest of considerable industrial importance, for in the application of lacquers, it is only the non-volatile components which remain in the finished product, and without a solvent recovery system, the volatile portion is always lost. The optimum solvent mixture dissolves the cellulose compound most rapidly, because the least viscous solutions are formed and the particles diffuse most rapidly away from the dissolving material. Solutions so prepared are usually the clearest due to a higher degree of dispersion. They are also generally more stable because tendency to jellify is reduced to a minimum[2].

That the optimum solvency in a mixture should and does possess the maximum fluidity and tenuity follows from the fact that with the maximum degree of dispersion comes the nearest approach to a true (molecularly dispersed) solution with its characteristically low viscosity. The explanation of variation in composition of the optimum solvent mixture with concentration and temperature, may be sought, according to E. Mardles, in the concept of the molecular complexity of the dispersed cellulose derivative.

A solution of a cellulose ether or ester in a binary mixture of liquids is essentially a ternary system, and the respective specific characters of the components differ; also there comes a differential change in degree of molecular complexity with variation in concentration.

It would be of considerable technical interest to deter-

1. J. S. C. I. 1920, **39**, 172-T.
2. E. Mardles, Trans. Faraday Soc. 1923, **18**, Part 3.

mine the underlying causes for the fact that the lower aliphatic alcohols and carbocyclic alcohols by themselves are ready solvents of most types of cellulose ethers, whereas the higher alcohols, or the hydrogenated phenols with alcoholic characters do not show this property at all, or to a much less pronounced degree. If the chemical structure of the solvents and the non-solvents is taken into consideration, it may be established that the products which show no oxygen in the molecule are of substantially non-dissolving action, whereas the presence of oxygen in the OH-group of the higher alcohols may also impart no solvent properties. Conversely, oxygen-containing molecules of such substances as contain the CO-group, e.g., esters of organic acids and also the ketones, consistently show a strong dissolving action, especially with those cellulose ethers of comparatively high degree of etherification, and which are insoluble in or little affected by water. The oxygen of the CO-group, doubly bound to carbon, appears to be the carrier of this important property. In the esters, both free valencies of the CO-group are saturated by two alkyls, one of which is directly bound to the carbon, and the other through an oxygen atom (R-CO-OR').

In the ketones, these are directly taken up by two alkyls without the interposition of oxygen (R-CO-R). For the execution of this dissolving action however, the ester or ketone-like character of the medium is not always present, as evidenced by the solubility of nitrocellulose, acetylcellulose and some of the cellulose ethers in concentrated acetic acid. Formic acid possesses this property, although to a much attenuated degree. It is conceded[1] that within a homologous series, the viscosity proportionally decreases with the size of the molecules, but according to A. Heinemann[2] the residual affinities and other constitutional influences which also determine the solvent properties, within certain ranges have a stronger dissolving effect than the

1. Nernst, Theoretical Chemistry, 1909, 310, 314.
2. Farben-Ztg. 1930, **36**, 270.

size of the molecules. There is a definite increase in reaction or solvent-power with augmenting carbon content, hence with increase in molecular size, for which the varying solvent powers of methyl alcohol as against ethyl alcohol are evident. Even with ethyl alcohol a solvent weakening is perceptible, while the higher alcohols show little or no solvent action[1]. K. Ziegler[2] feels that in the cellulose derivative lacquer field, the processes of a colloid-chemical nature will be brought nearer to their final explanation by means of "radical dissociations." E. Desparmet[3] has elaborated upon the generally accepted idea that with the same composition otherwise, cellulose ester solutions in ketones show a considerably lower viscosity than those prepared with equally high-boiling ester-type compounds. However, our experience is that this generalization does not apply with carbocyclic ketones as acetophenone.

The formation of various types of complex molecular compounds of cellulose esters and ethers with solvents and non-solvents can probably also be more or less satisfactorily explained by the theory of free radicals, upon which much work has been done in the field of tri-valent carbon and univalent oxygen atoms, it having been observed that in the union with cellulose compounds of solvents, the presence of carbon in combination with oxygen atoms produces in the solvent molecule an action tending to reduce viscosity, whereas the oxygen-free, genuine non-solvents induce an intumescing action upon the molecule, with which, as a rule, any rise in viscosity is connected.

Attempts to lay down basic generalizations of solvent capacity and ratio of dilution with non-solvents in connection with cellulose ethers, has met with the same difficulties as previously confronted those investigators working along similar lines with the better known cellulose nitrates and acetates, and that is the varying composition from an anal-

1. F. Zimmer, Farben-Ztg. 1930, **36**, 70.
2. Zts. ang. Chem. 1930, **43**, 915.
3. Le Cuir Technique, 1928, 56.

ytical viewpoint of the cellulose ether operated upon. By means of fractional precipitations, it has been possible to obtain from a technically usable cellulose ether, a whole series or fractions of bodies which have quantitatively varying alkyl or aralkyl content. In other words, at the commencement of the problem we are confronted with a chemically non-homogeneous body. Inasmuch as the usual methods of purification as vacuum distillation, sublimation or crystallization cannot be applied to these compounds (for possible exceptions see pp. 1312-1315 and 1334), all solvent determinations involving the cellulose ethers must be upon aggregates of etherified cellulose rather than with a clear-cut chemical individual. And the mass of solvent data which is obtainable from the literature, while representing most careful determinations, is all discountable by the fact that the precise composition of the compound is not known, and seldom the same between two investigators.

Therefore, unless and until a standard fractionally precipitated or crystallized etherized cellulose is available for accurate solvent determinations, previous results must be accepted *cum grano salis* for the above reason, which, of course, is no reflection upon the original investigator or the indefatigability of his work, and the results obtained must be interpretated as generalities rather than disclosing specific and duplicable information.

All neutral solvents and solvent combinations of the cellulose ethers produce more or less transparent, viscous solutions, from which the cellulose ether may be precipitated by the use of a sufficient amount of non-solvent, some liquids appearing to be better solvents than others, dissolving the cellulose ethers either more rapidly or more completely, and yielding solutions of varying viscosities. Similarly, a mixture of liquids oftens forms a better solvent than either liquid separately, and a cellulose ether in suspension in either of two liquids may be united and will then pass into solution. These are examples of

non-solvents or partial solvents becoming excellent dispersing agents on mixing.

In the study of solvents of colloidal bodies as the cellulose ethers, there is the difficulty of determining the relative solvent power of the dissolvants, since there appears to be complete miscibility in some cases[1]. With the organosols of cellulose ethers the characteristic rapid rise in viscosity coincidental with increase in concentration is of such a degree that all but the lower concentration sols are very viscous and intractable unless the ether has been subjected to a definite viscosity-reducing treatment, so that the existence of a saturation condition, as in the case of crystalline bodies, cannot be readily demonstrated in the usual manner. And another disturbing factor enters and that is that when an apparent saturation state has been obtained, submission of the solution to elevated temperature or to a trace of volatile acid (as acetic) and heat, or a volatile alkali (as ammonia) and heat, so reduces the viscosity that additional cellulose ether may be dissolved in what heretofore appeared to be a saturated solution. Therefore viscosity diminishes apparent solubility, because the solubility of any one cellulose ether only becomes definite as to quantitative results, when the solubility determination is accompanied by a statement as to the relative viscosity.

Estimation of insoluble matter in the sols of a cellulose ether solution is not directly indicative of the solvent power or capacity, since the insoluble portion is different in properties from the dissolved material and usually has a higher ash content. Furthermore, as we have experimentally proven, it is possible to take the undissolved portion of a cellulose ether solution, add the same solvent thereto, heat the mixture under pressure, and then add the same to the original solution when a clear solution results indicating finally a complete solubility, the viscosity of the heated portion being considerably less than the original solution in which the afterwards heated portion was initially insoluble.

1. T. Graham, J. C. S. 1864, **17**, 318.

The determination of viscosity on the assumption (and it is purely an assumption) that the best solvent gives solutions of minimum viscosity, while applicable in the majority of instances, yet has many exceptions. The factors which make for solubility in the cellulose ethers are three, the ether, the viscosity of the solution, and the third which is inseparable from the second, i.e., the interposition of heat or the presence of viscosity-reducing chemicals in minute amounts.

The temperature factor is also of much importance in connection with the dissolving of the cellulose ethers, especially those which are partially or wholly soluble in water or have a diminished resistivity to water. There are types of methyl- and ethyl-cellulose known which are soluble in water below 16°, but which, when the temperature is raised much above 16°, begin to precipitate. And it is an observable peculiarity with such ethers, that when substantially completely precipitated by means of hot water, the solubility in cold water is lessened as the result of the hot water treatment. Furthermore, there are known types of cellulose ethers insoluble in water, hot or cold, which upon reducing the water to a frozen condition and then gradually thawing, are found to have dissolved when the water again liquefies. No such analogous solvent actions are to be found with the acetylcelluloses or cellulose nitrates.

Another readily observable peculiarity with water-insoluble alkylcelluloses, is that with two different (say) ethylcelluloses, each in a benzene-methyl alcohol mixture of the same percentage ratio, and in which either one is incompletely soluble, it is possible by pouring the mixtures together to mutually so dissolve the residues of both that a clear solution results, without the addition of more solvent. This phenomenon appears unexplainable.

P. Schützenberger[1] has pointed out that cellulose triacetate soluble in nitrobenzene on warming, precipitates in a gelatinous form upon cooling. This may be merely analo-

1. Compt. rend. 1869, **68**, 814.

gous to the production of what might be correctly called a supersaturated solution, but cellulose ethers are known in which the converse is true, i.e., an incompletely soluble ethylcellulose in warm water gradually goes into solution as the water cools. The method of observing the transition temperature of the dispersion medium from a complete solvent to a partial or non-solvent has been used to appraise the relative solvent capacity of liquids for cellulose esters in a research on solvents suitable for aeronautical varnishes and airplane wing dope formulas[1], upon the principle that the lower this temperature, the better the solvent. The point of precipitation is indicated by the first observable opalescence, as in the case where a mixture of liquids is cooled below the temperature of complete miscibility, indicating the transition from a true solution to a coarse dispersion. Our experience with this method is that it is prone to lead to fallacious results on acccount of the diminution in viscosity superinduced by the heating treatment which gives higher solubility factors than a solubility determination where no extraneous heat was applied. This may readily be demonstrated with cellulose ethers of maximum etherification by making a saturated solution (as by rotating a solution for 24 hrs. in the presence of glass beads or marbles) where a small residue is left. It is possible to incorporate this residue into a clear solution in the same mixture by the mere application of heat and further agitation.

E. Mardles operating upon cellulose acetate and nitroacetate (acetonitrate)[2], reports there appeared no correlation between solubility of cellulose acetate and its chemical composition, as determinable from an examination of a large number of samples. This generalization holds true with the cellulose ethers. Viscosity attenuation may be so conducted that solvency in a single solvent or solvent combination may be at least 50% greater that the solvency

1. E. Mardles, Moses and Willstrop, Brit. Advisory Com. for Aeronautics, Rept. 368.
2. J. S. C. I. 1923, **42**, 128-T.

before artificial viscosity reduction was applied thereto, and yet by quantitative analysis the cellulose ethers before and after viscosity reduction are analytically indistinguishable. Mardles found that with a typical non-solvent for acetylcellulose as hexane, the curve relating the precipitation temperature and composition, approached a rectilinear function, but with benzene or alcohol there was a decided sag in binary mixtures with benzyl alcohol. Although a liquid may be a solvent of a cellulose ester at a temperature at and below its boiling point at atmospheric pressure, it often happens, as with alcohol, benzene, methylethyl ketone for acetylcellulose, that it becomes a solvent at higher temperatures. Anhydrous ethyl alcohol became a solvent for a particular sample of cellulose acetate at 120°, and industrial alcohol at 100°. If the cellulose acetate used was of that partial hydration degree represented by complete solubility in anhydrous acetone and incipient plasticity in alcohol-free chloroform, the above results are explainable.

He accentuates the idea that liquids which are solvents are sufficiently attracted toward the cellulose ester to form complexes with it, and states that since there is a rapid decrease in solvent power with ascent in a homologous series, there is a corresponding decrease in solvent power as the molecular weight becomes greater. Therefore, any addition to the solvent which tends to decrease its association or to simplify the molecular size, increases the solvent power. This is somewhat analogous to the theories of G. Barr and L. Bircumshaw[1] and of M. Byron[2]. J. Bain[3] emphasizes that solvation is the prime factor, but suggests that in a mixture of solvents there are more kinds of molecules to be attracted to different portions of the cellulose molecule, and therefore to solvate it more exhaustively, than there are in a pure liquid. This general thesis appears highly specu-

1. Trans. Faraday Soc. 1921, **16**, 99.
2. J. Phys. Chem. 1926, **30**, 1116.
3. J. Phys. Chem. 1926, **30**, 239.

lative to us. H. Barthelemy[1] has made an interesting contribution to the study of cellulose acetate solutions, many of the points being equally applicable to cellulose ether solvent combinations.

In an investigation of the refractometric determination of absorption of organic substances from liquid mixtures by

1. Chim. et Ind. 1931, **25**, 819; abst. C. A. 1931, **25**, 3827; J. S. C. I. 1931, **50**, 905-A. He finds that on progressive addition of water, methyl alcohol or ethyl alcohol to an acetone solution of cellulose acetate the viscosity decreases to a minimum and then increases. This confirms the opinion previously expressed that the phenomenon was due to an internal mol. modification of the system related to the presence of alcoholic hydroxyl groups; so it may be concluded that, when cellulose acetate is dissolved in a complex solvent containing at least one compound containing an alcoholic hydroxyl group, a selective adsorption of the alcoholic hydroxyl groups occurs at the surface of the cellulose acetate micelles. This adsorption produces a modification of the interfacial surface tension between the complex solvent and the dispersed micelles, which results in a better "lubrication" of the micelles and hence in a decrease in viscosity as the latter is merely a measure of the "internal friction" of the mols. Addition of increasing amounts of water to acetone decreases the surface tension of the liquid progressively (no min.); so that the viscosity-water curve of cellulose acetate solutions is really the resultant of 2 antagonistic phenomena, adsorption of hydroxyl by the micelles and precipitation of the micelles by large proportions of hydroxyl. After several days' contact with methylene chloride or with chloroform, cellulose acetate gives a homogeneous, highly refractive mass, having an enormous viscosity (unmeasurable by the Baume viscosimeter); addition of methyl alcohol very rapidly reduces the viscosity, which falls to a minimum and then rises to the point where flocculation occurs; the curve is not symmetrical with respect to an axis parallel to the viscosity axis and passing through the minimum of the curve. Cellulose acetate swells considerably in contact with trichlorethane, but with no sign of solution. Dichlorethane and tetrachlorethane give curves similar to those of methylene chloride and chloroform, but the values of the viscosities are higher. Flocculation by successive additions of chlorinated hydrocarbons to acetone solutions could be used for the fractionation of cellulose acetate according to micelle size. Addition of progressive amounts of ethyl ether or benzene to acetone solutions of cellulose solutions increases the viscosity according to a parabolic curve, there being no previous formation of a complex with minimum viscosity. The viscosity of solutions of cellulose acetate of low concentration (up to about 7-8%) in dry acetone as a function of concentration is expressed by the equation: $\log v = \log h + kC$, or $v = h10^{kC}$, in which h and k are constants, and C is the concentration in g. per 100 cc. The straight lines thus obtained with different samples of cellulose acetate in the same solvent pass through a common origin, which is not coincident with the viscosity of the pure solvent. This is explained by the fact that no account is taken of the possible influence of variations in the surface tension of the different solutions, and especially that there is too great a variation in the times of flow.

cellulose esters, T. Tomonari[1] has found that compound formation between cellulose nitrate or acetate with acetone or cyclohexanone mixed with alcohols or inert diluents may be studied by measurements of n of the liquid mixture. While it is a fact that up to the present time the cellulose ethers have not been studied very fully, it appears they are less polar than the lower cellulose esters, and in accord with this presumption, it has been found that whereas the acetylated celluloses of industrial importance are insoluble in hydrocarbons, the cellulose ethers dissolve in such bodies as tetra- and deca-hydronaphthalene, (see pp. 1315, n. 6; 1336), ethylbenzene (p. 51, n. 3) and dimethylaniline (p. 51, n. 4), liquids in which the cellulose acetates are insoluble.

For determining the viscosity of concentrated (22-30%) solutions, the Stokes falling-sphere method gives good results provided the following precautions are observed: let the solution stand 12 hours before placing in the constant temperature (25°) oven, leave at least 3 hours in the oven before determining the viscosity; determine the time of falling of only 1 ball in any given solution, let the ball fall exactly in the center of the tube containing the solution. The curve of viscosity (c. g. s.) against concentration is a straight line expressed by $\log v = kC$, or $v = 10^{kC}$, in which k is a constant, passing through the origin of the axis (corresponding to the viscosity of the pure solvent); the viscosity at all concentrations in a given solvent can therefore be found from the determination of the viscosity at a single concentration, and this is equally applicable to acetone containing water. At high concentrations of cellulose acetate the minimum viscosity is reached at higher water contents of the acetone than at low concentrations of cellulose acetate, which confirms that there is selective affinity between the acetate micelles and the hydroxyl groups of the water. Dropping a number of steel balls at close intervals and at exactly the same place through the solution until the time required to fall through a given distance becomes constant for successive balls, gives a measure of the true viscosity of the solution, and the difference between it and the time of falling of the first ball gives a measure of the "rigidity." The first ball (for determining the apparent viscosity) should preferably be 7/32 in. in diameter, the succeeding ones ¼ in., and the final one (which gives the true viscosity after constant speed has been attained) 7/32 in. By strong illumination of the solution during the determination in consequence of the Tyndall effect, the balls in falling are seen to produce a tubular-like path, successive balls following this path and enlarging it; after standing for several hours, the tube-like path disappears. The measurement of "rigidity" meets a much-felt want in the plastics industry, as plastic properties depend on it much more than on viscosity.

1. Cellulosechem. 1932, **13**, 101; abst. J. S. C. I. 1932, **51**, 717-B.

W. Lee[1] has conducted an investigation of practical utility in determining the solvent capacity of a number of

1. His results as applied to cellulose acetate are epitomized herewith, results with the cellulose ethers being in general in accord. *Trimethylethylene,* in the cold, action slight or *nil; cumene,* cold, strong swelling; *p-cymene,* cold, moderately strong swelling, hot, difficult to disperse; *tetrahydronaphthalene,* cold, action only slight, hot, dispersed appreciably on boiling, but with difficulty; *pinene,* cold, fairly strong swelling, hot, difficult to disperse; *ethyl acetate,* cold, solvent; *ethyl acetoacetate,* cold, solvent; *ethyl cyanoacetate,* cold, solvent; *ethyl trichloracetate,* cold, action only slight, hot, dispersed completely, but with difficulty at boiling point; *amyl formate,* cold, no action, hot, no apparent dispersion, inert liquid; *amyl valerate,* cold, action *nil* or slight, hot, did not disperse inert liquid; *butyl stearate,* cold, no action, hot, insoluble; *ethyl orthoformate,* cold, action *nil* or slight; *ethyl oxalate,* cold, solvent; *ethyl cinnamate,* cold, action slight, hot, dispersed almost completely, but with difficulty on boiling; *methyl benzoate,* cold, solvent; *isoamyl benzoate,* cold, moderate swelling, hot, dispersed readily and completely on moderate heating, solvent; *methyl salicylate,* cold, moderate action; *butyl phthalate,* cold, action slight, hot, solvent; *phenyl butyrate,* cold, action slight, hot, very little action on heating moderately with agitation; *ethyl collidinedicarboxylate,* cold, action slight; *vinyl acetate,* cold, fair swelling; *citronellyl acetate,* cold, swelling slight; *allyl bromide,* cold, strong swelling; *n-undecoic acid,* cold, action slight, hot, completely soluble on boiling; *undecenoic acid,* cold, action slight, hot, soluble; *lactic acid,* cold, pronounced action; *pyruvic acid,* cold, strong swelling; *oleic acid,* cold, action slight, hot, solvent; *acetonitrile,* cold, solvent; *diethylacetonitrile,* cold, action *nil* or slight; *phenylacetonitrile,* cold, solvent; *chloracetaldehyde,* cold, solvent; *aldol,* cold, action slight, hot, dispersed completely on gentle warming; *heptaldehyde,* cold, action *nil* or slight; *cinnamaldehyde,* cold, solvent; *salicylaldehyde,* cold, solvent; *citronellal,* cold, fairly strong action, hot, dispersed only slowly; *furfuraldehyde,* cold, solvent; *furfuryl alcohol,* cold, solvent; *cyclo-hexanol,* cold, action slight to moderate, hot, solvent; *iso-* and *tert-amyl alcohol,* cold, action *nil* or slight; *dibrompropyl alcohol,* cold, very strong action, solvent; *cineole,* cold, action slight, hot, could not disperse on boiling; *terpineol,* cold, moderate action, hot, solvent; *cinnamyl alcohol,* cold, action slight to fair, hot, solvent; *trimethylene glycol,* cold, action only slight; *diethylcarbinol,* cold, action *nil* or slight, hot, could not disperse on boiling; *phenyldimethylcarbinol,* cold, action moderate, hot, dispersed almost completely on boiling; *dimethyl-n-butylcarbinol,* cold, action *nil* or slight, hot, could not disperse; *diacetone alcohol,* cold, solvent; *methyl tolyl sulfide,* cold, action slight to moderate, hot, solvent; *thiophen,* cold, slight swelling; *pyrrole,* cold, solvent; *pyridine,* cold, solvent; *methylpyridine,* cold, solvent; *piperidine,* cold, solvent; *iso-quinoline,* cold, action slight; *xylidine,* cold, solvent; *phenylhydrazine,* cold, strong action, solvent; *diethylamine,* cold, action *nil* or slight; *benzylmethylamine,* cold, strong action, solvent; *triethanolamine,* cold, action slight; *methyl p-tolyl ketone,* cold, fairly strong swelling, hot, solvent; *iodobenzene,* cold, action slight, hot, partial dispersion only on boiling; *benzylidene chloride,* cold, moderate action, hot, solvent; *ethylene glycol monomethyl ether,* cold, no appreciable action observed, hot, solvent; *tetra nitromethane,* hot, could not disperse.

liquids for cellulose acetate, celluloid and rubber, and has also attempted to correlate the chemical structure of organic liquids with their solvent properties and swelling capacity. In 40 of the 60 tests made, it was found that swelling at room temperature was followed by ready dispersion as a result of heating, whereas when the swelling was initially absent, little or no dispersion resulted from raising the temperature. M. Deschiens[1] has studied the solubility of cellulose acetate graphically in ternary mixtures by means of triangular co-ordinates, and S. Sheppard and S. Sweet[2] have discussed solution and de-solution of cellulose esters by homologous series of carbon compounds, their work being accompanied by a bibliography.

In a discussion of "solvent balance," so necessary in the formulation of lacquers from cellulose ethers and esters, P. Symons[3] has recorded some unusually comprehensive and painstaking data on the dilution ratios of various solvents, which is reproduced herewith as Tables XVII to XX. It is to be observed that the addition of a small percentage of alcohol, up to 10% of the solvent mixture, materially decreases the viscosity, and that the tolerance of the solvent for diluent is increased where a percentage of alcohol is present. Inasmuch as the "cost" factor is paramount in lacquer production, considerable art has to be exercised in

Table XVII. Benzene-Alcohol.

Benzene / Alcohol	100 / 0	90 / 10	80 / 20	70 / 30	60 / 40	50 / 50	40 / 60	30 / 70	20 / 80	10 / 90	0 / 100
Acetone	4	8	30	66	144	286	150	67	50	38	50
Amyl Acetate	2	6	26	53	102	286	106	54	38	30	50
Butyl Acetate	2	8	24	54	108	286	110	56	40	34	50
Butyl Cellosolve	2	5	15	48	116	286	116	52	38	29	50
Cellosolve	6	10	18	28	92	286	94	37	32	24	48
Cellosolve Acetate	2	6	16	42	98	286	102	42	34	24	34
Cyclohexanone	4	6	18	40	106	286	106	42	34	26	50
Cyclohexyl Acetate	2	5	16	42	102	286	104	40	30	25	48
Ethyl Acetate	2	8	26	58	118	286	132	62	45	34	50
Ethyl Lactate	6	10	26	58	120	286	130	62	46	34	50
Methyl Acetate	4	7	18	48	98	286	100	42	34	28	50
Methyl Acetone	6	12	27	48	118	286	118	50	38	30	50
Methylethyl Ketone	6	13	34	62	138	286	142	66	54	42	50

1. Rev. gen. mat. Plast. 1930, **6**, 387; abst. C. A. 1930, **24**, 6005.
2. J. Phys. Chem. 1932, **36**, 819.
3. Brit. Plastics (Synthetic & Applied Finishes), 1932, **2**, #22, 95.

Table XVIII. Toluene—Alcohol.

Toluene / Alcohol	100 / 0	90 / 10	80 / 20	70 / 30	60 / 40	50 / 50	40 / 60	30 / 70	20 / 80	10 / 90	0 / 100
Acetone	3	6	26	56	108	146	110	60	46	32	50
Amyl Acetate	2	6	21	50	82	122	82	50	38	28	50
Butyl Acetate	2	6	24	53	99	137	106	59	38	30	50
Butyl Cellosolve	3	6	16	48	112	148	114	48	37	26	48
Cellosolve	6	9	19	38	78	115	80	34	26	25	50
Cellosolve Acetate	1	5	15	38	77	108	74	39	26	22	50
Cyclohexanone	3	6	18	38	78	106	82	38	27	24	48
Cyclohexyl Acetate	2	6	15	41	78	122	78	40	27	22	49
Ethyl Acetate	2	6	24	54	98	146	102	55	42	32	50
Ethyl Lactate	3	10	23	54	114	158	114	56	45	34	50
Methyl Acetate	3	9	18	42	91	132	94	42	33	28	50
Methyl Acetone	3	7	15	30	68	116	74	34	20	15	28
Methylethyl Ketone	4	6	18	46	114	150	118	50	38	30	50

Table XIX. Xylene—Alcohol.

Xylene / Alcohol	100 / 0	90 / 10	80 / 20	70 / 30	60 / 40	50 / 50	40 / 60	30 / 70	20 / 80	10 / 90	0 / 100
Acetone	2	3	6	29	50	80	54	38	30	21	50
Amyl Acetate	2	6	23	46	74	110	78	52	34	27	50
Butyl Acetate	3	7	22	46	72	106	70	48	35	26	50
Butyl Cellosolve	4	5	17	34	64	106	64	40	34	30	50
Cellosolve	5	8	15	26	60	102	62	30	26	22	50
Cellosolve Acetate	2	3	12	32	62	96	60	36	24	19	50
Cyclohexanone	4	6	18	34	65	106	63	39	30	26	50
Cyclohexyl Acetate	2	6	14	34	65	106	66	38	26	22	50
Ethyl Acetate	2	6	16	43	80	112	80	54	38	30	50
Ethyl Lactate	3	6	18	44	74	104	59	43	40	24	50
Methyl Acetate	2	4	10	18	48	72	50	38	24	20	50
Methyl Acetone	3	5	10	18	34	54	38	23	14	10	50
Methylethyl Ketone	2	6	14	36	66	106	66	38	34	26	50

Table XX. White Spirit—Alcohol.

0.780 Wh. Sp. / Alcohol	100 / 0	90 / 10	80 / 20	70 / 30	60 / 40	50 / 50	40 / 60	30 / 70	20 / 80	10 / 90	0 / 100
Acetone	1	1 5	2	3	4	6	8	11	18	30	50
Amyl Acetate	0.5	1	1.5	4	6	10	16	98	128	96	50
Butyl Acetate	0.5	1	1.5	4	7	10	17	110	138	98	50
Butyl Cellosolve	0.25	0.5	1	2	2.5	3	4	8	16	28	50
Cellosolve	...	0.5	0.75	2	8	12	16	22	30	39	50
Cellosolve Acetate	....	0.5	1	2	5	8	12	18	24	36	50
Cyclohexanone	...	1	2	4	6	10	13	18	24	34	50
Cyclohexyl Acetate	1	2	2	2	4	9	24	102	128	86	50
Ethyl Acetate	....	1	2	3	4	6	14	106	130	90	50
Ethyl Lactate	....	1	2	3	6	10	12	22	32	40	50
Methyl Acetate	....	1	2	3	6	8	9	12	18	32	50
Methyl Acetone	....	....	1	1.5	2	2.5	4	6	10	16	50
Methylethyl Ketone	0.5	1	1.5	2	4	5	6	9	16	30	50

order to produce the maximum of desirable workability at the minimum cost, which can be accomplished only by a careful consideration of the factors involved in dilution ratios as affecting the final product.

With mixed solvents, a number of variables enter into consideration, especially as to those solvents which disperse

the cellulose ethers more readily, or which widely disperse varying types of the cellulose ethers only when incorporated in certain proportions or within closely definable limits. The solvent properties which are sometimes latent in the single solvent may be developed in a mixture, in many cases there being evidence of the formation of complexes between the ingredients. P. Chaumeton and V. Yarsley[1] have shown that mixtures of toluene and alcohol will not disperse all types of cellulose acetate; with the higher esters, solution is effected only on warming, while with the over-ripened product (industrially inferior), the addition of a small amount of acetone is usually necessary, but such solutions usually gelate on standing. K. Werner and H. Englemann (see p. 841, n. 2)[2] state that while the action of heat on the dispersion of cellulose acetate in certain solvents can be regarded only in the light that the internal friction of the sols is less at higher temperatures, there is a range of about 51-55% acetic acid, over which dispersion in a mixture of equal parts ethyl alcohol and benzene is obtained only on warming. The critical temperature for this change they give as 70-71°. Above this point, and practically up to the boiling point of the mixture, dispersion readily takes place, yielding thin liquids, while in the lower neighborhood of this point, gelatinization of the product takes place with a considerable inclusion of the solvent, amounting in some cases to 100% on the weight of dry cellulose acetate. These dispersions usually set to a more or less transparent jelly.

In respect to general considerations of plasticizing agents, softeners and extensifiers, a good plastifier for cellulose ethers or esters is one that is insoluble in water, substantially odorless, has a high retentivity in combination with the cellulose derivative, and which hydrolyzes or splits off acid or halogen slowly or not at all. The volatility alone is no accurate criterion, for camphor readily volatilizes at normal room temperature and sublimes with ease, whereas,

1. Brit. Plastics, 1930, **2**, #15, 128.
2. Zts. ang. Chem. 1929, **42**, 438; abst. C. A. 1929, **23**, 4569; J. S. C. I. 1929, **48**, 468-B.

due to the courtesy of Dr. J. N. Goldsmith, the Author has in his possession articles fabricated by Alexander Parkes and exhibited by him at the International Exhibition, London, in 1862, in which the original camphor content as stated by him is substantially the same as found by analysis by ourselves seventy years later.

Strictly speaking, the terms "plasticizer" and "softener" are misnomers when applied to cellulose ether and ester compositions, although "thermoplasticizer" is a definite expression. The first two terms, therefore, are not to be used in a too literal interpretation. Primarily, a softener is not a compound or body which induces softness in a cellulose derivative, but rather one which imparts flexibility and also usually elasticity, properties substantially absent in the ester or ether *per se*. Of the manner in which these compounds induce this desired property we know but little, most of the speculative reasons which have been advanced lacking corroboration in actual practice phenomenon. The inference is that they act in the manner of an internal lubricant or friction-reducing body, as solid media in which the colloidal particles may move with greater freedom in rather narrowly confined limits. Until there is elucidated the structure of colloidal materials from the standpoint of geometrical configuration and the arrangement and linking up of the individual entities, it seems impossible to propound a rational theory of the manner in which plasticizing bodies function.

If and when and not until such an explanation is forthcoming, will we be in a position to predicate with any reasonable degree of accuracy the suitability or non-suitability of a particular plasticizer for a definitely stated purpose.

A too narrowly circumscribed interpretation of these terms often leads to erroneous conclusions. While it is true that the line of demarcation between direct solvents and plasticizers is indefinite, the one gradually and imperceptibly blending into the other, this twilight zone between the two is so broad and embraces so many suitable compounds,

that the solution of this problem of almost incomprehensible complexity, is nevertheless one of immense practical interest in the logical development of the technics of this art. Many cellulose ether direct solvents are good plasticizers, but the converse is less often true.

The general concept of a plasticizer is one that harmoniously knits together a cellulose ether into a non-separable whole, but softener and plasticizer as terms are purely relative, their correct application depending largely upon several not definitely characterized variables, and the ultimate purpose for which the plasticized compound is designed. If a plasticizer is considered as a body compatible with the cellulose ether physically, or perhaps chemically binding it into an indistinguishable whole so that as a chemical entity it remains behind after dissipation of the volatile solvent portion, then the time or extent to which it will remain in intimate association with the cellulose ether, depends in a great measure upon the distribution of the cubical contents of the product, that is, whether (say) 100 gms. are cast as a cube of one inch, and therefore with an exposed evaporable surface area of six square inches, or whether the same weight is distributed out in a thin film of many times greater superficial area.

While the primary function of plasticizers is to induce and conserve flexibility, they also in many instances increase water resistivity, minimize ultimate shrinkage, and impart fire-retardant qualities. For this reason the vapor pressure of the plasticizer must be low at the temperature at which the finished article is designed to be used, and there should be no deleterious reaction between plasticizer and cellulose derivative. As H. Wolff[1] has shown, the definite or absolute evaluation of a named plasticizer is impossible without concrete knowledge as to the physical constants of the particular derivative with which it is to be associated, and the use and conditions under which the finished product are to

1. Farben-Ztg. 1930, **35**, 750.

be placed. The rotation of ingredients in compounding is also often of considerable importance.

While the range of available plasticizers for cellulose acetate is less than those suitable for the nitrocelluloses, those applicable to the cellulose ethers as a class appear to exceed both the nitro- and acetyl-celluloses by virtue of the much wider solvent capacity of the etherified celluloses. There has as yet been no compound found which occupies the chair of Professor Emeritus with the cellulose ethers, as does natural camphor with the nitrocelluloses. Our feeling is that without a doubt such a compound or series of compounds is or are existent, but when someone unwittingly or otherwise stumbles upon, reasons out, or synthesizes such a body, the cellulose ethers by virtue of their relatively low inflammability, wide solvent capacity, exceedingly high stability and inertness towards concentrated alkalis and acids, will rapidly supercede the nitrated and acetated celluloses in practically all fields of application involving the dissolved condition.

N. Ishii[1] has examined the plasticizing effect of solid plastifiers on cellulose acetate in film form, and has drawn the following generalizations:

1. Attempts were made to study the form of combination between the cellulose acetate and plasticizers by causing acetylcellulose films to swell in ethyl alcohol containing various amounts of plasticizers. Cellulose acetate is swelled by alcohol only to a limited degree, and the cellulose acetate alcoholic gel thus formed apparently acts as a plasticizer solvent.

2. The efficiency of a plasticizer increases with the affinity, viscosity and surface tension of the combination of plasticizer-acetylcellulose.

3. Increase in plasticity is ascribed to the permanent state of the swollen cellulose acetate, in which state the mutual cohesive power of the micelle is decreased by the

1. J. Cellulose Inst. Tokyo, 1931, **7**, #10, 51, 235; abst. J. S. C. I. 1932, **51**, 96-B.

intra-micellar swelling, the spaces between the structural units are enlarged, and the slipping capability among the micelle or the structural units is increased by the "inner lubricating effect" of the plasticizer.

P. Chaumeton and V. Yarsley[1] have compiled Tables showing the important constants of some of the more common cellulose ether and ester solvents (Table XXI) and plasticizers (Table XXII) which are reproduced herewith.

Table XXI. Physical Constants of Cellulose Ether and Ester Solvents

Solvent	B. P. °C.	S. G. 15°C.	R. I. 15° C.	Time of Evaporation. Ether equals 1	% Sol. in water at 20° C.	Action on Diluents, Oils, Gums, Resins						
						Benzene	Toluene	Castor Oil	Shellac	Copal	Glyptal Resins	Ester Gum
Methyl acetone	50/70	0.830	. .	2.3	S.∞.	S	S	S	P	S	S	S
Ethyl formate	53/58	0.927	1.360	....	10	S	S	S	I	I	S	S
Acetone	56	0.7912	1.3599	2.1	S ∞.	S	S	S	P	S	S	S
Methyl acetate	55/60	0.93	1.362	2.2	31.9	S	S	S	I	I	S	S
Chloroform	61	1.49	1.447	...	0.5	S	S	I	I	I	S	S
Ethyl acetate	77	0.901	1.3690 (25°C)	2.9	8.6	S	S	S	P	I	I*	S
Methylethyl ketone	80	0.815	1.379	4.0	24	S	S	S	I	S	S	S
Dimethyl cellosolve	85	0.878 (20°C)	1.3839 (20°C)	4.2	S	S	S	S	I	SS	S	P
1.4-Dioxane	101	1.0338 (20°C)	1.4232	16	S	S	S	S	S	G	S	S
Methyl cellosolve	124	0.975	1.40 (25°C)	34	S	S	S	I	S	G	S	P
Ethylene chlorhydrin	128	1.21	. .	....	S	S	S	S	I	SS	P	SS
Methylcellosolve acetate	141	0.992	1.4025 (25°C)	35	S	S	S	I	S	SS	S	P
Tetrachlor-ethane	147	1.601	1.495	....	I	S	S	I	I	P	S	S
Cellosolve acetate	153	0.978	1.405 (25°C)	52	22	S	S	S	S	G	SS	S
Ethyl lactate	154	1.035	1.4118 (20°C)	80	S.∞.	S	S	S	S	P	S	S
Cyclohexanol	160	0.945	1.1466	403	5	S	S	S	S	P	S	S
Diacetone alcohol	166	0.945	1.4204 (20°C)	147	S	S	S	S	P	P	S	SS
Glycol monoacetate	182	1.108 (20°C)	....	606	S	S	S	I	I	I	I	I
Glycol diacetate	190	1.11	1.415 (20°C)	650	I	SS	SS	I	I	I	I	I
Benzyl alcohol	205	1.051	1.541	1767	3	S	S	S	P	S	S	S

Key—S.∞., =soluble in all proportions; S, =soluble; SS, =slightly soluble; P, =partially soluble; G, =swells; *, =soluble on addition of alcohol.

1. Brit. Plastics, 1930, **2**, #16, 177.

Table XXII. Physical Constants of Cellulose Ether and Ester Plasticizers

Plasticizer	M.P. °C	B.P °C	S.G. (15°C)	R.I. (15°C)	% Sol. in water at 20°C	Action on Diluents, Oils, Gums, Resins						
						Benzene	Toluene	Castor Oil	Shellac	Copal	Ester Gum	Glyptal Resins
Triacetin	—	258	1.161	1.433	6	S	S	P	P	S	P	S
Diacetin	—	259	1.19	—	S∞	I	I	P	S	I	I	S
Diethyl phthalate	—	290/300	1.13	1.500 (25°C)	I	S	S	S	P	SS	S	S
Dibutyl phthalate	—	325	1.05	1.495	0.04 (25°C)	S	S	S	P	S	S	P
Benzyl benzoate	19	324	1.126	1.569	I	S	S	S	P	S	S	P
Butyl oleate	—	357/370	0.88	—	I	P	P	S	I	S	S	P
Dimethylcyclohexanyl adipate	—	decomp 225/232 (12 mm)	1.011	—	—	S	S	P	I	SS	S	P
Dimethylcyclohexanyl methyladipate	—	216/224 (12 mm)	1.009	—	—	S	S	P	I	P	S	P
Diamyl tartrate	—	400	1.06	1.45	I	S	S	S	S	P	S	S
Triphenyl phosphate	45/48	410	—	—	I	S	S	I	I	I	I	I
Tricresyl phosphate	—	430/440	1.189	1.498 (25°C)	0.02 (25°C)	S	S	S	P	S	S	S
p-Toluene methyl sulfonamide	78	—	—	—	I	S	S	—	—	-	—	—
p-Toluene sulfonamide	137	—	—	—	I	P	P	—	—	—	—	—

According to H. Messer[1], from a chemical viewpoint the approach to the ideal of a solvent for cellulose derivatives as cellulose acetate is one with the essential structure of acetone and methyl and ethyl acetate reproduced in a non-

1. J. S. C. I. 1931, **50**, 386-T. Sodium salicylate and chloracetone were combined and the free hydroxyl group then acetylated, giving rise to $OAc.C_6H_4.CO_2CH_2Ac$. Thus a compound containing two ester groups in addition to the acetone radical was obtained, i.e., a large molecule (high-boiling) with three gelatinizing groups attached. If, instead of salicylic acid, benzoic acid is used, the compound $C_6H_5CO_2CH_2Ac$ results. On account of the inert nature of the benzene nucleus in this example, the gelatinizing effect of the side chain is reduced. If, however, another side chain is present as in the first example, both side chains retain almost all their original softening power. Should it be desired to use aromatic acids other than the hydroxy-acids, it is advised to select those with two carboxyl groups such as phthalic acid, so that an ester of the type $C_6H_4(CO_2CH_2Ac)_2$, diacetonyl phthalate, is obtained. Here the benzene nucleus is combined with two acetonyl ester groups (in all, four gelatinizing groups), so that the depressing effect of the heavy nucleus is far less apparent than in the benzoic ester.

An analogous effect may be had by combining hydroxy- or dicarboxy-aromatic acids with methyl or ethyl acetate, and may be made

volatile compound, i.e., the keto-grouping in the acetone, or ester-grouping in the acetate combined with a high-boiling nucleus which is in itself a moderately good softener, thus giving a plasticizer with very high boiling point.

A. Kraus[1] has examined in detail and evaluated the following plasticizing bodies: tritolyl phosphate, dibutyl and diamyl phthalates, tributyl phosphate, butyl stearate, castor oil, "casterol," "ricol," "sipalin special" and "sipalin MOM," and tabulated their volatility and viscosity, while H. Wolff and I. Rabinowicz[2] have determined the loss of weight at 80° of various plasticizers, including a new material "Hydropalat CY."

The following is a synopsis of the classification of the solvents, non-solvents and plasticizing and softening bodies enumerated and described herein. While some of them have been described as having been experimented with only as to their dissolving or colloiding capacity in connection with perhaps the nitrocelluloses or cellulose acetate, yet

from the sodium salts of the aromatic acids and chloracetic ester with subsequent acetylation in the case of hydroxy-acids, giving $AcO.C_6H_4.CO_2CH_2.CO_2Et$ from salicylic acid, and $C_6H_4(CO_2CH_2.CO_2Et)_2$ from phthalic acid. All of these esters have the desired properties of a satisfactory softener, being water-insoluble and therefore very stable towards hydrolysis. Starting again from the fact that ester groups are good gelatinizers, endeavors have been made to combine diacetin and aromatic or aliphatic mono- and di-carboxylic acids, the compounds $AcO.C_6H_4.CO.CH(CH_2.OAc)_2$ from salicylic acid and $C_6H_4(CO_2.CH(CH_2.OAc)_2)_2$ from phthalic acid, quantitative yields being readily obtained. Products of this type are thick, syrupy liquids which do not crystallize at —20° and have high boiling points, the phthalic acid derivative refusing to distil, even at 300° under 1 mm. It differs from triacetin in being insoluble in and practically non-hydrolyzable by water. It is a general principle that the connection radical—in this case carbonic acid—should be small; if large, it should be a dicarboxylic or hydroxycarboxylic acid, and not such a compound as benzoic acid.

A product similar in structure to these glyceryl esters is manufactured by C. F. Boehringer & Soehne under the name Glyacol, and has proven an excellent plastifier, being non-volatile, and a water-insoluble syrupy liquid. Whereas methyl and ethyl phthalates are good softeners, the higher phthalic esters are considered superior because less volatile, but the longer the side chain the more is the gelatinizing effect depressed, that is, a gain in non-volatility in this ester type is nullified by the relatively poor softening power.

1. Farbe. u. Lack, 1932 121, 135; abst. J. S. C. I. 1932, **51**, 392-B.

2. Farben-Ztg. 1932, **37**, 585; abst. J. S. C. I. 1932, **51**, 271-B.

the feverish search which is going on for new and desirable cellulose ether and ester dissolvants should include a trial of those compounds described as advantageous in the older arts, as being possibly of decided advantages in connection with the various types of cellulose ethers:

Inorganic Compounds (page 1796).

Hydrocarbons, Aliphatic (1799), Aromatic (1801). Dioxydiphenyldimethylmethane (1810).

Halogen Substituted, Methanes (1811), Ethanes (1815), Ethylenes (1821).

Haloid Aromatic Hydrocarbons (1825).

Alcohols, Aliphatic. Methyl (1829), Ethyl (1832), Propyl (1834), Butyl (1835), Amyl (1836), Dihydric Alcohols (1837), Chlorhydrins (1839), Glycol Derivatives (1845), Polyhydric Alcohols (1856).

Aromatic Alcohols, Phenol (1858), Polyhydric Phenols (1859), Benzyl Alcohol (1862).

Aldehydes. Aliphatic (1864), Aromatic Aldehydes (1867), Aldol (1868).

Ethers (1869), Acetal (1873), 1.4-Dioxane (1875).

Ketones, Aliphatic (1877), Diacetone Alcohol (1884), Mesityl Oxide (1886), Acetoxime (1887), Aromatic Ketones (1888).

Acids, Aliphatic (1890), Glycine (1893), Aromatic Acids (1894).

Esters, Phosphoric (1895), Carbonic and Resorcindicarboxylic (1906), Inorganic (1908), Formic (1909), Acetic (1912), Acetoacetic (1929), Propionic (1932), Levulinic (1934), Butyric (1935), Valerianic and Higher (1937), Glycollic, Acetoglycollic, Thioglycollic (1941), Phenoxyacetic and Naphthoxyacetic (1942), Lactic (1942), Oxalic (1947), Malonic (1948), Succinic and Malic (1949), Maleic and Fumaric (1950), Tartaric (1950), Citric (1952), Adipic (1953), Acrylic and Crotonic (1953), Glyceric (1954), Abietic (1954), Carbamic and Urethanes (1955), Carbanilic (1957), Benzoic and Salicylic (1957), Naphthenic

(1965), Anisic (1966), Mandelic (1966), Phthalic (1967), Cinnamic (1978), Oxanilic and Oxynaphthylaminic (1979).

Polymethylene Derivatives, Cyclo-Compounds (1979).

Cyclopentanol and Cyclohexanol Esters (1988).

Vinyl Compounds (1993).

Furan or Furfurane Group (1995).

Sulfones (2000).

Sulfoxides (2001).

Nitro Aromatic Bodies (2002), Nitronaphthalin (2005).

Amines and Amides, Aliphatic (2006), Aromatic (2007), Anilids (2019).

Ureas, Guanidines (2026).

Pyridine, Quinoline, Acridine (2031).

Toluenesulfonate Compounds (2033).

Sulfonamides (2035).

Essential Oils, Terpenes (2044).

Camphor (2048).

Resins and Waxes (2052).

Esterified Oils (2056).

Proteids, Albumen, Casein (2056).

Polysaccharides, Sugars (2058).

Reduction in Inflammability (2058).

Flash Points of Solvents (2060).

Inorganic Compounds. To a limited extent various salts, usually water-soluble and preferably also dissolvable in alcohol and other organic solvents, have been used as direct solvents. Unfortunately, many of the salts which otherwise are applicable, have a well developed hydroscopicity, another drawback being their water-solubility and hence lack of stability towards moisture.

Zinc nitrate and chloride[1], basic lead acetate[2], calcium resinoleate[3], sodium oleate[4], boric acid[5], sulfur dioxide[6], sul-

1. W. Dreaper and H. Tompkins, D. R. P. 113786.
2. J. Crane, U. S. P. 1329583; abst. J. S. C. I. 1920, **39**, 249-A.
3. C. Schroeder, L. Levi and A. Lasche, U. S. P. 951582.
4. T. Whittelsey, E. P. 206520; abst. C. A. 1924, **18**, 1184.
5. Titanine, Ltd., and P. Bowles, E. P. 136927; abst. Kunst. 1921, **11**, 15.
6. H. Parkes, E. P. 1866, 1879. Nitrogen Corp. and J. Clancy, E. P. 189416. Ital. P. 212139.

fur dissolved in chloroform[1], zinc nitrate or iodide[2], calcium thiocyanate (sulfocyanide)[3], and liquid sulfur dioxide indicate some of the salts and inorganic combinations which have been used as dissolvants and gelatinizers, primarily in connection with the nitrocelluloses.

Carbon Bisulfide has been found to be an excellent solvent for the cellulose ethers, especially ethyl- and benzylcellulose of higher etherification, some of the desirable dissolving media being carbon bisulfide with ethyl ether 5:1, with benzene 9:1, with butyl alcohol 19:1, or ethyl ether-benzene 9:1, the latter having a constant boiling point of 60°[4]. Mixtures of cellulose ethers dissolve with equal facility.

Benzene with carbon bisulfide constitutes an excellent but highly inflammable solvent mixture[5]. For instance, when a triethylcellulose which dissolves to a clear solution in benzene, is treated with a mixture of 92% CS_2 and 8% benzene, in proportion to produce a solution containing 8% ethylcellulose, a somewhat milky solution results. From this turbid solution clear films may be cast, which have a tensile strength enhanced to the extent of 20-25% with equal extensibility as compared with films made from the same ethylcellulose dissolved in pure benzene and treated under similar conditions.

1. P. Leder, U. S. P. 974285.
2. A. Parkes, U. S. P. 257607.
3. Manchester Oxide Co., F. P. 494234. Holl. P. 8351. Dan. P. 27195. Norw. P. 37627. Ital. P. 171138. Manchester Oxide Co. and R. Clayton, E. P. 123784. H. Dreyfus, E. P. 284798. Cites E. P. 281084. F. Beck, D. R. P. 357972. Soc. pour la Fabrication de la soie Rhodiaseta, E. P. 246430. I. G. Farbenindustrie, Swiss P. 143668. F. P. 674761. Farbenfabriken vorm. F. Bayer & Co., D. R. P. 281374. Naamlooze Vennootschap Nederlandsche Kunstzijdefabriek and F. Beck, Holl. P. 9656.
4. I. G. Farbenindustrie, E. P. 297676; abst. C. A. 1929, **23**, 2822; Chem. Zentr. 1929, I, 592. F. P. 653583; abst. C. A. 1929, **23**, 3808; Chem. Zentr. 1929, I, 2940.
5. *Ibid.* E. P. 295942; abst. C. A. 1929, **23**, 2293; J. S. C. I. 1930, **49**, 99-B; Brit. Plastics, 1930, **1**, #10, 446; Chem. Zentr. 1928, II, 2760. Belg. P. 350769. F. P. 653297; abst. C. A. 1929, **23**, 3807; Chem. Zentr. 1929, II, 3261. Swiss P. 133158. D. R. P. 520411; abst. C. A. 1931, **25**, 2850.

It is also claimed that if a triethylcellulose as above is dissolved in pure carbon bisulfide or pure acetone, a solution in a mixture of 7% ethylcellulose containing acetone 4 and CS_2 96 parts "has three times the extensibility of and the same tensile strength as a film made from a pure acetone solution under the same conditions."

If a solution of 8% 2.5-ethylcellulose (2:5 ethyl groups per C_6 cellulose molecule)[1] containing 84% CS_2 and 16% ethyl ether be made, when worked up at 24°, numerous small bubbles appear, whereas the same solution worked up at +5° yields a clear and correspondingly strong and lustrous film. As another example, a mixture of 92% ether and 8% CS_2 containing 9% of a 2.5-ethylcellulose worked up at 20° produces a non-transparent film enclosing many bubbles, and of very poor tenacity and extensibility. But the same solution when manipulated at +3°, and only raised to a higher temperature, namely 30-40° after the first drying, yields a film practically bubble-free.

Carbon bisulfide in limited amounts was used in the early days of the pyroxylin plastic industry as a solvent of cellulose nitrate[2] and of xyloidine[3], but was soon abandoned on account of the toxicity and disagreeableness of the vapor.

Ammonia, anhydrous, so-called "liquid ammonia," now an article of commerce in unlimited amounts, has been found an efficient rapid solvent for both pyroxylin and some types of acetylcellulose. The ester may be dissolved in liquids in which they are initially insoluble by means of the addition of a relatively small amount of anhydrous ammonia[4], transferring the treated ester into the liquids and evaporating the ammonia, or[5] the ester may be com-

1. I. G. Farbenindustrie, E. P. 302667; abst. Silk J. 1929, **5**, #59, 72; Kunst. 1931, **21**, 16; Chem. Zentr. 1929, I, 1875.
2. H. Parkes, U. S. P. 265337.
3. D. Spill, U. S. P. 97454.
4. Nitrogen Corp. and J. Clancy, E. P. 190694; abst. J. S. C. I. 1923, **42**, 1126-A. U. S. P. 1439293; abst. J. S. C. I. 1923, **42**, 180-A; Chem. Ztg. 1923, **47**, 27. Ital. P. 212138.
5. *Ibid.* E. P. 182488; abst. C. A. 1922, **16**, 4346; J. S. C. I. 1923, **42**, 1171-A.

pletely dissolved in anhydrous ammonia, subsequent admixture with volatile non-solvent being carried out in the atmosphere. In this way cellulose nitrates in aliphatic or aromatic alcohols either alone or admixed with esters of these alcohols or with carbon bisulfide, carbon tetrachloride, chloroform, ethyl chloride, tetrachlorethane, benzene, benzine or naphthalene may be obtained. Liquid sulfur dioxide, preferably substantially pure and free from moisture, dissolves both nitrocellulose and acetated cellulose, and possesses the advantage of non-inflammability and ready removability from the finished product by simple evaporation[1].

Ammonia has been used in preparing celluloid substitutes[2], as a pyroxylin precipitant[3], in the acetation of cellulose[4] and as a pyroxylin solvent with chlorethane.

The Internationale Celluloseester Ges.[5] have advocated the use of sodium and potassium bromides and iodides; ammonia nitrate, cupric chloride or potassium bichromate as a solvent for cellulose formate. Bromine[6] has been employed in the manufacture of methyl- and ethyl-cellulose.

Aliphatic Hydrocarbons. None of the paraffin, olefin or acetylene hydrocarbons are solvents of nitrocellulose or the acetylated celluloses, but do dissolve some of the cellulose ethers, notably the water-insoluble ethylcelluloses (the so-called triethylcelluloses). They are used primarily as diluents in amounts well under the precipitation point of the cellulose derivative in lacquers, enamels and varnishes. The petroleum hydrocarbons are the most inexpensive water-immiscible bodies used in conjunction with solvents in this art. The hydrocarbons in admixture from *n*-hexane (b. pt. 71°) to decane, are the usual cuts employed. The

1. Nitrogen Corp. and J. Clancy, E. P. 189416; abst. J. S. C. I. 1923, **42**, 1171-A. Ital. P. 212137. Can. P. 234321.
2. H. Dreyfus, U. S. P. 1501206.
3. C. Schwartz, U. S. P. 1398804.
4. W. Bonner, U. S. P. 1173336.
5. D. R. P. 266600; abst. C. A. 1914, **8**, 573; J. S. C. I. 1914, **33**, 196. D. R. P. 267557; abst. J. S. C. I. 1914, **33**, 196.
6. L. Lilienfeld, U. S. P. 1188376.

A. Burwell petroleum products adapted for use in nitrocellulose coating compositions comprehend the range 173-297° b. pt., covering the kerosene fractions[1]. B. Lougovoy[2] limits the fractions to 100-150°, the distillate containing some unsaturated hydrocarbons from cracking operations.

Petroleum ether, b. pt. 40-60°, sp. gr. 0.63-0.67 comprises mainly *n*-hexane. It is miscible with some types of etherified cellulose without turbidity, but too volatile for general use in lacquers.

Petroleum spirit, Ligroin, Benzoline, Benzine, Gasolene, Lythene, comprises mainly hexanes and heptanes, with usually small amounts of octanes. It has been used as a cheap non-solvent in pyroxylin lacquers[3], cellulose acetate precipitant[4], celluloid substitute formation[5], cellulose nitrate solvent mixture[6], in electric insulation formulas[7], lacquer manufacture[8], varnish preparations[9] and paint removers[10], ceresin[11], vaseline in cellulose acetate compositions[12] and as an ethylcellulose solvent[13] and in petroleum

1. U. S. P. 1791711. 2. U. S. P. 1855681.

3. C. Ellis, U. S. P. 1529056. E. P. 23544, 1912. F. P. 471104. O. Schmidt, T. Eichler and O. Allemann, U. S. P. 1166790. E. P. 21368, 1912. F. P. 459006. See also D. R. P. 263404, 272391. Aust. P. 64393. Swiss P. 64710.

4. H. Levey, U. S. P. 1330543.

5. U. S. P. 1245976, 1245983, 1245984, 1427645.

6. U. S. P. 1152625, 1158265, 1160979, 1196144, 1267445, 1329386, 1341710, 1355976, 1356440, 1398525, 1439293.

7. U. S. P. 1123401, 1245976, 1245980, 1245981, 1245984, 1248447, 1255139, 1448556, 1492155.

8. U. S. P. 1185514, 1195673, 1245981, 1245982, 1427645.

9. U. S. P. 1133432, 1156119, 1159258, 1191390, 1195673, 1226760, 1242161, 1280861, 1307805, 1326917, 1411050, 1427645, 1432110, 1436820, 1458493, 1488274.

10. U. S. P. 1130499, 1143110, 1143111, 1147848, 1147849, 1156119, 1189803, 1280162, 1381485, 1483587.

11. C. Claessen, D. R. P. 163668. The I. G. Farbenindustrie (E. P. 282172; abst. J. S. C. I. 1928, **47**, 155-B. Cf. E. P. 227147, 229714, 237030, 238390; abst. J. S. C. I. 1925, **44**, 189, 338, 784) has described as solvents for cellulose esters catalytic hydrogenation products of carbon oxides or fractions from these products or the products of their acylation which are superior, and which are miscible with aliphatic alcohols or their esters, and aliphatic and aromatic hydrocarbons.

12. G. Convert, F. P. 421843; abst. J. S. C. I. 1911, **30**, 415; Kunst. 1911, **1**, 174.

13. L. Lilienfeld, U. S. P. 1188376; abst. C. A. 1916, **10**, 2145.

products[1]. The A. Wacker Ges. solvent[2] for lacquers is 1-hydroxy-3-alkoxybutanes. Bis(hydroxyaryl)ethane has been recommended in methylcellulose compositions[3] and for admixture with ethylcellulose, and 2.2-bis(hydroxyphenyl)-propane in celluloid substitutes[4], as an acetylcellulose plasticizer[5], motion picture fabrication[6], for electric insulation[7], and in the production of acetone[8].

Methylal, Dimethoxymethane, Methylenedimethylate, Methylenedimethyl Ether, a colorless, volatile liquid of chloroformic odor and pungent taste, easily soluble in water, alcohol, ether and oils, has sp. gr. 0.872 at 15°, b. pt. 42°, has been proposed for combining with cellulose acetate[9], for the formation of celluloid substitutes[10] and the manufacture of cellulose ester lacquers[11]. Nitromethane, both mono-nitro and tetra-nitro, has been proposed as cellulose ether solvent. L. Lilienfeld[12] combined the lower monohydroxy aliphatic alcohols with nitromethane in the proportion, for example, of 10 parts water-insoluble ethylcellulose dissolved in a mixture of 20-60 parts nitromethane and 80-40 parts methyl or ethyl alcohol.

Aromatic Hydrocarbons. Many of these are direct solvents of the cellulose ethers, their solvent capacity being augmented by the addition thereto of the lower monohydroxy aliphatic alcohols as methyl or ethyl alcohols. Methyl-, ethyl- and benzyl-celluloses have been described

1. U. S. P. 35687, 262077, 1079773, 1175791, 1365049. E. P. 22309, 1910.
2. F. P. 704145; abst. C. A. 1931, **25**, 4638.
3. L. Lilienfeld, U. S. P. 1505044.
4. U. S. P. 1156969, 1158960, 1158961, 1158962, 1188356.
5. U. S. P. 1156969, 1158960, 1158963, 1158964.
6. U. S. P. 1158961, 1158962, 1158963.
7. U. S. P. 1156969, 1158962, 1397144.
8. U. S. P. 1188356, 1225748, 1225749, 1225750.
9. H. Dreyfus, F. P. 432264; abst. J. S. C. I. 1912, **31**, 24; 1913, **32**, 19; Kunst. 1914, **4**, 360.
10. *Ibid.* U. S. P. 1181859; abst. C. A. 1916, **10**, 1789.
11. L. Baekeland, U. S. P. 1217115; abst. C. A. 1917, **11**, 1279.
12. U. S. P. 1599569; abst. C. A. 1926, **20**, 3567; J. S. C. I. 1926, **45**, 1010-B; Ann. Rep. S. C. I. 1926, II, 131, 368; Rev. gen. mat. Plast. 1927, #1, 46; Chem. Zentr. 1927, II, 380.

which dissolve in a mixture of benzene (or toluene) and alcohol within the wide range of 10:90 to 90:10. Benzene and toluene are cellulose acetate precipitants[1].

Benzene is the term used in this work rather than benzol, and toluene and xylene instead of toluol and xylol. Benzene is found in the trade usually as "Benzol 100%," water-white, 100% distilling within 2° and not above 100°, sp. gr. 0.875-0.885; "90% Benzol," 90% distilling at not above 100°, sp. gr. 0.875-0.883; and "50% Benzol," in which 50% distills at not above 100° or 90% at not above 120°, sp. gr. 0.868-0.880. Benzene is largely used as a diluent in the cellulose ether industry, and in addition to being a solvent for the cellulose ethers, it dissolves aluminum naphthenate (see p. 107), benzylcellulose (pp. 10, 230, 248, 249, 278), butylbenzylcellulose (p. 278), butylcellulose solvent (p. 278), cellulose acetate solvent (pp. 484, 1039), cellulose acetate colloidant (pp. 553, 660, 800, 908, 912), cellulose acetobutyrate solvent (p. 559), cellulose dilaurate solvent (p. 538), ethylbenzylcellulose solvent (p. 278), and for the crystallization of triethylcellulose (p. 116).

As a few of the preferred solvent combinations utilizing benzene may be mentioned, with acetone and benzyl alcohol[2], alcohol[3], carbon tetrachloride[4], butyl or amyl acetates[5], ethyl glycol[6], and with methyl or ethyl alcohols. Benzene has also been employed in the cellulose ester and ether

1. G. Bonwitt, D. R. P. 237151; abst. C. A. 1912, **6**, 1526; J. S. C. I. 1911, **30**, 1232; Wag. Jahr. 1911, **57**, II, 506; Chem. Zentr. 1911, II, 500; Chem. Ztg. Rep. 1911, **35**, 456; Zts. ang. Chem. 1911, **24**, 1838; Kunst. 1911, **1**, 340; Zts. Chem. Ind. Koll. 1911, **9**, 318.

2. D. Sutherland, U. S. P. 1320290; abst. C. A. 1920, **14**, 131; J. S. C. I. 1919, **38**, 954-A; Kunst. 1920, **10**, 149. E. P. 131082; abst. J. S. C. I. 1919, **38**, 834-A; Chim. et Ind. 1921, **5**, 577; Ann. Rep. S. C. I. 1920, **5**, 324; Kunst. 1920, **10**, 134; 1922, **12**, 6. Can. P. 195559.

3. D. Sivet, F. P. 517356; abst. Mon. Sci. 1923, (5), **13**, 4.

4. W. Jenkins and Imperial Chemical Industries, Ltd., E. P. 305148; abst. C. A. 1929, **23**, 4819.

5. I. G. Farbenind. A.-G., E. P. 294912; abst. C. A. 1929, **23**, 2050; J. S. C. I. 1928, **47**, 762-B.

6. S. Shipley and G. Given, U. S. P. 1533616; abst. C. A. 1925, **19**, 1784.

art in film manufacture[1], especially photographic films[2], in finish removers[3], electric insulation[4], lacquer production[5], molded articles and thermoplastic bodies[6], motor fuels[7], paints[8], paint removers[9], as a phenol-aldehyde condensate solvent[10], plastic production[11], varnish fabrication[12], in var-

1. U. S. P. 1199395, 1217027, 1347801, 1363763, 1400196, 1434432, 1440006, 1441181, 1480016, 1488608, 1501206, 1508928.

2. U. S. P. 1188797, 1226339, 1226341, 1240344, 1357614, 1395905, 1405448, 1405449, 1405490, 1429179, 1441142, 1441181, 1488294, 1500393, 1512751, 1518417, 1519659.

3. U. S. P. 1140449, 1145365, 1147851, 1147852, 1160394, 1167462, 1167469, 1167640, 1167641, 1172773, 1173628, 1185641.

4. U. S. P. 1131578, 1149171, 1159257, 1179357, 1181800, 1185074, 1194201, 1209333, 1216265, 1216266, 1233415, 1233416, 1234381, 1245981, 1246810, 1248638, 1286370, 1300218, Re-15199, 1332860, 1370666, 1383740, 1398143, 1425784, 1427911, 1439056.

5. U. S. P. 262077, 495263, 518388, 555596, 595355, 598649, 694946, 805466, 841509, 893987, 972464, 981178, 1015155, 1015156, 1021569, 1035108, 1039782, 1084702, 1118498, 1135026, 1148168, 1152625, 1185514, 1195090, 1195673, 1216265, 1216266, 1234381, 1245981, 1245982, 1347801, 1354154, 1411035, 1437170, 1480016, 1488608. See D. R. P. 10210, 17089, 210519, 250421, 254784, 263404, 272391, 279638, 281265, 295764, 302460, 307075, 336476, 352905, 397919. Aust. P. 47899, 56488, 64393. Swiss P. 47559, 51952, 52115, 64710, 66510. Jap. P. 32242.

6. U. S. P. 1175791, 1185074, 1209333, 1216265, 1216266, 1220401, 1286370, 1300218, Re-15199, 1354154, 1368753, 1370666, 1398143, 1425784, 1427690, 1439056.

7. U. S. P. 1360872, 1361153, 1363870, 1378858, 1388531, 1398947, 1412233, 1414759, 1419910, 1420007, 1423048, 1423049, 1423050, 1423058, 1425136, 1428885, 1428913, 1460767.

8. U. S. P. 1131578, 1133433, 1167264, 1179176, 1179413, 1189549, 1192756, 1204629, 1209333, 1216265, 1216266, 1242161, 1370195, 1408325, 1451092, 1515439.

9. U. S. P. 1129770, 1130499, 1143110, 1143111, 1143130, 1143387, 1143877, 1143878, 1147848, 1147849, 1147850, 1173628, 1185641, 1189803, 1189804, 1201181, 1204851, 1229247, 1235721, 1273307, 1281156, 1328080, 1381485, 1406175, 1495547, 1499101, 1516064.

10. U. S. P. 1191390, 1209333, 1216265, 1216266, 1252507, 1261615, 1277904, 1309581, 1354154, 1368753, 1370666, 1396021, 1398143, 1398144, 1401633, 1404792, 1414139, 1439056.

11. U. S. P. 1146787, 1173337, 1175791, 1185074, 1188797, 1189549, 1191801, 1194201, 1209333, 1234381, 1245981, 1357614, 1395905, 1405490, 1425784, 1427690, 1427911, 1440006, 1474830, 1488608.

12. U. S. P. 1131578, 1133432, 1133433, 1159257, 1159258, 1167264, 1191390, 1195673, 1204697, 1209333, 1216265, 1216266, 1226760, 1234381, 1242161, 1251863, 1347801, 1354154, 1357614, 1370195, 1395905, 1405490, 1408325, 1411050, 1413666, 1436820, 1440006, 1441181.

nish removers[1] and as a rubber solvent[2].

Ethylbenzene has been patented by S. Carroll[3] as a cellulose ether dissolvant, in conjunction with methyl or ethyl alcohols or acetates, a mixture of ethylbenzene-methyl acetate (10:90) dissolving about 20% of its weight of water-insoluble ethylcellulose, to form a thick, viscous flowable solution suitable for film manufacture.

Toluene, Toluol, is a cellulose precipitant (pp. 811, 1043) although used in acetylcellulose plastic (p. 442), and there are types of cellulose acetate (p. 484) which partially or wholly dissolve in toluene. Nearly all types of the cellulose ethers dissolve in toluene, and probably all in toluene aided by methyl or ethyl alcohol, except those cellulose ethers of relatively low degree of etherification. Benzylcellulose dissolves in toluene (p. 248). Toluene has been used as a plastifier with camphor in acetylcellulose combinations[4], a mixture of toluene with ethyl or butyl acetates being a favorite nitrocellulose lacquer combination[5]. In cellulose nitrate solutions[6], as a cellulose ether solvent[7], and in cellulose acetate compositions[8], toluene is most used.

Toluene boils at 110-112°, sp. gr. 0.867-0.87, dissolves

1. U. S. P. 1129770, 1130499, 1143110, 1143111, 1143130, 1143387, 1147848, 1147849, 1147850, 1185641, 1189803, 1189804, 1201181, 1229247, 1235721, 1273307, 1281156, 1328080, 1381485, 1414139, 1437170, 1499101, 1516064.

2. U. S. P. 1146414, 1193883, 1217213, 1217214, 1217215, 1220401, 1228680, 1300263, 1302064, 1302065, 1312452, 1316295, 1350533, 1371157, 1377152, 1389574, 1395396, 1395409, 1424668, 1427134, 1427754, 1431455, 1443012, 1446039, 1463780, 1463884, 1464143, 1467356, 1467749, 1469563, 1482336, 1482340, 1487880, 1492123, 1492580, 1496500.

3. U. S. P. 1467093; abst. J. S. C. I. 1923, **42**, 1065-A; Chem. Met. Eng. 1923, **29**, 679.

4. A. Eichengruen, U. S. P. 1015156; abst. C. A. 1912, **6**, 685 D. R. P. 238348, 254385, 295764. Aust. P. 47899. Belg. P. 222416. Can. P. 129265. Swiss P. 52115.

5. F. Vivas, E. P. 286724; abst. J. S. C. I. 1929, **48**, 610-B.

6. U. S. P. 1130499, 1195673, 1321633, 1321634, 1323624, 1329386, 1393239, 1397173.

7. U. S. P. 1217027, 1217028, 1441143, 1469816.

8. E. Robinson, U. S. P. 1310841; abst. C. A. 1919, **13**, 2443. H. Matheson, U. S. P. 1488608; abst. C. A. 1924, **18**, 1908; Chem. Age, 1924, **32**, 206. Can. P. 198972.

copal, mastic, sandarac, elemi, guaiac, coumarone, benzyl abietate, and is miscible with castor and linseed oils.

The solvent of Canadian Industries, Ltd., comprises a benzenoid hydrocarbon[1], and balloon fabric dope of F. Clouth[2] utilizes cellulose acetate and anthracene oil, or creosote oil[3]. Creosote has also been used as a direct pyroxylin solvent[4], as indicated in the processes of S. Bennett[5], L. Desvaux[6], Palewski & Morin Co.[7], and A. Eichengruen[8].

Xylene, Xylol, in its commercial form, consists of a mixture of the three isomeric xylenes, *m*-xylene predominating. Sp. gr. 0.862-0.865, b. pt. 90% between 135-145°. The vapor of toluene and xylene is toxic. The cellulose ether composition of S. Carroll[9] comprises xylene with methyl or ethyl alcohol in equal parts, 1 part ethylcellulose of maximum ethylation dissolving in 5 parts of the above mixed solvent. The E. Flaherty pyroxylin composition contains xylene[10].

Phenanthrene has been used by G. Spica[11] and by F. Nathan, W. Rintoul and F. Baker[12] as a nitrocellulose ancillary gelatinizing agent.

Cymene, Cymol, Methyl*iso*propylbenzene, has been described by Farbenfabriken vorm. F. Bayer & Co.[13] along

1. Can. P. 292962.
2. D. R. P. 319723; abst. J. S. C. I. 1920, **39**, 568-A; Ann. Rep. S. C. I. 1920, **5**, 324; Chem. Zentr. 1920, IV, 19.
3. F. Clouth, D. R. P. 324944; abst. Chem. Zentr. 1920, IV, 648.
4. F. Greening, U. S. P. 172995, 401269. E. P. 2044, 1875; 2481, 1883; 8842, 1886; 5344, 1889; 22019, 1894. F. P. 110571, 184247. Belg. P. 77879.
5. U. S. P. 578714.
6. F. P. 450746; abst. Chem. Ztg. 1913, **37**, 254.
7. F. P. 491490; abst. Chim. et Ind. 1920, **3**, 811; Chem. Ztg. 1919, **43**, 733.
8. Swiss P. 52115; abst. Kunst. 1912, **2**, 99.
9. S. Carroll, U. S. P. 1431905; abst. C. A. 1922, **16**, 4346; J. S. C. I. 1922, **41**, 894-A; Chem. Zentr. 1923, II, 358; Chem. Ztg. 1922, **46**, 1134. See U. S. P. 1188376.
10. E. Flaherty, U. S. P. 1323624.
11. E. P. 126013; abst. C. A. 1919, **13**, 2280. See E. P. 14004, 1914.
12. E. P. 12742, 1912; abst. J. S. C. I. 1913, **32**, 991. F. P. 459539; abst. C. A. 1914, **8**, 3238.
13. D. R. P. 336476.

with xylyl chloride, benzylidene chloride, *p*-xylylene chloride, phenanthrene, anthracene and the xylenes as suitable non-solvent diluents in cellulose ester formulas, but the boiling point is so high (175°) that low-boiling solvents are contraindicated with them due to the fact that in the normal evaporative process, the increment of non-solvent increases, and often reaches a point before solidification of the cellulose ester where precipitation ensues. It is recommended to mix cellulose ethers with the above, and where high boilers are used as solvents, excellent lacquers result which, however, solidify very slowly. E. Rouxeville[1] mixes the complex and variable products resulting from the treatment of oil of turpentine with sulfuric acid with cymene, terebene, diterebene or colophene to produce thinners. *p*-Cymene has recently come into some prominence as a lacquer thinner[2]. With 71% cyclohexanol it forms a constant boiling mixture at 159°.

The trimethylbenzenes, pseudocumene and mesitylene, and *iso*propylbenzene (cumene) are of minor interest in this connection.

Naphtha, Solvent Naphtha, Solvene, is found in commerce as "light grade," b. pt. 110-160°, consisting primarily of toluene, the three xylenes, ethylbenzene and propylbenzene. The "heavy grade" boils at 165-190°, sp. gr. 0.88-0.91 and chiefly contains pseudocumene, mesitylene, ethyl-*p*-xylene, hemimellithene, indene, durene and coumarone hydrocarbons. The heavy grade is unsuitable for cellulose ester or ether lacquers on account of its high boiling point and low volatlity. The nitrocellulose composition of V. Richmond[3] is amyl acetate 59, coal tar naphthan 36.5; that of A. Sanderson & Sons[4], acetone 5.25, amyl acetate 4.87, ethyl alcohol 7.5, benzene 11 and solvent naphtha 1.5. The

1. E. P. 13023, 1907. F. P. 376269. Belg. P. 200494.
2. P. Groggins, U. S. Paint & Varnish Mfrs. Assoc. Circ. No. 311. For mfr. of cymene see U. S. P. 1185654, 1223158, 1314920, 1488278.
3. E. P. 154942.
4. E. P. 284435; abst. J. S. C. I. 1928, **47**, 259-B.

D. Carnegie[1] nitrocellulose solvent and coating composition combines a low boiling naphtha with ethyl acetate 30 and ethyl alcohol 35. Naphtha and chloroform constitute the solvent portion of the F. Golby and H. Ahrle formula[2]. A cellulose acetate plastic has been patented of *a*-naphthyldihydrocarbon[3].

The cellulose ether composition of L. Lilienfeld[4] is for manufacturing moldable masses from ethyl- or benzylcellulose plasticized "by the addition of oily products obtained by the action of acetylene on tar oil constituents boiling above 140° in the presence of aluminum chloride, or[5] oils obtained from naphtha with sulfuric acid, being fractions boiling 180-300°.

Naphthalene, Napthalin, has been used to a limited extent as a succedaneum for camphor in pyroxylin thermoplastic production. The methods and directions as laid down by Societe Generale pour la Fabrication des Matieres Plastiques[6], J. Jarvis[7], Düsseldorfer Celluloid-

1. Can. P. 309861; abst. C. A. 1931, **25**, 3184.
2. E. P. 17427, 1910. For data on cuprene (carbene), see W. Herzog, Chem. Ztg. 1931, **56**, 461.
3. B. Szelinski, D. R. P. 202720; abst. Zts. ang. Chem. 1908, **21**, 2428; Chem. Zentr. 1908, II, 1837; Chem. Ztg. Rep. 1908, **32**, 594; Wag. Jahr. 1908, **54**, II, 540.
4. U. S. P. 1563204; abst. C. A. 1926, **20**, 503. U. S. P. 1625415; abst. C. A. 1927, **21**, 2054. E. P. 149317; abst. C. A. 1921, **15**, 434. E. P. 149319; abst. C. A. 1921, **15**, 419. E. P. 163271; abst. C. A. 1922, **16**, 159. F. P. 417392; abst. C. A. 1913, **7**, 1987. F. P. 521000; abst. Chem. Zentr. 1921, IV, 826. F. P. 16144, Addn. to F. P. 417392. D. R. P. 357707; abst. Chem. Zentr. 1922, IV, 964. Aust. P. 54719, 90010, 91535. Dan. P. 29621. Ital. P. 210/526. Norw. P. 37755. Swed. P. 54449. See U. S. P. 1625416. E. P. 171661. F. P. 535132. D. R. P. 504226.
5. L. Lilienfeld, U. S. P. 1625416; abst. C. A. 1927, **21**, 2054; J. S. C. I. 1927, **46**, 519-B; Plastics, 1927, **3**, 608. E. P. 171661; abst. C. A. 1922, **16**, 1301; J. S. C. I. 1922, **41**, 53-A; Chem. Zentr. 1922, II, 544; Kunst. 1923, **13**, 9. F. P. 535132; abst. Caout. et Gutta. 1922, **19**, 11495; Chem. Zentr. 1922, IV, 274. D. R. P. 504226; abst. C. A. 1930, **24**, 5444. Can. P. 249773; abst. Chem. Zentr. 1926, I, 2757. Aust. P. 91680. See U. S. P. 1563203, 1563204, 1625415. Dan. P. 29621.
6. D. R. P. 117542; abst. Mon. Sci. 1901, (4), **57**, 165. Chem. Zentr. 1901, I, 352; Jahr. Chem. 1901, **54**, 900; Wag. Jahr. 1901, **47**, II, 609. F. P. 292983. See U. S. P. 543197.
7. U. S. P. 1343135; abst. C. A. 1920, **14**, 2418; Paper, 1921, **27**, #21, 26; J. S. C. I. 1920, **39**, 541-A; Chem. Ztg. 1920, **44**, 810.

fabrik[1], L. Arbez-Carme[2], J. Chaubet[3], Sudheim & Koppen[4], E. I. du Pont de Nemours & Co.[5], British Celanese, Ltd.[6], I. Ginsberg[7], and J. Stevens[8] are typical. C. Ellis[9], A. Eichengruen and T. Becker[10] and A. Wohl[11] indicate the use of naphthalene with other bodies in connection with cellulose ester liquid and solid compositions.

The Rheinische Gummi- und Zelluloidfabrik[12] have described as adjuncts to nitrocellulose, *a*- and *b*-phenylnaphthalene and *a*- and *b*-benzylnaphthalene, while O. Silberrad[13] has described *a*- and *b*-methylnaphthalene, di-, tri- and tetra-methylnaphthalene in connection with pyroxylin compounds.

Tetra- and Deca-hydronaphthalene, Tetralin and Decalin. 1.2.3.4-Tetrahydronaphthalene, obtained by the incomplete catalytic hydrogenation of naphthalene, is a non-toxic liquid, oxidizing on exposure to the air to resinous products. Sp. gr. 0.975-0.98, b. pt. 205-212°. A powerful resin and oils solvent[14]. Decahydronaphthalene results from the complete dehydrogenation of naphthalene, boiling at 189-190°, sp. gr. 0.89. H. Morris prepares printing inks by dissolving a cellulose ether with dyes and pigments in a mixture of tetrahydronaphthalene, butyl alcohol, toluene

1. E. P. 17069, 1912; abst. Kunst. 1914, **4**, 155. F. P. 446270; abst. C. A. 1913, **7**, 1972.
2. F. P. 372512; abst. J. S. C. I. 1907, **26**, 634.
3. E. P. 13287, 1899; abst. J. S. C. I. 1900, **19**, 552. See E. P. 20279, 1899.
4. D. R. P. 7784, Addn. to D. R. P. 6051; abst. Dingl. Poly. 1879, **233**, 429; Ber. 1897, **12**, 2390; Wag. Jahr. 1880, **26**, 949.
5. E. P. 308230; abst. J. S. C. I. 1929, **48**, 483-B.
6. E. P. 301497; abst. Silk J. 1929, **5**, #58, 78; Chem. Zentr. 1929, I, 1751.
7. Rubber Age, 1921, **10**, 165; abst. C. A. 1922, **16**, 361.
8. U. S. P. 543197. See U. S. P. 269340, 269341, 269344, 269345, 517987.
9. U. S. P. 999490; abst. J. S. C. I. 1911, **30**, 1051.
10. U. S. P. 738533; abst. J. S. C. I. 1903, **22**, 1100.
11. D. R. P. 139669; abst. Chem. Zentr. 1903, I, 744.
12. D. R. P. 140480; abst. Chem. Zentr. 1903, I, 906.
13. E. P. 19381, 1912; abst. J. S. C. I. 1913, **32**, 843. See E. P. 13860, 13861, 1911. Belg. P. 246526.
14. Akt. Ges. fuer Anilin-Fabrikation, D. R. P. 369944; abst. Chem. Ztg. 1923, **47**, 73.

and methylethylglycol[1]. The cellulose ether composition of S. Sheppard[2] utilizes tetra- and deca-hydronaphthalenes as a direct solvent of water-insoluble ethylcellulose, until a homogeneous viscous solution is obtained, which is then thinned down with lower boiling solvents as methyl or ethyl alcohol. The cellulose lacquer formula of J. Johnston[3] employs tetrahydronaphthalene with other solvents.

Diamylene, 1.1.2.3.3-pentamethylpentene-1, is a polymerization product chiefly of triethylethylene, a colorless, oily liquid, b. pt. 150-170°, sp. gr. 0.775 at 20°[4]. The solvent properties are somewhat analogous to those of turpentine. Dixylylethane[5], glyceryldibenzyl ether, *m*-styrenedibutyl phthalate and butyl stearate have been proposed as coating compositions with cellulose esters. The nitrocellulose diluent of the Carbide & Carbon Chemical Corp.[6] comprises ethylbenzene and *iso*propyl benzene alone, or in conjunction with "cellosolve"[7]. In the presence of methyl acetate[8], diphenylmethane (b. pt. 260°, m. pt. 25°, sp. gr. 1.06 at 25°) becomes an energetic cellulose ether solvent for both ethyl- and benzyl-cellulose. Diphenylethane, ditolylethane, dixylylethane, dinitrodiphenylethane are all solvents of nitrocellulose and cellulose acetate, being used preferably about 16% on the weight of low viscosity cellulose acetate, or 40% on pyroxylin, the auxiliary solvent being acetone 80, diacetone alcohol 20 for the acetate, or ethyl acetate 90, butyl acetate 10 for the nitrate[9].

Bibenzyl, a white solid melting at 51.8° and boiling

1. H. Morris, E. P. 320410; abst. C. A. 1930, **24**, 2622.
2. U. S. P. 1441181; abst. C. A. 1923, **17**, 1141; J. S. C. I. 1923, **42**, 180-A; Chem. Met. Eng. 1923, **28**, 366; Chem. Zentr. 1923, I, 1122; Kunst. 1923, **13**, 92; 1925, **15**, 26.
3. E. P. 294158; abst. C. A. 1929, **23**, 2050.
4. E. P. 138113, 173750, 209128, 259293.
5. W. Lawson, Can. P. 312341; abst. C. A. 1931, **25**, 4138.
6. Can. P. 294500.
7. J. Davidson, E. P. 304759; abst. C. A. 1929, **23**, 4836; J. S. C. I. 1930, **49**, 872-B; Brit. Plastics, 1930, **2**, #17, 100.
8. S. Carroll, U. S. P. 1467095; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.
9. E. I. du Pont de Nemours & Co., E. P. 312604; abst. C. A. 1930, **24**, 961; J. S. C. I. 1930, **49**, 780-B.

at 248°, while not a strong solvent for nitrocellulose alone, admixed with acetone it becomes a good solvent[1]. Ethylbenzene (mono-ethylbenzene) diethylbenzene, hexaethylbenzene, butylbenzene, propylbenzene and pentylbenzene (amylbenzene), especially in conjunction with monoethyl ether of ethyleneglycol[2] constitute a nitrocellulose dissolving combination especially adapted for lacquer manufacture. *m*-Styrene (styrol) combined with triphenyl phosphate and nitrocellulose[3], forms the waterproofing composition of C. Burke and W. Lawson. Polystyrenes as hexahydropolystyrene and *a*-polymethylstyrene[4] have been patented as stiffening materials for textiles, felt and paper.

In the preparation of plastic masses from cellulose derivatives, it has been proposed to employ dimethoxydiphenylethane, dibenzyldioxydiphenylethane or other alkyl, oxyalkyl, or carboxyalkyl ethers of ethylidenediphenols[5], or ethylidenediphenyl or dibenzoyldiphenylethane phosphates or *p*-toluenesulfonates[6]. Or, pyroxylin may be admixed with toluene, ethyl or butyl acetates and a copper resinate[7].

Dioxydiphenyldimethylmethane obtained as a condensation product by reacting upon phenol with acetone, has been made the basis of a cellulose nitrate or acetylcellulose plastizant by W. Beatty[8], who combines nitrocellulose 8, dioxydiphenyldimethylmethane 20, with a solvent as amyl

1. J. Davidson, U. S. P. 1617237; abst. J. S. C. I. 1927, **46**, 214-B; Chem. Zentr. 1927, I, 2147. Can. P. 268571; abst. C. A. 1927, **21**, 2384.
2. J. Davidson, U. S. P. 1834050.
3. U. S. P. 1862565.
4. I. G. Farbenindustrie, A.-G., F. P. 709141; abst. C. A. 1932, **26**, 1135. D. R. P. 534636; abst. Chem. Zentr. 1931, II, 2385.
5. A. Voss, D. R. P. 369536, Addn. to D. R. P. 367560; abst. Kunst. 1923, **13**, 69.
6. *Ibid.* D. R. P. 369535, Addn. to D. R. P. 367560; abst. Kunst. 1923, **13**, 69.
7. L. Barensfeld, D. R. P. 508556; abst. C. A. 1931, **25**, 834.
8. U. S. P. 1156969 (assigned to G. Beadle); abst. C. A. 1915, **9**, 3358; J. S. C. I. 1915, **34**, 1204; Mon. Sci. 1917, **84**, 28; Kunst. 1916, **6**, 98. U. S. P. 1158960; abst. C. A. 1916, **10**, 275; Mon. Sci. 1917, **84**, 28; Kunst. 1916, **6**, 63. U. S. P. 1158961; abst. C. A. 1916, **10**, 275. U. S. P. 1188356; abst. C. A. 1916, **10**, 2146; J. S. C. I. 1916, **35**, 923; Mon. Sci. 1917, **84**, 60; Ann. Rep. Soc. Chem. Ind. 1917, **2**,

acetate and/or acetone. Camphor or camphor substitutes may be added, covering those bodies "specified on pages 248 to 257 of the publication entitled *Nitro-Cellulose Industries,* by Worden, 1911 edition."

Halogen Methanes of interest in the cellulose ether industry comprise the chlorine compounds only. Tribrommethane (bromoform) and tri-iodomethane (iodoform) have not been used to any appreciable extent, due principally to the powerful odor and cost.

Methyl Chloride, Monochlormethane (p. 1251), methyl bromide (p. 1254) and methyl iodide (p. 1255) have been mentioned.

Methylene Chloride, Dichlormethane, Methylene Dichloride, is a colorless, faintly ethereal smelling liquid, extremely stable and non-corrosive even with excess water at elevated temperatures, sp. gr. 1.3361 at 20°/4°, b. pt. 39.8°. Has a slightly anaesthetic action (see pp. 154, 200, 806, 877). Methylene chloride dissolves cellulose acetate (see pp. 539, 639, 781, 996, 998, 1016, 1038), cellulose ethers (pp. 50, 230), ethylcellulose (p. 284) and the wood ethers (p. 290). The cellulose ether composition of S. Carroll[1] combines methylene chloride with the lower aliphatic alcohols as methyl and ethyl alcohol, water-insoluble ethylcellulose dissolving in this menstruum in the cold. The British Celanese Ltd.[2] dissolve the cellulose ethers in methylene chloride augmented by butyl or amyl alcohols, ethylene glycol, monoethyl glycol, hexahydrophenol, methylcyclohexanol, ethyl lactate, tartrate or phthalate, or diacetone

140. E. P. 18822, 1912; abst. C. A. 1914, **8**, 572; J. S. C. I. 1913, **32**, 907; Chem. Ztg. Rep. 1913, **37**, 645; Kunst. 1914, **4**, 76. E. P. 18499, 1913; abst. C. A. 1915, **9**, 377; J. S. C. I. 1914, **33**, 746. F. P. 447645; abst. C. A. 1913, **7**, 2115; J. S. C. I. 1913, **32**, 283; Mon. Sci. 1914, **81**, 14; Chem. Ztg. Rep. 1913, **37**, 144; Kunst. 1913, **3**, 116. Aust. P. 63966; abst. Kunst. 1914, **4**, 257. Belg. P. 252594; abst. Kunst. 1913, **3**, 276. Can. P. 147578; abst. C. A. 1913, **7**, 2127. Can. P. 147579; abst. C. A. 1913, **7**, 2128. D. R. P. Anm. B-68616, 1912; abst. Chem. Ztg. 1914, **38**, 818; Kunst. 1914, **4**, 280. F. P. 447645; abst. J. S. C. I. 1913, **32**, 283.

1. U. S. P. 1467102; abst. J. S. C. I. 1923, **42**, 1065-A.
2. E. P. 315279; abst. C. A. 1930, **24**, 1740.

alcohol. W. Moss[1] prefers a mixture of methylene chloride and ethyleneglycol or its monoethyl ether, and A. Eichengrün[2] a combination of methylene chloride, trichlorethylene and dichlorethylene. The cellulose acetate lacquer of G. Goerner[3] comprises methylene chloride as the predominating ingredient, as does the lacquer formula of C. Dreyfus[4]. Plasticized products from cellulose ethers have been described[5] employing a mixture of di- and tetra-chlormethane, a representative formula being to dissolve 1 part ethylcellulose insoluble in water in 5 parts carbon tetrachloride and an equal amount of methylene chloride, with the preferable addition of 0.5-1 part ethyl alcohol. It is also possible to employ 7 parts carbon tetrachloride to 3 parts methylene chloride or conversely.

Methylene chloride has also been used as a cellulose acetate solvent[6], fire extinguishing composition[7], and in the preparation of hexamethylenetetramine[8].

Trichlormethane, Chloroform, on account of its anaesthetic properties has not been extensively used in cellulose ester and ether technics. The chloroform-soluble cellulose acetate is inferior to the acetone-soluble, and the nitrated celluloses are insoluble in chloroform. A direct cellulose ether solvent composition has been detailed by J. Donohue[9] of chloroform and ethyl alcohol, equal parts by weight, which dissolves ethylcellulose without the application of heat to a clear, viscous solution. The S. Carroll ethylcellulose dissolvant[10] involves admixing chloroform with methyl or ethyl acetates, viscous, flowable solution result-

1. U. S. P. 1844365; abst. Plastics, 1932, **8**, #5, 221.
2. D. R. P. 508153; abst. C. A. 1931, **25**, 813.
3. U. S. P. 1384188; abst. C. A. 1921, **15**, 3746.
4. Can. P. 306829; abst. C. A. 1931, **25**, 812.
5. I. G. Farbenind., E. P. 346040; abst. J. S. C. I. 1931, **50**, 643-B.
6. H. Dreyfus, U. S. P. 1181859, 1181860. G. Goerner, U. S. P. 1384188.
7. H. Mork, U. S. P. 1246641, 1246642.
8. A. Carter and A. Coxe, U. S. P. 1459971, 1499001, 1499002.
9. U. S. P. 1394505; abst. C. A. 1922, **16**, 494.
10. U. S. P. 1464169, 1464170; abst. C. A. 1923, **17**, 3253.

ing. W. von Neuenstein[1] has discussed the colloidal-chemical relationships of solutions of various cellulose ethers and esters, and finds that Ostwald's "peptization rule" applies, as with chloroform solutions of cellulose acetate.

Chloroform has sp. gr. 1.49-1.5, b. pt. 61.2°, non-inflammable, soluble 0.5% in water. It dissolves acetic acid (pp. 905, 1005), acetic anhydride (p. 605), benzylcellulose (pp. 10, 230), cellulose acetate (pp. 319, 324, 336, 813, 1016), cellulose benzoate (p. 1021), cellulose dilaurate, dipalmitate, distearate (p. 538), cellulose ethers (pp. 8, 230, 244), dimethylhydrocellulose (p. 76) and methylcellulose acetate (p. 27). It has been used for the production of celluloid substitutes[2], in acetylcellulose combinations[3], as an ethylcellulose solvent[4], for photographic film manufacture[5] and in general plastics fabrication[6].

Tetrachlormethane, Carbon tetrachloride, Pyrene, Tetra, Benzinoform. Carbona is a mixture of carbon tetrachloride and benzine. A widely used solvent and diluent, being colorless, non-inflammable, toxic, decomposing into carbonyl chloride (phosgene) upon exposure to the air. Sp. gr. 1.61-1.63, b. pt. 76.8°. The ethylcellulose of L. Lilienfeld[7] is soluble in carbon tetrachloride. W. Webb[8] has

1. Kolloid Zts. 1927, **41**, 163; abst. C. A. 1928, **22**, 897.
2. U. S. P. 1158960, 1181858, 1181859, 1181860, 1188798, 1199798, 1217027, 1242783, 1245476, 1386576, 1420028.
3. U. S. P. 1132384, 1158960, 1165179, 1175791, 1180704, 1181857, Re-14338, 1181858, 1181859, 1181860, 1188798, 1195673, 1199798, 1199799, 1199800, 1201260, 1217722, 1236578, 1236579, 1242783, 1244107, 1244108, 1244347, 1244348, 1244349, 1245476, 1258913, 1265216, 1275884, 1286172, 1296847, 1319229, 1338661, 1355976, 1355978, 1384188, 1386576, 1388472, 1420028, 1421341, 1429295, 1444786, 1494816, 1494830, 1516225.
4. U. S. P. 1188376, 1217027, 1217028, 1394505, 1405487, 1418405, 1431906, 1432366, 1432367, 1432368, 1437792, 1437828, 1437829, 1441181, 1464169, 1469816, 1505043, 1505044.
5. U. S. P. 1188798, 1199799, 1199800, 1229485, 1229487, 1281080, 1357614, 1388472, 1394505, 1418405, 1431906, 1432366, 1432367, 1432368, 1437828, 1437829, 1441181, 1500393, 1519659.
6. U. S. P. 1158960, 1175791, 1188798, 1199800, 1229485, 1229487, 1245981, 1281080, 1357614, 1386576, 1388472, 1405487, 1437792.
7. U. S. P. 1217027, 1217028. E. P. 149319. The M. Thau (U. S. P. 1793726) non-inflammable nitrocellulose lacquer contains CCl_4. See Swiss P. 66509.
8. U. S. P. 1418413; abst. C. A. 1922, **16**, 2780.

described a cellulose ether composition, the fluid portion consisting of a mixture of ethyl alcohol and carbon tetrachloride within the limits of 95:5 to 5:95—a very wide range. A mixture of carbon tetrachloride with methyl, ethyl, propyl, butyl and amyl acetates constitutes an excellent direct cellulose ether solvent and colloiding medium[1]. J. Donohue[2] has covered by patent issuance the production of cellulose ether solutions utilizing mixtures of carbon tetrachloride and benzene, ethylcellulose of the water-insoluble type dissolving to a transparent solution in a mixture of equal parts of these two liquids. In the cellulose ester art, the processes of H. Parkes[3], A. Schwenterley[4], S. Brick[5], F. Vivas[6], E. Knoevenagel[7], H. Mork[8], and L. Lederer[9] are illustrative. Carbon tetrachloride has been used extensively as a component in finish removers[10], fire extinguishers[11], paint remover[12], and as an antimony trichloride solvent[13]. A liquid product for preventing mist or rain drops on glass has been evolved[14], comprising nitrocellulose with tetrachlorethane, alcohol, glycerol and nicotine. Tetracol, Spectral, Tetraform, Katarine, and Phoenixine are trade names for carbon tetrachloride.

1. W. Webb, U. S. P. 1434465; abst. C. A. 1923, **17**, 467.
2. U. S. P. 1434432; abst. C. A. 1923, **17**, 467.
3. U. S. P. 265337. See E. P. 1866, 1879. F. P. 132495. Belg. P. 56230. D. R. P. 10210.
4. U. S. P. 1447734.
5. U. S. P. 1389574, 1389575; abst. C. A. 1922, **16**, 145.
6. U. S. P. 1800120. E. P. 206724; abst. C. A. 1929, **23**, 522.
7. U. S. P. 981574; abst. J. S. C. I. 1911, **30**, 126.
8. U. S. P. 972464; abst. J. S. C. I. 1910, **29**, 1245.
9. U. S. P. 902093; abst. J. S. C. I. 1908, **27**, 1130. U. S. P. 999236; abst. J. S. C. I. 1911, **30**, 1050.
10. U. S. P. 1140449, 1147851, 1147852, 1160394, 1167640, 1167641, 1169783, 1172772, 1173628.
11. U. S. P. 1151255, 1154161, 1190160, 1190161, 1236622, 1243149, 1246640, 1246641, 1246642, 1270392, 1270393, 1270394, 1270395, 1270396, 1270397, 1292743, 1292744, 1364952, 1385081, 1400906, 1402711, 1403191, 1421428, 1428207, 1506963.
12. U. S. P. 1130499, 1143110, 1143111, 1147849, 1147850, 1173628, 1189803, 1189804, 1328080, 1406175, 1499101.
13. U. S. P. 1388824, 1388825, 1388826, 1388827, 1388828, 1388829, 1418609.
14. Compagnie Internationale des Industries Chimiques "Interchimic," F. P. 702349; abst. C. A. 1931, **25**, 4372.

Nitromethane, Mononitromethane, isomeric formhydroxamic acid, boils at 101°, has been proposed as a nitro- and acetyl-cellulose solvent[1], in the preparation of films and plastics. Farbenfabriken vorm. F. Bayer & Co.[2] and Chemische Fabrik Griesheim-Elektron[3] have proposed the use of tetranitromethane as a cellulose ester solvent, and C. Claessen[4] has given directions for its manufacture. Nitroethane boils at 113° and 1-nitropropane at 130° and 1-nitro-*n*-butane at 151°.

Halogen Ethanes. Each of the six hydrogens in ethane may be replaced by halogen, giving rise to six different compounds for the same halogen.

Monochlorethane, Ethyl chloride, see p. 1267. Ethyl bromide, see p. 1275. Ethyl iodide, see p. 1276. C. Wagishauser[5] has described a cold lacquer in which nitrocellulose is dissolved in a mixture of ethyl chloride and methyl alcohol to which benzene may be added. It is intended for sealing the caps of bottles. The cellulose ether composition of S. Carroll[6] combines ethyl iodide (boils at 72°, and has the very high sp. gr. of 1.93-1.94 at 15°) with methyl acetate, the range of the two solvents being stated as from 90:10 to 10:90. An excellent viscous film making dope is said to result by dissolving triethylcellulose 1 in 5 parts of a mixed solvent containing ethyl iodide and methyl acetate in equal proportions. A hydrochlorated ethyl chloride (Wigger's or Mialke's or Aran's anesthetic ether, polychlorated hydrochloric ether) which is a mixture of di-, tri-, tetra-, penta- and hexa-chlorethane, dissolves the etherified celluloses best in conjunction with lower boiling aliphatic alcohols or their acetates.

Dichlorethane, sym-Dichlorethane, Ethylidene chloride (not dichlorethylene) is a colorless liquid smelling

1. E. Fischer, D. R. P. 201907; abst. C. A. 1909, **3**, 491.
2. E. P. 24299, 1909. F. P. 384079; abst. C. A. 1909, **3**, 1690.
3. D. R. P. 281877, 290544, 291299.
4. D. R. P. 184229; abst. J. S. C. I. 1908, **27**, 183.
5. E. P. 10222, 1912; abst. J. S. C. I. 1913, **32**, 34.
6. U. S. P. 1467099; abst. Chem. Met. Eng. 1923, **29**, 679.

somewhat like chloroform, toxic, b. pt. 80-85°, sp. gr. 1.25-1.26 at 20°, soluble 0.1° in water at 20°, and dissolves in 0.5% of water at the same temperature. It has been used as a solvent for the cellulose ethers[1], cellulose acetate[2], cellulose esters[3], and to clarify acetylcellulose solutions (see p. 1030). Readily dissolves camphor, mastic, sandarac, elemi, dammar, ester gum, coumarone, zinc and aluminum resinates, and methyl-, ethyl- and benzyl-cellulose.

Trichlorethane, Methyl chloroform, Monochlorethylene chloride, Vinyl trichloride, *aab*-Ethane trichloride, may be made by reaction between acetylene, chlorine and HCl[4]; by first preparing vinyl chloride and transforming this into *aab*-ethane trichloride[5]; or by mixing ethylene with Cl in the proportion of 2:1 at 20-30°, then fractionally distilling, the product containing 70% of trichlorethane[6]. Vinyl chloride and Cl may also be passed in the presence of 1.1.2-trichlorethane in the presence of a chlorine carrier as antimony pentachloride[7]. Trichlorethane has been employed as a cellulose acetate solvent in the processes of H. Dreyfus[8] and J. Clancy[9].

1-Brom-2-chlorethane has been patented as both a cellulose ether[10] and cellulose ester[11] solvent.

Tetrachlorethane, Acetylene tetrachloride, Calcitone, Carbitone, Westron, Vitrol, Vitran, Acetosol, Tetraline (not to be confused with Tetralin) is a colorless, heavy liquid, decidedly toxic, being three or four times more so than chloroform. Tetrachlorethane is a solvent for nitro-, acetyl-,

1. S. Carroll, U. S. P. 1429188, 1464170.
2. W. Lindsay, U. S. P. 1199799, 1199800, 1265217, 1388472.
3. F. Klatte and A. Rollett, U. S. P. 1241738. D. R. P. 281687. H. Dow, U. S. P. 1339552.
4. I. G. Farbenindustrie, E. P. 344592; abst. C. A. 1932, **26**, 155.
5. *Ibid.* E. P. 349097; abst. J. S. C. I. 1931, **50**, 917-B. F. P. 687307; abst. C. A. 1931, **25**, 715.
6. A. Maier, D. R. P. 522959; abst. C. A. 1931, **25**, 3670.
7. Consort. f. Elektrochem Ind., E. P. 341781; abst. C. A. 1931, **25**, 4893. F. P. 690767; abst. C. A. 1931, **25**, 1264.
8. U. S. P. 1181860; abst. C. A. 1916, **10**, 1789. Swiss P. 63584.
9. U. S. P. 1439293. E. P. 190694. F. P. 553547.
10. W. Webb, U. S. P. 1432373.
11. H. Dow, U. S. P. 1339552. Compare E. P. 12406, 13100, 1910. F. P. 418347.

ethyl and benzyl-cellulose, resins, waxes, rubber, sulfur and oils. Sp. gr. 1.6, b. pt. 144-147°. It forms azeotropic mixtures containing 9% glycol, b. pt. 145°; 55% cyclohexanone, b. pt. 159°; and 32% amyl acetate, b. pt. 150°. H. Mork[1] and J. Zdanowich[2] have furnished details for the stabilization of acetylcellulose using tetrachlorethane. A cellulose ether composition has been described by R. Stinchfield[3] the solvent portion of which comprises tetrachlorethane and ethyl acetate or its equivalent or tetrachlorethane and methyl or ethyl alcohol[4]. Ethylcellulose of maximum ethylation dissolves in either of the above mixtures in the cold, forming transparent solutions suitable for casting into films.

In the production of cellulose esters, the published formulas of J. de Girves[5], L. Clement and C. Riviere[6], G. Convert[7], H. Mork[8], A. Bacigalupi[9], L. Lederer[10], E. Langfeldt[11], J. Matray[12] and S. Peachey[13] all utilize tetrachlorethane. Cellulose acetate has been combined with caoutchouc by means of the harmonious solvent tetrachlorethane[14], and the earlier acetate filaments were produced from a mixture of this solvent and denatured alcohol[15]. A small amount (0.1-1%) of a paraffin hydrocarbon as liquid

1. U. S. P. 1607474; abst. C. A. 1927, **21**, 1322.
2. E. P. 200186; abst. C. A. 1924, **18**, 329. Can. P. 258765; abst. C. A. 1926, **20**, 2411. Aust. P. 105804.
3. U. S. P. 1432365; abst. C. A. 1923, **17**, 341.
4. U. S. P. 1432364; abst. C. A. 1923, **17**, 341. See U. S. P. 804960, 1009116. E. P. 27258, 1910. F. P. 427562.
5. F. P. 35669, Addn. to F. P. 660935; abst. C. A. 1930, **24**, 4175.
6. U. S. P. 1168164. F. P. 449253. U. S. P. 1173931. F. P. 461058.
7. F. P. 421843; abst. J. S. C. I. 1911, **30**, 415.
8. U. S. P. 1107222; abst. C. A. 1914, **8**, 3371.
9. E. P. 29273, 1910.
10. E. P. 11625, 1909; abst. J. S. C. I. 1909, **28**, 1030. F. P. 402072; abst. J. S. C. I. 1909, **28**, 1221.
11. U. S. P. 1397103; abst. C. A. 1922, **16**, 653.
12. F. P. 477294; abst. J. S. C. I. 1916, **35**, 597.
13. E. P. 121091; abst. J. S. C. I. 1919, **38**, 110-A.
14. Soc. Anon. des Etablissements Hutchinson, E. P. 129630; abst. C. A. 1919, **13**, 3028.
15. H. Mork and C. Coffin, U. S. P. 1551112; abst. C. A. 1926, **20**, 115.

petroleum dissolved in tetrachlorethane acts as a preservative[1]. "Solvace" is a cellulose acetate plastifying solvent combination containing tetrachlorethane 25, triacetin 20, perchlorethylene 11, alcohol 15 and acetone 10.

Pentachlorethane, a colorless, noninflammable and toxic liquid, sp. gr. 1.685-1.71, and boiling at 159°, is a solvent for some of the cellulose ethers, for cellulose acetate, dammar, elemi, sandarac and mastic. Known in the arts as Pentaline. The cellulose ether solvent as described by S. Carroll[2] as especially suitable for water-insoluble ethylcellulose, combines pentachlorethane and methyl or ethyl alcohols. W. Lindsay[31] uses equal volumes pentachlorethane and methyl alcohol as a cellulose acetate solvent, or cellulose acetate in conjunction with pentachlorethane and/or a large number of other solvents[4]. Pentachlore-

1. E. Zuckermandel, U. S. P. 1835682; abst. C. A. 1932, **26**, 999.
2. U. S. P. 1434427; abst. J. S. C. I. 1923, **42**, 50-A. F. P. 408396.
3. U. S. P. 1041112; abst. C. A. 1912, **6**, 3517.
4. U. S. P. 1199800, "The following solvents are included." Amyl acetate, fusel oil, chloroform, dichlorethylene, ethylene chloride, methyl alcohol, ethyl alcohol, camphor, borneol, salol, diphenylamine, diacetanilid, chlorhydrin derivatives, amyl butyrate, amyl salicylate, oil of anise seed, benzyl alcohol, benzyl acetate, benzyl benzoate, benzyl ether, bornyl acetate, oil of camphor (heavy), carvene, oil of cedar leaves, oil of cedarwood, acetodichlorhydrin, oil of eucalyptol, methyl salicylate, nitrobenzene, pentachlorethane, phenyl-ether, benzyl salicylate, safrol, oil of sassafras, terpineol, amyl benzoate, amyl formate, oil of anise, anisic aldehyde, anisol, benzyl butyrate, benzyl formate, oil of camphor (light), carvol, cinnamylic alcohol, oil of citronella, oil of cloves, oil of eucalyptus, eugenol, ethyl cinnamate, oil of fennel, geraniol formate, geranyl acetate, oil of hedeoma, iso-eugenol, isosafrol, oil of juniper berries, oil of mace, methyl cinnamate, methyl anthranilate, methylene acetate, methyl nitrobenzoate, methyl oleate, ethyl oleate, methyl phenyl acetate, methyl benzoate, ethyl benzoate, oil of nutmeg, oenanthic ether, oil of pennyroyal, oil of peppermint, phenyl ethyl alcohol, oil of pine needles, oil of rosemary, oil of rue, oil of sage, oil of spike, oil of spruce, terpinyl acetate, oil of thyme, benzoic ether, oil of cinnamon. U. S. P. 1244107, Toluene sulfonamid, benzene sulfonamid, ethyl acetanilid, methyl acetanilid, ethyl alcohol, chloroform, epichlorhydrin, acetodichlorhydrin, dichlorethylene, ethylene chloride, trichlorhydrin, pentachlorethane, acetochlorhydrin, acetylene tetrachloride, ethyl chloracetate, acetone, ethyl acetate, di-acetochlorhydrin, triphenyl phosphate, tricresyl phosphate, naphthalene, camphor, tetrachlorethyl acetanilid, trichlormethyl acetanilid. U. S. P. 1244108, toluenesulfonamid, benzenesulfonamid, paraethyltoluolsulfonamid. U. S. P. 1244347, 1244348, 1244349, Ethyl alcohol, tricresyl phosphate, naphthalene, camphor, tetrachlorethylacetanilid, trichlor-

thane and acetone[1], or alcohol[2], or amyl acetate with pentachlorethane, and trichlorethylene[3] are some of the dissolving combinations considered suitable. The processes of L. Collardon[4], L. Lilienfeld[5], B. Gaisenband and C. Piestrak[6] and Farbenfabriken vorm. F. Bayer & Co.[7] indicate the range of solvent combinations which have been proposed.

Hexachlorethane, Carbon hexachloride, Perchlorethane, Carbon trichloride, is a solid whereas the previously described members are all liquids. Boils about 185°. Soluble

methylacetanilid, toluene sulfonamid, paraethyltoluolsulfonamid, benzene sulfonamid, ethyl acetanilid, methyl acetanilid, chloroform, epichlorhydrin, acetodichlorhydrin, dichlorethylene, ethylene chloride, trichlorhydrin, pentachlorethane, acetochlorhydrin, acetylene tetrachloride, ethyl chloracetate, acetone, ethyl acetate, di-acetochlorhydrin. U. S. P. 1388472, Borneol, salol, diphenylamine, amyl butyrate, amyl salicylate, oil of anise seed, benzyl alcohol, benzyl acetate, benzyl benzoate, benzyl ether, benzoic ether, bornyl acetate, oil of camphor (heavy), carvene oil, oil of cedar leaves, oil of cedar wood, oil of cinnamon, acetodichlorhydrin, oil of eucalpytol, methyl salicylate, nitro benzol, pentachlorethane, phenyl ether, benzyl salicylate, safrol, oil of sassafras, terpineol, amyl benzoate, amyl formate, oil of anise, anisic aldehyde, anisol, benzyl butyrate, benzyl formate, oil of camphor (light), carbol, cinnamylic alcohol, oil of citronella, oil of cloves, oil of eucalyptus, eugenol, iso-safrol, juniper berries (oil of), ethyl cinnamate, oil of fennel, geraniol formate, geranyl acetate, oil of hedeoma, iso-eugenol, oil of mace, methyl cinnamate, methyl anthranilate, methylene acetate, methyl nitrobenzoate, methyl oleate, ethyl oleate, methyl phenyl acetate, methyl benzoate, ethyl benzoate, oil of nutmeg, oenanthic ether, oil of pennyroyal, oil of peppermint, phenyl ethyl alcohol, oil of pine needles, oil of rosemary, oil of rue, oil of sage, oil of spike, oil of spruce, terpinyl acetate, oil of thyme, amyl acetate.

1. D. Reid, U. S. P. 1095999; abst. C. A. 1914, **8**, 2124.
2. H. Dreyfus, E. P. 20976, 1911. F. P. 432047. Swiss P. 63854.
3. Akt. Ges. f. Anilinfabr., Swiss P. 66509.
4. U. S. P. 1105619; abst. C. A. 1914, **8**, 3244.
5. U. S. P. 1563205. "The following solvents are included." *m*-Dixylylethane, benzene, camphor, naphthalene, resins, phenol-aldehyde condensation products, oils, rubber, gutta-percha, balata, metallic resinates and oleates, waxes, paraffins, fats, methyl alcohol, glacial acetic acid, formic acid, pyridine, quinoline, picoline, epichlorhydrin, acetone, pentachlorethane, nitrobenzene, ethyl acetate, amyl acetate, butyl acetate, tetrachlorethane, trichlor-ethylene, acetylene dichloride, carbon tetrachloride, chloroform, xylene, nitrophenols, turpentine oil, phenylethers.
6. F. P. 483316; abst. C. A. 1918, **12**, 995.
7. E. P. 14364, 1910. F. P. 417250. Swiss P. 52438. Aust. P. 46991.

in alcohol, ether and oils. Insoluble in water. A plastic has ben described[1] combining 19% each hexachlorethane with *b*-naphthol in the presence of volatile solvents. Alone it is a non-solvent of all forms of nitrocellulose acetylcellulose. H. Hands and Spicers Ltd[2] have described cellulose ether solutions containing hexachlorethane, penta-, hexa- and hepta-chlorpropane, mono- or tri-glyceryl benzoate, resorcin diacetate, ethyl oleate and cyclohexanol.

iso-Propyl bromide in the presence of a solvent such as acetone, dissolves cellulose ethers, nitrocellulose and the cellulose acetates[3]. The proportion of *iso*propyl bromide to acetone is about 1:20. As a lacquer composition utilizing acetylcellulose, H. Hands[4] recommends a formula composed of heptachlorpropane 2.5-4, mono-*b*-naphthyldiphenyl phosphate 20, mono-*b*-naphthyldicresyl phosphate 4, tricresyl phosphate 4, especially useful for the casting of films which are odorless. Dichlorpropane (trimethylene dichloride, *iso*propylidene chloride, acetone chloride, chloracetol) in the hands of P. Seel[5] is a direct solvent for the cellulose ethers, for film formation water-insoluble ethylcellulose being dissolved in 4-6 parts of dichlorpropane. If more rapid setting of the film is desired, methyl alcohol may be added. The chlorpropanes may be prepared by passing Cl into amyl alcohol above 65°[6], or by introducing HCl into *n*-propyl alcohol[7].

Amyl Chloride, n-Amyl chloride, a colorless liquid, boils at 106.6° at 740 mm., sp. gr. 0.9013 at 20°. 2-Chlorpropane, methylpropylcarbin chloride, boils at 103-105°, sp. gr. 0.912 at 0°. O. Amend[8] has described a pyroxylin solvent consisting of amyl chloride, amyl chloral, monochlorvaleralde-

1. Societe Leduc, Heitz et Cie., F. P. 429788.
2. E. P. 279139. Can. P. 275323. New Zealand P. 57726. Australia P. 5297, 15187.
3. S. Carroll, U. S. P. 1813661; abst. Chem. Zentr. 1932, I, 1464.
4. E. P. 346339; abst. Chem. Zentr. 1931, II, 3178.
5. U. S. P. 1429169; abst. C. A. 1922, **16**, 3758.
6. H. Buc, U. S. P. 1391758; abst. J. S. C. I. 1921, **40**, 827-A.
7. C. Jones and H. Buc, U. S. P. 1440683.
8. U. S. P. 371021. Re-10879. U. S. P. 372100; abst. Chem. Ztg. 1887, **11**, 1432.

hyde and dichlorvaleraldehyde. Amyl chloride (chlorpentane) has been used in amylcellulose manufacture[1], and as a cellulose nitrate solvent[2]. Technical amyl chloride now available is said to consist of *n-*, *iso-*, and *ter*-amyl chloride, 2-, and 3-chlorpropane and 1-chlor-2-methylbutane. It has a sp. gr. of about 0.88 at 20°, and a boiling range of 85-109°.

Amylene Dichloride, a commercial product consisting primarily of 2.3-dichlorpropane, has a b. pt. 138°, sp. gr. 1.085 at 20°. First described as a nitrocellulose by F. Sparre[3]. Amylene diacetate and hexylene diacetate[4] dissolve pyroxylin.

Halogen Ethylenes. Ethylene, C_2H_4 may have one, two, three or four hydrogens substituted by halogen, giving rise with chlorine, for instance, of chlorethylene or vinyl chloride, C_2H_3Cl; dichlorethylene, $C_2H_2Cl_2$; trichlorethylene; and perchlorethylene, C_2Cl_4. All four compounds have been used in the cellulose ether and ester art.

Chlorethylene, Monochlorethylene, Vinyl chloride, a gas, boils at —18° to —15°. Usually employed in the polymerized state as an ester as vinyl acetate, propionate, butyrate, etc.

Dichlorethylene, a colorless, mobile liquid, b. pt. 55°, sp. gr. 1.29. The physical constants vary in the commercial solvent due to the preponderance of one isomer over another. Non-inflammable and moderately toxic, slowly liberating HCl on contact with water. Soluble in water less than 0.3% at 15.6°. Its low boiling point and correspondingly high evaporative tendency render losses high in the use of this solvent unless precautions are taken. It dissolves sandarac, the softer copals, elemi, mastic and dammar readily, shellac less easily, and amber not at all. At least 85% commercial dichlorethylene should distill

1. G. Young, U. S. P. 1504178; abst. C. A. 1924, **18**, 3272.
2. F. Sparre, U. S. P. 1148258; abst. C. A. 1915, **9**, 2593; J. S. C. I. 1915, **34**, 924. E. P. 29963, 1912; abst. J. S. C. I. 1914, **33**, 502.
3. U. S. P. 1148258. E. P. 29963, 1912.
4. W. Masland, U. S. P. 1084702; abst. C. A. 1914, **8**, 1010.

within the limits of 54-59°. Used alone it is a non-solvent of nitrocellulose and chloroform-soluble and acetone-soluble cellulose acetate. In conjunction with alcohol and methyl and ethyl acetates it has pronounced solvency. The Farbenfabriken vorm. F. Bayer & Co.[1] use dichlorethylene-ethyl alcohol as an acetylcellulose dissolvant. Flexible films are said to result when 20 parts acetylcellulose are mixed with 65 parts dichlorethylene and 15 parts ethyl alcohol[2]. Or[3], 12 parts cellulose acetate are mixed with 73 parts dichlorethylene and 15 parts ethyl alcohol and the mixture gently heated. H. Dreyfus[4] combines dichlorethylene with anisol, phenetol, chloranisols, safrol and benzyl alcohol, and C. Dreyfus[5] admixes dichlorethylene and ethyl alcohol each 30, with 40 of benzene as a vehicle for cellulose ester lacquers. The cellulose ether solvent of S. Carroll[6] comprises ethylene chloride with methyl or ethyl alcohols, triethylcellulose being readily soluble therein, or ethylene chloride

1. E. P. 16932, 1910. F. P. 418309. U. S. P. 988965 by T. Becker. Aust. Anm. 5592-10.

2. Prepared preferably according to Farbenfabriken vorm. F. Bayer, D. R. P. 153350; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Zentr. 1904, II, 625; Jahr. Chem. 1904, 1168; J. C. S. 1904, **86**, i, 853; Chem. Ind. 1904, **27**, 538. D. R. P. 159524; abst. Chem. Zentr. 1905, II, 527; Zts. ang. Chem. 1905, **18**, 1636; Jahr. Chem. 1905-08, II, 984; J. C. S. 1906, **90**, i, 6; Chem. Ind. 1905, **28**, 535. E. P. 21628, 1901; abst. J. S. C. I. 1902, **21**, 870. F. P. 317007; abst. J. S. C. I. 1902, **21**, 870. U. S. P. 734123; abst. J. S. C. I. 1903, **22**, 961. U. S. P. 790565; abst. J. S. C. I. 1905, **24**, 686. Ital. P. 62042. Aust. P. 31391.

3. *Ibid.* E. P. 24067, 1906; abst. J. S. C. I. 1907, **26**, 1213. F. P. 371447; abst. J. S. C. I. 1907, **26**, 340. For solvent action of dichlorethylene and epichlorhydrin upon cellulose and celluloid, see H. Flemming, Chem. Ztg. 1895, **19**, 1550; abst. J. C. S. 1896, i, 333; 1898, i, 396.

4. F. P. 432264. Belg. P. 241251.

5. Can. P. 293642. See C. Abel, E. P. 9962, 1904; abst. J. S. C. I. 1905, **24**, 248. Akt. Ges. für Anilin Fabrikation, E. P. 17953, 1913; abst. C. A. 1915, **9**, 388. F. P. 339654, 349884; abst. J. S. C. I. 1905, **24**, 855. F. P. 461034; abst. C. A. 1914, **8**, 2482; J. S. C. I. 1914, **33**, 93; Chem. Ztg. 1913, **37**, 1405. D. R. P. 161213; abst. Chem. Zentr. 1905, II, 663. W. Gruber, D. R. P. 488989; abst. C. A. 1930, **24**, 2316; Chem. Zentr. 1930, II, 637. Belg. P. 259073, 354852. Akt.-Ges. für Anilin Fabrikation, Aust. P. 24952.

6. U. S. P. 1429188; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1922, **41**, 807-A; Chem. Zentr. 1922, IV, 1183.

and methyl or ethyl acetates[1]. Cellulose nitrate lacquers have been described in which the predominating solvent portion is di- or tri-chlorethylene. Dichlorethylene with benzene[2], or with amyl acetate or acetone, indicates the general solvent combinations found most suitable. Modern methods for manufacturing dichlorethylene have been disclosed by the I. G. Farbenindustrie[3] and Consortium fuer Elektrochemische Industrie[4]. Dichlorethylene is a good solvent for caoutchouc[5].

In addition to use as a cellulose ether[6] and cellulose acetate solvent[7], dichlorethylene has been used in celluloid substitutes and similar plastics[8].

Ethylene chlorbromide with methyl or ethyl alcohols[9], with methyl or ethyl ether[10], or with methyl or ethyl acetates[11] or ethylene bromide with the latter, constitutes an acceptable solvent for water-insoluble ethylcellulose and both low and high viscosity benzylcellulose. A mixture of ethylene chlorbromide, ethyl alcohol and ethyl acetate produces a very efficient cellulose ether solvent. Propylene

1. S. Carroll, U. S. P. 1464170; abst. J. S. C. I. 1923, **42**, 1065-A; Kunst. 1924, **14**, 44; Chem. Zentr. 1923, IV, 809.
2. B. Lach, E. P. 6031, 1912.
3. F. P. 702361; abst. C. A. 1931, **25**, 4285; Chem. Zentr. 1931, II, 1191. E. P. 349872; abst. J. S. C. I. 1931, **50**, 917-B.
4. E. P. 348346; abst. J. S. C. I. 1931, **50**, 796-B. F. P. 694054; abst. C. A. 1931, **25**, 1843; Chem. Zentr. 1931, I, 1514.
5. Siemens and Halske Akt.-Ges., F. P. 386017; abst. C. A. 1909, **3**, 1819; J. S. C. I. 1908, **27**, 759. See E. Fischer, D. R. P. 211186; abst. C. A. 1909, **3**, 2633.
6. L. Lilienfeld, U. S. P. 1217027, 1217028.
7. U. S. P. 1181858, 1199800, 1244107, 1244108, 1244347, 1244348, 1244349, 1388472. See also 1027616, 1206222, 1224485, 1231123, 1235283, 1237076, 1315542, 1315545, 1496675, 1509603, 1540748, 1645791, 1645792, 1645793. E. P. 108602, 126511, 136489, 147908, 147909, 148139, 148366, 158836, 166767, 177362, 214293. D. R. P. 210705, 218466, 245532, 248255, 258473, 280975, 282672, 298931, 299074, 313650, 326729, 332677, 354344, 358729, 374141, 404999, 405384, 410470, 442342. F. P. 520319, 532735, 533295, 533296, 535210, 586582. Aust. P. 88625, 108421, 108424. Can. P. 203124. Norw. P. 31349.
8. U. S. P. 1181858, 1181859, 1217027, 1241738.
9. W. Webb, U. S. P. 1432373; abst. C. A. 1923, **17**, 341; J. S. C. I. 1922, **41**, 978-A.
10. H. Dow, U. S. P. 1339552.
11. S. Carroll, U. S. P. 1467100; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.

chloride, a colorless liquid of bland odor and containing a mixture of monochlorpropylene and isomeric dichlorpropanes has been patented by P. Seel as a cellulose ether dissolving liquid admixed with acetone or methyl or ethyl alcohols or acetates[1]. A celluloid substitute has been described[2] containing "bromethylene."

Trichlorethylene, Westrosol, Tri, Trieline, Ethylene trichloride, has been described as an efficient cellulose ether solvent when admixed in equal proportions with ethyl alcohol, water-insoluble, which will dissolve 20% of its weight of cellulose ether at ordinary temperatures[3]. W. Lindsay has described the use of trichlorethylene with methyl alcohol (5:2)[4], and this same solvent with *p*-toluenesulfonamid[5] for acetylcellulose lacquer and thermoplastic formation. In the recovery of plasticizing and softening agents from acetylcellulose waste[6], trichlorethylene has been recommended. The anti-acid mineral lacquer of J. de Girves[7] includes trichlorethylene and tetrachlorethane. For trichlorethylene preparation, the J. MacMillan[8] and Consortium fuer Elektrochem. Industrie processes are representative[9].

Trichlorethylene is a colorless, heavy, strongly refractive and toxic liquid, practically insoluble in water but miscible in all proportions without turbidity with methyl, ethyl, butyl or amyl alcohols or acetates, acetone, pyridine, ben-

1. U. S. P. 1467071; abst. C. A. 1923, **17**, 3788; J. S. C. I. 1923, **42**, 1065-A; Chem. Zentr. 1923, IV, 962; Kunst. 1925, **15**, 27.
2. F. Klatte and A. Rollett, U. S. P. 1241738; abst. J. S. C. I. 1917, **36**, 1185. D. R. P. 281687; abst. J. S. C. I. 1915, **34**, 623.
3. S. Carroll, U. S. P. 1467105; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.
4. U. S. P. 1027616; abst. C. A. 1912, **6**, 1989; J. S. C. I. 1912, **31**, 583.
5. U. S. P. 1229486; abst. C. A. 1917, **11**, 2276; J. S. C. I. 1917, **36**, 869-A.
6. P. Aron, F. P. 622074; abst. J. S. C. I. 1928, **47**, 121-B; Chem. Zentr. 1927, II, 655.
7. F. P. 35669, Addn. to F. P. 660935; abst. C. A. 1930, **24**, 4175. F. P. 660935; abst. C. A. 1930, **24**, 252.
8. U. S. P. 1397134; abst. Chem. Tech. Uebers, 1922, **46**, 3.
9. F. P. 665138; abst. C. A. 1930, **24**, 866. E. P. 302321; abst. C. A. 1929, **23**, 4231.

zene, toluene and a solvent of dammar, sandarac, elemi, mastic and the softer copals, including coumarone, benzyl abietate and synthetic resins. Sp. gr. 1.4702 at 17.5°/17.5°, b. pt. 88°. A. Zimmer[1] has employed trichlorethylene in treating starched linen with acetylcellulose, and G. Koller[2] combines trichlorethylene with mono- or poly-phenols as a slowly evaporating solvent combination.

Tetrachlorethylene, Perchlorethylene, Eteline, a colorless, refractive liquid of heavy narcotic odor, sp. gr. 1.62 at 19°, b. pt. 121°. It has been patented by G. Koller as a solvent of acetylcellulose in combination with phenol[2,7], and by S. Carroll[3] as a cellulose ether solvent when accompanied by methyl or ethyl alcohol, in the proportion of equal weights of alcohol and perchlorethylene, in which triethylcellulose dissolves to the extent of 20% to form a transparent viscous, readily flowable solution.

Haloid-Substituted Aromatic Hydrocarbons. Both the chlorine, bromine and iodine substituted aromatic hydrocarbons have found substantial application in cellulose ether technique, being unusually stable, inexpensive and obtainable in large quantities.

Halogen Benzenes. J. Donohue has discovered that mono-brom- and dibrom-benzenes and -toluenes are strong solvents of the cellulose ethers in the presence of methyl and ethyl alcohols as subservient solvents[4], equal weights of brombenzene and methyl alcohol dissolving 20% by weight of water-insoluble ethylcellulose to a clear, transparent solution. Monobrombenzene and dibrombenzene

1. E. P. 12406, 1910; abst. J. S. C. I. 1911, **30**, 206. D. R. P. 242786; abst. C. A. 1912, **6**, 2182. U. S. P. 1025731; abst. C. A. 1912, **6**, 1994. G. Koller (D. R. P. 266781) mixes cellulose esters with mono- or polyatomic phenols and tri- or per-chlorethylene and thereby forms plastic celluloid-like masses of industrial value.

2. E. P. 4744, 1911; abst. J. S. C. I. 1912, **31**, 328; C. A. 1912, **6**, 2315. F. P. 440133; abst. J. S. C. I. 1912, **31**, 680. D. R. P. 266781; abst. C. A. 1914, **8**, 573. U. S. P. 1079773.

3. U. S. P. 1450714; abst. C. A. 1923, **17**, 1887; J. S. C. I. 1923, **42**, 494-A.

4. U. S. P. 1552799; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, I, 795; Caout. et Gutta. 1926, **23**, 13316. See U. S. P. 1188376.

which act equivalently, do not of themselves dissolve the cellulose ethers to a sufficient extent.

Monochlorbenzene (chlorbenzol), a colorless liquid of mild odor, relatively harmless from a toxic viewpoint, boils at 132°, sp. gr. 1.113. Immiscible with water. It is useful in preparing lacquers with a crackle or matt surface. S. Carroll[1] has described cellulose ether compositions obtained by mixing monochlorbenzene with methyl, ethyl, propyl, butyl or amyl alcohols, either singly or in various mixtures, ethyl- and benzyl-cellulose being particularly soluble. Monoiodobenzene (iodobenzene), b. pt. 188° in the presence of acetone dissolves both the cellulose ethers, acetylcellulose[2], cellulose acetostearate, acetomalate, or nitroacetate. Dichlorbenzene and monochlornaphthalene in the hands of Zuehl & Eisemann[3], and also trichlorbenzene[4] have been advocated as cellulose ester plastifying bodies. J. Stevens way back in 1897 brought forth a series of bodies which have had some use in celluloid plastics in special compositions[5], comprising nitrobenzyl chloride, nitrochlortoluene (m. pt. 82°), dichlorbenzene (benzol bichloride) m. pt. 53°, *p*-chlornitrobenzene, *p*-dibrombenzene, *p*-nitrobenzene, and the tetrachloride, *a*-di-, *b*-di- and *b*-mono-chlorides of naphthalene. Included in this category are also phenol trichloride and tribromide and monobromcamphor (bromcamphor, camphor monobromide).

Di-, tri-, tetra-, penta- and hexa-fluor(or chlor- or brom-)benzene(or toluene or xylene) constitute a series of 45 bodies[6] having solvent characteristics in conjunction with other and lower boiling direct solvents. Di-, tri-, tetra-, penta-, hexa-, hepta- and octo-fluor(or chlor- or brom-)-naphthalene constitute a series of 21 plastifying possibili-

1. U. S. P. 1411708; abst. C. A. 1922, **16**, 1915; J. S. C. I. 1922, **41**, 267-A; Caout. et Gutta. 1922, **19**, 11653; Chem. Tech. Uebers. 1922, **46**, 295.
2. S. Carroll, U. S. P. 1813662.
3. D. R. P. 128956; abst. Mon. Sci. 1903, (4), **59**, 4.
4. I. Frankenburg, Ltd., R. Frankenburg and F. Betteridge, E. P. 17156, 1903; abst. J. S. C. I. 1904, **23**, 906.
5. U. S. P. 583516.
6. Zühl & Eisemann, D. R. P. 128956.

ties of relatively higher boiling points. Trichlorbenzene has been described by H. Dreyfus[1] as a desirable acetylcellulose plastifiant.

Halogen Toluenes. Mono- and di-chlortoluene dissolve cellulose acetate[2], and *a*-bromtoluene is a solvent for benzylcellulose, benzyl dextrin and benzyl starch[3]. Bromtoluene with dicyanodiamide and acetone is said to produce an excellent plastifier for acetylcellulose. The Farbenfabriken vorm. F. Bayer & Co. for nitrocellulose and J. Donohue for cellulose ethers[4] have described certain aliphatic derivatives of toluene, which in presence of auxiliary solvents as the lower aliphatic alcohols constitute valuable plastifying and flexilizing bodies. They include benzyl chloride and bromide, benzotrichloride, benzal chloride and bromide and benzotribromide. In addition, as desirable for nitrocellulose plastification, are phenanthrene, anthracene, cymol, xylylene, xylyl chloride, *p*-xylylene dichloride and the naphthalene chlorides.

Halogen Naphthalenes. According to S. Carroll monochlornaphthalene with methyl acetate[5] or methyl, ethyl or *iso*propyl alcohols[6] constitutes excellent cellulose ether solvents, especially for ethylcellulose of maximum ethylation, the presence of chloroform not being necessary. Monochlornaphthalene, piperidine and acetone are claimed as a useful solvent mixture for acetylcellulose[7], and *a*-monochlornaphthalene or tetrachlornaphthalenes for ethylcellulose in the presence of chloroform and denatured alcohol[8].

1. F. P. 432264.
2. H. Dreyfus, F. P. 432264.
3. *Ibid.* U. S. P. 1451330. G. Young, U. S. P. 1504178.
4. U. S. P. 1552798; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Chem. Zentr. 1926, I, 540; Caout. et Gutta. 1926, **23**, 13316; Ann. Rep. S. C. I. 1926, **11**, 618. See U. S. P. 1188376.
5. U. S. P. 1467091; abst. C. A. 1923, **17**, 3789; Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A. See U. S. P. 1188376.
6. U. S. P. 1437792; abst. C. A. 1923, **17**, 695, 878; J. S. C. I. 1923, **42**, 91-A; Chem. Zentr. 1923, II, 1123; Caout. et Gutta. 1923, **20**, 11931. See U. S. P. 1188376.
7. T. Murray and C. Staud, U. S. P. 1826667.
8. P. Seel, U. S. P. 1281080; abst. C. A. 1919, **13**, 73; J. S. C. I. 1919, **38**, 8-A; Chim. et Ind. 1919, **2**, 831. See U. S. P. 1188376.

1- or 2-Tetrahydronaphthalenesulfoethylamide (viscous, colorless oil, b. pt. 240-260° at 10 mm.), 1- or 2-tetrahydronaphthalenesulfo-oxyethylamide, tetrahydronaphthalenesulfamide (white powder, m. pt. 120-130°) or cresyl 1-, or 2-tetrahydronaphthalenesulfonate (tetrahydronaphthalenesulfoacid cresyl ester, m. pt. 240-260°) in conjunction with tetrahydronaphthalene, form the colloiding series for cellulose ethers and esters as evolved by A. Steindorff and G. Balle[1].

As a mixed solvent for both nitro- and acetyl-cellulose, or for nitrocellulose alone[2], tri- and tetra-chlornaphthalenes and anthracenes have been described with butyl alcohol or fusel oil as auxiliary liquids; and α-monochlornaphthalene with butyl alcohol and fusel oil[3] has been described. Other uses of tetrachlornaphthalene are as a solvent for benzylcellulose or phenylethylcellulose (see p. 224), stencil sheet manufacture (p. 268), reduction of inflammability in nitrocellulose (p. 506), and for incorporation with benzylcellulose (p. 224). Naphthalene dichloride (dichlornaphthalene), naphthalene trichloride (trichlornaphthalene), nitronaphthalin trichloride[4] and aniline trichloride are said to produce celluloid-like materials when incorporated with nitrocellulose. Nitrobenzene, nitrotoluene, nitronaphthalene, tetra-, penta- and hexa-hydro-toluene, -xylene, -cumene and -cymene comprise a series of 12 colloidants which combine plasticity with fire-retarding qualities[5].

Aliphatic Alcohols. The degree of solvency of the cel-

1. D. R. P. 368362; abst. J. S. C. I. 1923, **42**, 494-A; Kunst. 1923, **13**, 70; Chem. Zentr. 1923, II, 769. See D. R. P. 122272.
2. S. Carroll, U. S. P. 1354725; abst. C. A. 1921, **15**, 172. U. S. P. 1354726; abst. C. A. 1921, **15**, 172; J. S. C. I. 1920, **39**, 745-A; Kunst. 1921, **11**, 167; Caout. et Gutta. 1921, **18**, 11023.
3. P. Seel, U. S. P. 1342601; abst. C. A. 1920, **14**, 2418; J. S. C. I. 1920, **39**, 541-A; Chem. Ztg. 1920, **44**, 645.
4. E. Zühl, E. P. 10213, 1901; J. S. C. I. 1901, **20**, 831. F. P. 310942; abst. J. S. C. I. 1902, **21**, 65; Mon. Sci. 1902, (4), **58**, 174.
5. B. Gaisenband and C. Piestrak, F. P. 483316; abst. C. A. 1922, **16**, 4063; Caout. et Gutta. 1923, **20**, 11853.

lulose ethers and esters diminishes in this group with increasing molecular weight, i.e., methyl and ethyl alcohols in general, are more powerful solvents than are the butyl and amyl alcohols. With ethylcellulose and benzylcellulose, the solvency of the lower alcohol is often increased by the addition of aromatic hydrocarbons, and cellulose ethers are known which are insoluble in (say) either methyl alcohol or benzene, but which dissolve in varying proportions of the two when mixed.

Methyl Alcohol, Methanol, Wood alcohol, has long been used in the cellulose nitrate industry, commercial wood alcohol by virtue of the impurities which it contains being a more powerful dissolving agent than the pure chemical. Its primary uses are in the preparation of celluloid substitutes[1], acetylcellulose[2] and nitrocellulose[3] solvents, for the preparation of films[4] especially photographic films[5], in

1. U. S. P. 1153596, 1181860, 1188797, 1188798, 1188799, 1188800, 1217027, 1412762, 1420028, 1440006.

2. U. S. P. 1127871, 1128468, 1136248, 1143979, 1156894, 1160979, 1165179, 1173931, 1181860, 1185514, 1188797, 1188798, 1188799, 1196799, 1199395, 1199799, 1199800, 1203756, 1205822, 1226339, 1226340, 1226341, 1226342, 1244107, 1244108, 1244347, 1244348, 1244349, 1260977, 1265216, 1265217, 1298199, 1309980, 1384188, 1388472, 1395401, 1406224, 1408095, 1420028, 1440006, 1488608.

3. U. S. P. 1124012, 1127871, 1129770, 1135026, 1139112, 1143464, 1147850, 1160979, 1202490, 1250822, 1260977, 1290794, 1309981, 1320458, 1321611, 1321633, 1321634, 1322786, 1323792, 1329503, 1342601, 1342602, 1350274, 1354725, 1360759, 1360763, 1369596, 1370878, 1370922, 1380258, 1385229, 1396592, 1398239, 1398939, 1408095, 1415059, 1418405, 1429153, 1429174, 1431900, 1431906, 1432368, 1434453, 1434454, 1439293, 1441185, 1441203, 1456782, 1466733, 1493207, 1493208, 1497137, 1497138, 1503835, 1508457, 1510739.

4. U. S. P. 1199395, 1217027, 1354725, 1405487, 1429153, 1429169, 1429174, 1434426, 1437792, 1440006, 1450714, 1450715, 1450716, 1479955, 1488608, 1494469, 1494470, 1494471, 1494472, 1494473, 1494474, 1494475, 1494476, 1514283.

5. U. S. P. 1188797, 1188798, 1188799, 1188800, 1199799, 1199800, 1203756, 1226339, 1226340, 1226341, 1226342, 1226343, 1229485, 1229487, 1281080, 1342602, 1388472, 1415059, 1418405, 1429179, 1429188, 1431900, 1431905, 1431906, 1432364, 1432368, 1432373, 1432374, 1434453, 1434454, 1441143, 1441185, 1444333, 1486245, 1494479, 1500366, 1518417.

general plastic production[1], and as a varnish remover[2]. As a solvent for the cellulose ethers[3], especially ethylcellulose it has found a wide application. In the cellulose industry as a solvent, it has found general use in England[4], Canada[5], France[6], Germany[7], Austria[8], Switzerland[9], and in the earlier development of this art in the United States[10].

In connection with the cellulose ethers in general, and triethylcellulose in particular, the following solvent com-

1. U. S. P. 1188797, 1188798, 1188799, 1188800, 1199800, 1203756, 1226340, 1226343, 1229485, 1229486, 1229487, 1281080, 1388472, 1405487, 1437792, 1440006, 1479330, 1488608.
2. U. S. P. 1129770, 1130499, 1133639, 1143110, 1143111, 1143130, 1143387, 1147848, 1147849, 1147850, 1173628, 1181361, 1184164, 1185641, 1189803, 1189804, 1204851, 1273307, 1328080, 1516064.
3. U. S. P. 1217027, 1217028, 1405487, 1411708, 1418405, 1429169, 1429179, 1429188, 1431905, 1431906, 1432364, 1432373, 1432374, 1434426, 1434427, 1437792, 1441143, 1450714, 1450715, 1450716, 1467092, 1467093, 1467094, 1467095, 1467096, 1467097, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105, 1469812, 1469813, 1469816, 1469825, 1469826, 1469862, 1469863, 1473217, 1473218, 1473219, 1494469, 1494470, 1494471, 1494472, 1494473, 1494474, 1494475, 1494476, 1497955, 1500366, 1518417.
4. E. P. 2484, 1878; 1866, 1879; 466, 1883; 15121, 1884; 8442, 1886; 5791, 1887; 8253, 1887; 10393, 1889; 12684, 1890; 6542, 1892; 6543, 1892; 7784, 1893; 22137, 1893; 13139, 1894; 22019, 1894; 6858, 1896; 17602, 1897; 28613, 1897; 20092, 1899; 4863, 1903; 9962, 1904; 28376, 1904; 4390, 1908; 1441, 1910; 13692, 1910; 14586, 1910; 10222, 1912; 23777, 1912; 2465, 1913; 714, 1914; 1262, 1914; 140, 1915; 7956, 1915; 112483, 127027, 128215, 131647, 133972, 160225, 164032, 164033, 184197, 184671, 187847, 189942, 209727, 230663, 231161, 238485, 243030, 243031, 243350, 276834.
5. Can. P. 78060, 196151, 196925, 196926, 260463.
6. F. P. 184548, 233727, 324121, 344501, 374395, 387791, 398028, 408396, 412797, 415945, 430440, 432264, 433013, 439721, 464646, 466911, 472423, 553547, 580882, 595155, 596838.
7. D. R. P. 80776, 86740, 118052, 161213, 176121, 267992, 281265, 287745, 302460, 307075, 352905.
8. Aust. P. 17684, 47899, 99665.
9. Swiss P. 47559, 51952, 52115, 53760.
10. U. S. P. 59888, 91393, 97454, 233558, 239423, 239424, 239425, 269340, 269344, 294577, 311203, 315357, 329273, 366231, 381354, 410204, 410205, 410206, 410207, 410208, 410209, 422195, 434330, 437499, 440921, 458663, 463039, 471422, 471469, 478543, 479305, 489684, 494790, 494791, 494792, 494793, 495263, 502546, 507964, 517987, 528812, 542692, 543108, 551456, 552209, 552934, 552935, 553270, 556017, 559392, 561624, 562626, 568106, 570728, 587096, 592895, 595355, 597144, 598649, 601927, 602797, 610861, 610953, 621433, 622294, 623963, 630945, 697790, 797373, 888516, 893987, 961360, 982370, 999490, 1009116, 1015155, 1015156, 1021569, 1027486, 1027615, 1027616, 1027617, 1027618, 1035108, 1041112, 1041113, 1041114, 1041115, 1041117, 1076215, 1082543, 1124012.

binations containing methyl alcohol have been recommended: chloroform 90-25, methyl alcohol 10-75[1]; toluene 50-75, methyl alcohol 50-25[2]. For dissolving pyroxylin and the cellulose ethers simultaneously[3], a mixture of methyl alcohol 45, ethyl acetate 20 and chloroform 35 has been found efficient.

Methyl alcohol forms constant boiling point mixtures with the following: 85% acetone, b. pt. 55.9°; 60% benzene, 58.3°, 79% carbon tetrachloride 55.7°, 63% cyclohexane 54.2°, 86% carbon bisulfide 37.6°, 80% chloroform 64.7°, 84% ethyl formate 51°, 81% methyl acetate 54°, 38% *n*-heptane 60.5°, 73% *n*-hexane 50°, and 64% trichlorethylene, b. pt. 60.2°.

The potency of methyl alcohol as a solvent is greatly augmented by the presence of a small amount of acetone for cellulose nitrates and acetates, and a small amount of ethyl acetate or benzene or both, for the etherified celluloses. The physical constants of methyl alcohol are too well known to be here repeated.

Glycide is epihydrin alcohol. Phenylglycide and phenol ethers of glycide[4], as well as glycidol (epihydrin alcohol, epihydric alcohol, *b*-epoxypropyl alcohol) have been described and patented as plastifying bodies of the cellulose esters[5]. Lacquers are said to be obtainable with acetylcellulose and glycidol containing up to 40% water.

1. S. Carroll, U. S. P. 1405487; abst. C. A. 1922, **16**, 1316; J. S. C. I. 1922, **41**, 213-A; Chem. Zentr. 1922, II, 881; Caout. et Gutta. 1922, **19**, 11653.

2. *Ibid.* U. S. P. 1441143; abst. C. A. 1923, **17**, 938; J. S. C. I. 1923, **42**, 180-A; Chem. Met. Eng. 1923, **28**, 271; Chem. Zentr. 1923, II, 1122; Kunst. 1923, **13**, 92.

3. *Ibid.* U. S. P. 1431906; abst. C. A. 1922, **16**, 4346; J. S. C. I. 1922, **41**, 894-A; Chem. Zentr. 1923, II, 424; Kunst. 1924, **14**, 91.

4. H. Danzer, assignor to Cie. Gen. de Phono. Cinemato. et Appareils de Precision, U. S. P. 1089910; abst. C. A. 1914, **8**, 1551; Mon. Sci. 1914, **81**, 106; Kunst. 1914, **4**, 275. E. P. 13239, 1912; abst. C. A. 1913, **7**, 3840; J. S. C. I. 1912, **31**, 1120; Chem. Ztg. Rep. 1913, **37**, 592; Kunst. 1913, **3**, 73. F. P. 443031; abst. J. S. C. I. 1912, **31**, 1008. Swiss P. 61929; abst. C. A. 1914, **8**, 2124; Kunst. 1914, **4**, 98. Swiss P. 63585; abst. C. A. 1914, **8**, 2252; Kunst. 1914, **4**, 216.

5. E. Glietenberg, D. R. P. 495040; abst. C. A. 1930, **24**, 3387.

Acetol. Acetyl carbinol, Acetylmethyl alcohol, 1-Hydroxy-2-propanone, Propanolon, Oxyacetone, Pyroracemic alcohol, has been patented as a cellulose acetate solvent by H. Dreyfus[1], and used to prevent decomposition of copper ammonia solutions[2]. The Deutsche Hydrierwerke A. G.[3] have described esters of these keto-alcohols with monobasic aliphatic or aromatic carboxylic acids as cellulose ether solvents or softening agents, acetol acetate, laurate and levulinate (pyroracemic acetate, laurate and levulinate) being specified. Acetol salicylate (salacetol, salantol) has been patented as a pyroxylin plastifier[4], being white crystals, m. pt. 71°, and soluble in hot water and alcohol. Not to be confounded with salacetin, a mixture of 43% acetanilid, 21% sodium bicarbonate, 20% sodium salicylate.

The word "acetol" has been protected by U. S. Trade Mark 233752, as a name for cellulose acetate by Societe Chimique Usine du Rhone.

Ethyl Alcohol, Ethanol, Grain Alcohol, has been used from the inception of the cellulose ester art as a solvent[5], in the earlier days in combination with ether in the familiar

1. F. P. 432264; abst. C. A. 1913, **7**, 3414. E. P. 20975, 1911; abst. C. A. 1913, **7**, 890. U. S. P. 1181859, 1181860; abst. C. A. 1916, **10**, 1789. Belg. P. 241251; abst. Mon. Sci. 1913, **78**, 392. Swiss P. 65051 (Addn. to Swiss P. 63585). Swiss P. 65057; abst. Chem. Ztg. 1914, **38**, 501.

2. British Cellulose Syndicate and V. Mertz, E. P. 1148, 1909. Belg. P. 222298. F. P. 411592. See U. S. P. 954984.

3. D. R. P. 547039, Addn. to D. R. P. 535168; abst. C. A. 1932, **26**, 3667.

4. J. Stevens, U. S. P. 572134.

5. U. S. P. 35687, 91393, 97454, 112370, 150722, 209570, 251410, 262077, 265337, 269341, 269342, 269345, 286212, 304229, 329313, 381354, 410205, 410207, 410209, 463039, 470451, 471422, 494790, 494791, 494792, 494793, 495263, 502546, 502547, 503401, 503402, 504905, 517987, 518388, 542692, 551456, 552209, 553270, 559823, 559824, 566349, 568106, 572134, 578714, 595355, 598649, 602797, 610728, 610861, 628463, 797373, 830493, 874879, 888516, 894108, 928235, 942395, 951582, 961360, 979431, 988965, 996191, 999490, 1005454, 1015155, 1015156, 1027486, 1027614, 1027615, 1027616, 1027617, 1027618, 1039782, 1041113, 1041114, 1041116, 1041118, 1045895, 1067785, 1076216, 1079773, 1089960, 1124012, 1128468, 1140174, 1153596, 1158217, 1161063, 1165179, 1175791, 1181858, 1181859, 1181860. E. P. 2359, 1855; 639, 1858; 1695, 1867; 3102, 1869; 1208, 1871; 2484, 1878; 959, 1865, 1866, 1879; 3072, 1882; 466, 5974, 1883; 5433, 1884; 5413, 1886; 383, 5791, 16330, 1887; 5344, 1889; 8823, 1891; 7688, 1892; 7277, 7784, 1893; 13139, 15327, 1894;

collodion formula or some modification of it. In France[1] and Germany likewise[2], alcohol has been a favorite component in acetylcellulose and nitrocellulose compositions. Anhydrous alcohol (about 99.7% absolute)[3] has been employed extensively during the past few years, it being an excellent dissolving medium for low viscous nitrocelluloses. The L. Clement[4], Pathe Cinema[5] cellulose acetate processes depend upon anhydrous ethyl alcohol for the main solvent effect. Various partially and completely denatured alcohols, sold under the trade names of "Al-Kol"[6], "Wi-Alc"[7], "Shellacol"[8], and "Alcol-Oil"[9] are widely used. Ansol M, is substantially absolute ethyl alcohol[10]. The following azeotropic mixtures with ethyl alcohol are known: with water 4.43%, b. pt. 78.15°; 67.63% benzene, b. pt. 68.24°; 32% toluene, b. pt. 76.7°; 79% *n*-hexane, b. pt. 58.6°; 69.5% cyclohexane, 64.9°; 60% methylethyl ketone, b. pt. 74.8°;

6389, 6858, 12693, 13198, 25779, 1896; 27534, 1897; 11927, 1898; 15355, 1899; 8301, 18744, 1901; 4863, 15696, 1903; 5280, 9962, 22245, 28376, 1904; 26201, 1905; 11397, 11928, 24214, 1907; 413, 1908; 11340, 12976, 24006, 1909; 6519, 10320, 10794, 13692, 16932, 18189, 21719, 29246, 29273, 1910; 6798, 10708, 16810, 20976, 20979, 21426, 1911; 3869, 10222, 18822, 28210, 1912; 7086, 2465, 6387, 25182, 1913; 714, 4668, 8126, 9270, 13100, 14042, 1914; 140, 7956, 12091, 1915.

1. F. P. 132495, 184548, 233727, 320133, 322457, 324121, 324718, 328054, 328658, 331819, 333824, 336970, 340622, 347303, 351555, 352853, 361954, 363090, 363592, 368004, 377039, 379589, 381195, 383478, 387179, 392505, 397429, 408396, 411126, 416843, 417250, 417319, 418309, 418347, 418744, 419530, 420212, 421843, 422763, 423774, 424820, 429788, 431090, 431711, 432047, 432264, 432483, 439721, 440955, 441146, 443031, 447645, 447664, 448808, 450746, 456261, 456729, 464617, 467800.

2. D. R. P. 10210, 17089, 27031, 86740, 93009, 163668, 168497, 169782, 175379, 180208, 180489, 185808, 202720, 210519, 211520, 220322, 222777, 240188, 244566, 249535, 250421, 254193, 254385, 254784, 255692, 267992, 268627, 277490, 279127, 279638, 281225, 281265, 281374, 295764, 364347, 372856, 375640.

3. U. S. P. 1562386, 1562544, 1564664. E. P. 226142, 243614. F. P. 587486, 601547, 601662. Can. P. 259662, 261371.

4. U. S. P. 1713512, 1713997; abst. C. A. 1929, **23**, 3573; J. S. C. I. 1929, **48**, 594-B; British Plastics, 1929, **1**, #3, 113. Can. P. 261371; abst. C. A. 1926, **20**, 3568; Chem. Zentr. 1927, I, 207.

5. F. P. 601546, 601547; abst. J. S. C. I. 1926, **45**, 533-B; Chem. Zentr. 1926, I, 3110.

6. U. S. Trade Mark, American Druggists Syndicate, 155041.

7. Western Industries Co., U. S. Trade Mark, 152355.

8. The Rossville Company, U. S. Trade Mark, 151232.

9. Electro Chemical Refineries, Inc., U. S. Trade Mark, 150523.

10. See H. Haines, Paint, Oil and Chem. Rev. 1924, **78**, #11, 10. B. Tunison, Drug and Chem. Markets, 1925, 277.

91% carbon bisulfide, b. pt. 42.4°; 19% tetrachlorethylene, b. pt. 78°; 73% trichlorethylene, b. pt. 70.9°; 93% chloroform, b. pt. 59.4°; 84.15% carbon tetrachloride, b. pt. 65°; 69.4% ethyl acetate, b. pt. 71.8°.

J. Brégeat[1] dehydrates cellulose ethers by treatment with substantially anhydrous ethyl alcohol, and L. Clement employs a mixture of anhydrous ethyl alcohol and acetone, 4:2. The ethylcellulose solvent propounded by S. Carroll[2] comprises benzene-ethyl alcohol 2:1, acetone being added if desired, to promote adhesion.

Propyl Alcohol, Propanol, has been used to a lesser degree than ethyl alcohol[3], for, although in general it has about the same solvent avidity for cellulose ethers and esters, the commercial commodity, being usually the collective lighter boiling fractions of fusel oil, varies considerably in physical constants and hence in action in lacquers and enamel compositions. A useful dissolving composition, as has been pointed out by W. Clough and C. Johns[4], is a mixture of *iso*propyl alcohol and *iso*propyl acetate, having a constant b. pt. 80.1° at 760 mm. pressure, and sp. gr. 0.824 at 15° when containing 47.5% acetate and 52.5% of the alcohol. The H. Dow formula[5] is propyl alcohol 55, ethylene chlorbromide 45 and benzyl acetate 5. S. Carroll[6] has published a cellulose ether composition especially applicable to water-insoluble ethylcellulose, combining methyl,

1. E. P. 226142; abst. C. A. 1925, **19**, 1629; J. S. C. I. 1925, **44**, 706-B; Plastics, 1926, **2**, 134; Ann. Rep. S. C. I. 1925, **10**, 147; Chem. Zentr. 1925, I, 2030; Kunst. 1925, **15**, 223; Schiess. & Spreng. 1925, **20**, 110. F. P. 587486; abst. Plastics, 1926, **2**, 134; Kunst. 1925, **15**, 224.
2. U. S. P. 1441142; abst. J. S. C. I. 1923, **42**, 203-A.
3. U. S. P. 410204, 471422, 559824, 1199799, 1265217, 1398239, 1431905, 1439293, 1439656, 1458256, 1533616, 1548932, 1552795, 1552796, 1552798, 1552799, 1552800, 1552801, 1552802, 1552804, 1552805, 1552806, 1580189, 1599569, 1618483. E. P. 5791, 1887; 194727, 236190. Can. P. 262784. F. P. 184548, 600178. Aust. P. 17684.
4. U. S. P. 1485071.
5. H. Dow, U. S. P. 1339552; abst. C. A. 1920, **14**, 2084.
6. U. S. P. 1444331: abst. C. A. 1923, **17**, 1329; Chem. Met. Eng. 1923, **28**, 510; J. S. C. I. 1923, **42**, 305-A; Chem. Zentr. 1923, IV, 342.

ethyl, propyl, *iso*propyl, *iso*butyl,*sec*butyl, amyl alcohol and/or fusel oil with phenylpropyl alcohol.

Propyl alcohol has been used as a solvent for nitrocellulose in conjunction with other liquids[1], for the cellulose ethers[2] and for cellulose esters in general[3].

Butyl Alcohol, Butanol, especially the *n*-butyl alcohol isomer is of paramount importance in the cellulose derivatives industry by virtue of the fact that it serves as the alkyl for a series of esters which are direct solvents, primarily *n*-butyl acetate. Butyl alcohol in combination has been used extensively as a cellulose nitrate solvent[4], as a direct solvent for the cellulose ethers[5] usually in conjunction with an aromatic hydrocarbon or an aliphatic acetic ester, being especially useful in fluid ethylcellulose mixtures[6]. In the production of photographic films[7] and in motor fuels[8], butyl alcohol has found a wide and increasing usefulness. *iso*Butyl alcohol has likewise been employed as a cellulose ether solvent[9] and for cellulose nitrate solutions as an adjunct to more active dissolving bodies[10]. The S. Carroll solvent combination for ethylcellulose[11] combines monochlorbenzene with propyl or butyl alcohols or fusel oil; W. Webb[12] combines butyl alcohol with methyl acetate; while phenetol, methyl alcohol and propyl or butyl alcohols constitute the

1. U. S. P. 1400196, 1485071.
2. U. S. P. 1411708, 1432364, 1432374, 1437792, 1479955.
3. U. S. P. 1429188, 1469812, 1469813, 1469862, 1469863.
4. U. S. P. 1321611, 1323624, 1370922, 1379596, 1380258, 1398239, 1429174, 1431900, 1434453, 1434454, 1437170, 1439293, 1441185, 1510739.
5. U. S. P. 1411708, 1429188, 1432364, 1432374, 1437952, 1469812, 1469813.
6. U. S. P. 1411677, 1434426, 1434427, 1437792, 1458256, 1469862, 1469863.
7. U. S. P. 1199799, 1342601, 1342602, 1415059, 1434453, 1434454, 1486245.
8. U. S. P. 1398947, 1412233, 1420006, 1420007, 1423048, 1423049, 1423050, 1423058, 1428913.
9. U. S. P. 1444331, 1479955.
10. U. S. P. 1341710, 1356440, 1398939, 1400196.
11. S. Carroll, U. S. P. 1411708; abst. C. A. 1922, **16**, 1915; J. S. C. I. 1922, **41**, 267-A.
12. U. S. P. 1432374.

cellulose ether dissolvant of others[1]. The solvent of E. Flaherty[2] contains *n*-butyl alcohol, a hydrocarbon and an alcohol of the paraffin series. *sec*-Butyl alcohol has been advocated by W. Lindsay[3] as a desirable nitrocellulose plasticizing agent.

1.1.1-Trichlor-2-methylpropyl alcohol (trichlor*ter*butyl alcohol, chlorbutol, chloretone)[4] and trichlorbutyl alcohol have been brought forward as desirable acetylcellulose plasticizing agents, but in practice have not proven satisfactory primarily on account of decomposition upon exposure to light with liberation of chlorine.

Amyl Alcohol, Pentasol, exists in 8 isomers, *iso*-butyl carbinol being the chief ingredient in fermentation amyl alcohol, and occurs as amyl angelate and amyl crotonate in Roman chamomile oil. Amyl alcohol has been patented as an ingredient in airplane wing dope[5], and as a solvent for celluloid[6], acetylcellulose mixtures[7], cellulose acetonitrate compositions[8], and in nitrocellulose mixtures. Amyl alcohol does not dissolve nitrocellulose, but exhibits the peculiar property that pyroxylin in the dissolved state can be admixed with amyl alcohol without precipitation to an attenuation of at least ten volumes amyl alcohol[9]. Many formulas for cellulose ether lacquers contain amyl alcohol as a prime

1. S. Carroll, U. S. P. 1479955; abst. C. A. 1924, **18**, 904; J. S. C. I. 1924, **43**, 213-B; Kunst. 1925, **15**, 83.
2. U. S. P. 1356440; abst. J. S. C. I. 1920, **39**, 817-A.
3. U. S. P. 1538861; abst. J. S. C. I. 1925, **44**, 587-B.
4. W. Bader and W. Dickie, U. S. P. 1536052; abst. C. A. 1925, **19**, 1948. H. Dreyfus, U. S. P. 1661169; abst. C. A. 1928, **22**, 1473; J. S. C. I. 1928, **47**, 295-B; Plastics, 1928, **4**, 688; Kunst. 1929, **19**, 162. W. Bader and W. Dickie, E. P. 195849; abst. C. A. 1923, **17**, 3789; J. S. C. I. 1923, **42**, 546-A. H. Dreyfus, E. P. 205195; abst. C. A. 1924, **18**, 1199; J. S. C. I. 1923, **42**, 1172-A; Kunst. 1924, **14**, 91; Chem. Zentr. 1924, I, 716.
5. L. Clement and C. Riviere, U. S. P. 1173931; abst. C. A. 1916, **10**, 1104. H. Dreyfus, U. S. P. 1363763; abst. C. A. 1921, **15**, 752; J. S. C. I. 1921, **40**, 114-A. F. P. 461058; abst. J. S. C. I. 1914, **33**, 20.
6. U. S. P. 1368954, 1421974.
7. U. S. P. 1160979, 1181758, 1199799, 1265217, 1363763.
8. U. S. P. 1173931.
9. U. S. P. 1129770, 1143464, 1147850, 1160979, 1181758, 1208358, 1320458, 1379596, 1388546, 1398239, 1400196, 1434453, 1434454, 1441185, 1510739.

component, usually in conjunction either with benzene or toluene, or with methyl or ethyl acetates[1]. Amyl alcohol is a cellulose formate precipitant[2].

Fusel Oil in the raw condition consists of propyl, butyl and amyl alcohols, and refined fusel oil, depending upon the cuts taken off in refining, comprises primarily *iso*-butyl and *iso*-amyl alcohols. The earlier nitrocellulose art often employed the terms fusel oil and amyl alcohol synonymously[3]. Fusol oil has been employed in acetylcellulose solvent mixtures[4], as a nitrocellulose dissolvant in conjunction with active solvents[5], and as a direct solvent for ethylcellulose[6], usually in the presence of benzene or methyl or ethyl acetates. Various essential oils have been proposed in conjunction with fusel oil[7] as cellulose ester dissolving media.

Methyl*iso*butyl carbinol (methylamyl alcohol)[8] has recently been advocated as a pyroxylin solvent in brushing lacquers, and allyl alcohol[9] as a solvent in nitrocellulose textile impregnating solutions.

Dihydric Aliphatic Alcohols. The dihydric alcohol, ethylene glycol (glycol, ethanediol), stands midway between the monohydric alcohol, ethyl alcohol, and the trihydric al-

1. U. S. P. 1411708, 1429188, 1432374, 1437952, 1467812, 1467813, 1469862, 1469863, 1479955.
2. U. S. P. 1153596.
3. U. S. P. 269343, 269344, 340026, 371021, 372100, 417202, 422195, 428654, 450264, 471422, 478543, 494790, 494791, 494792, 494793, 495263, 502546, 502547, 504905, 507749, 518386, 518387, 518388, 555596, 559823, 559824, 587211, 595355, 598649, 622727, 797373, 841509, 1117931, 1185514, 1199799. E. P. 491, 4668, 1885; 5791, 15771, 1887; 487, 1888; 5344, 10393, 1889; 9315, 20690, 1890; 7277, 7784, 1893; 17717, 1896; 870, 1799, 14293, 1910; 21015, 1913; 714, 5633, 1914.
4. U. S. P. 1165179, 1181758, 1185514, 1199799, 1199800, 1265217, 1309980, 1342603, 1370879, 1388472.
5. U. S. P. 1181758, 1309981, 1321611, 1370878, 1370922, 1379596, 1380258, 1398939, 1415059, 1419258, 1431950, 1432368, 1434453, 1434454, 1437170, 1441185, 1466733, 1508457.
6. U. S. P. 1411708, 1432354, 1479955.
7. J. Stevens, U. S. P. 269343, 269344.
8. R. Van Schaack, U. S. P. 1702181; abst. J. S. C. I. 1929, **48**, 924-B; Plastics, 1929, **5**, 391.
9. D. Sutherland and W. McLaren, E. P. 28613, 1897; abst. J. S. C. I. 1897, **16**, 1013.

cohol, glycerol. The next member in the glycol series is propylene glycol (trimethylene glycol, methyl glycol, propanediol, methylethylene glycol), and the next butylene glycol (tetramethylene glycol, ethyl glycol, butanediol, dimethylethylene glycol, ethylethylene glycol). Tetramethylethylene glycol is pinacone. There has been much confusion in the patent literature in the naming of these compounds.

Ethylene Glycol is a limpid liquid with properties midway between those of ethyl alcohol and glycerol, being colorless and odorless, b. pt. 197-198 at 760 mm., sp. gr. 116-118°. The S. Shipley brushing lacquer[1] comprises glycol 40, resin and toluene 25, and gasoline 35%. Although ethylene glycol possesses the inherent characteristics of a nonsolvent for water-insoluble ethylcellulose, it may be combined with a volatile solvent as methyl alcohol or acetate[2], and thereby impart to cellulose ethers softness and plasticity. The flowability of the composition may be modified by the amount of volatile solvent present. H. Dreyfus[3] has described employment of ethylene glycol, diethylene glycol, propylene glycol, trimethylene glycol and 1.2- and 1.3-butylene glycols as softeners for the acetylcelluloses, either alone or in combination with trichlormethyl-, tetrachlorethyl- or 2.4.6-tribromdi-acetanilid[4]. Glycol has been used in the preparation of electric insulation compositions[5], in cellulose ester plastics[6], as a cellulose ester colloidant[7] and in the formulation of dope for airplane wing fabrics[8]. Modern methods of manufacture are indicated in the note below[9].

1. S. Shipley, U. S. P. 1692584; abst. C. A. 1929, **23**, 722.
2. S. Carroll, U. S. P. 1735158; abst. C. A. 1930, **24**, 723; Cellulose, 1930, **1**, #2, 63.
3. F. P. 713847. See E. P. 355298.
4. W. Dickie and P. Sowter, E. P. 355330. F. P. 713846; abst. C. A. 1932, **26**, 1781. See E. P. 319073. F. P. 675745.
5. U. S. P. 1091627, 1091628, 1091732, 1098728, 1098776, 1108329.
6. U. S. P. 1098728, 1108329.
7. U. S. P. 1392849.
8. U. S. P. 1427941.
9. U. S. P. 1181697, 1206222, 1213367, 1213368, 1213369, 1215903, 1231123, 1231351, 1234886, 1235283, 1237076, 1253617, 1259757, 1259758, 1270759, 1307033, 1308796, 1308797, 1442386, 1454604, 1498781, 1498782.

Propylene glycol has recently appeared on the market as a solvent[1], and ethylthiodiglycol is used in printing pastes. Di- and tri-ethylene glycol, b. pt. 250° and 290° respectively, and ethylenepropylene glycol, have been described by G. Davidson[2] as acceptable nitrocellulose colloiding bodies. Tetraethyl glycol constitutes the solvent of Farbenfabriken vorm. F. Bayer & Co.[3], and glycolformal and glycerolmonoformal as cellulose ether solvents have been delineated by I. G. Farbenindustrie[4], who have also described the application of ethylene oxide, propylene oxide and butylene oxide as a solvent for both primary and partially hydrated acetylcellulose[5], preferably in conjunction with butyl phthalate.

Chlorhydrins, as ethylene chlorhydrin, CH_2ClCH_2OH, monochlorhydrin $CH_2ClCHOHCH_2OH$, dichlorhydrin $CH_2ClCHOHCH_2Cl$, and epichlorhydrin $CH_2ClCHOCH_2$, and especially their derivatives as the acetic compounds have been found valuable solvents and plastic-inducers in cellulose ether compositions, acetylcellulose solutions and nitrocellulose compounds.

Monochlorhydrin, in its commercial form, is a mixture of two isomers, *α*-monochlorhydrin preponderating. On account of its miscibility with water, tendency to development of acidity upon prolonged contact with moisture, and hygroscopicity, it has found a limited field of usefulness. It has been used in the explosives industry[6]. Sp. gr. 1.2,

1. E. Clayton and C. Clark, Textile Mfr. 1931, **57**, #684, 455.
2. U. S. P. 1693746; abst. C. A. 1929, **23**, 982; J. S. C. I. 1929, **48**, 554-B; Chem. Zentr. 1929, I, 1517; Plastics, 1929, **5**, 453; British Plastics, 1929, **1**, #3, 114.
3. Swiss P. 58410; abst. Chem. Ztg. 1913, **37**, 228.
4. E. P. 286789; abst. C. A. 1929, **23**, 513; J. S. C. I. 1928, **47**, 376-B; Chem. Zentr. 1928, I, 3016.
5. I. G. Farbenindustrie, A.-G., E. P. 346827; abst. C. A. 1932, **26**, 2053. Chem. Zentr. 1931, II, 3178.
6. See E. I. du Pont de Nemours Powder Co., U. S. P. 1040323; abst. Mon. Sci. 1913, **78**, 13; J. S. C. I. 1912, **31**, 1054. D. R. P. 229536; abst. J. S. C. I. 1911, **30**, 307. Chem. Fabrik Griesheim-Elektron, D. R. P. 238341; abst. C. A. 1912, **6**, 1660. Deutsche Sprengstoff Aktiengesellschaft, E. P. 26036, 1911; abst. J. S. C. I. 1912, **31**, 1147; C. A. 1913, **7**, 807. F. P. 370224, 370249; abst. Mon. Sci. 1908, (4), **68**, 78. F. P. 437315; abst. J. S. C. I. 1912, **31**, 557; C. A.

b. pt. 215-227°. Miscible with the usual range of organic solvents but not with vegetable oils, benzene, toluene, xylene or gasolene. The I. G. Farbenindustrie[1] have described acetylcellulose lacquers in monochlorhydrin, to which small amounts of aniline, pyridine or quinoline are added as stabilizers. In the L. Rosenthal acetylcellulose lacquer[2], a mixture of monochlorhydrin 40 and water 60 is used to dissolve cellulose acetate containing not less than 50% acetic acid.

Ethylene Chlorhydrin, Chlorethyl alcohol, Glycol chlorhydrin, is a colorless, highly refractive liquid of bland odor, sp. gr. 1.21, b. pt. 126-131°, miscible with water, alcohol and benzene—the latter if in the anhydrous condition. Boiling at 96°, this chlorhydrin forms a constant-boiling mixture with water, containing 58% of the latter. Recently it has been demonstrated that it possesses insidious toxic properties.

W. Webb[3] has described cellulose ether compositions containing ethylene chlorhydrin aided by alcohol, the recommended menstruum for water-insoluble ethylcellulose being 1 part cellulose ether and 2-3 parts each chlorhydrin and methyl alcohol. The cellulose ester fluid preparation of B. Eldred[4] utilizes ethylene, propylene and butylene chlorhydrins, all soluble in water, propylene chlorhydrin dissolving in water to the extent of 24%. Such a saturated

1912, **6**, 2674. D. R. P. 254709; abst. C. A. 1913, **7**, 807. Belg. P. 194975. Chem. Fabr. von Heyden, D. R. P. 263106; abst. C. A. 1913, **7**, 3820; J. S. C. I. 1913, **32**, 925. P. Walden and R. Swinne (Zts. Physik. Chem. 1912, **79**, 713; abst. Chem. Zentr. 1912, II, 791; Bull. Soc. Chim. 1912, (4), **12**, 1250; C. A. 1912, **6**, 2877; J. C. S. 1912, **102**, ii, 628) give the density of monochlorhydrin as follows: 25°/4°, 1.3181; 50°/4°, 1.2594; 70°, 1.2773.

1. D. R. P. 472311; abst. C. A. 1929, **23**, 2585.

2. D. R. P. 406426, Addn. to D. R. P. 383699; abst. Chem. Zentr. 1925, I, 908; J. S. C. I. 1925, **44**, 217-B. D. R. P. 439009, Addn. to D. R. P. 383699; abst. J. S. C. I. 1927, **46**, 661-B. See E. P. 228518; abst. Chem. Zentr. 1925, I, 2732.

3. U. S. P. 1444406; abst. C. A. 1923, **17**, 1329; J. S. C. I. 1923, **42**, 305-A; Chem. Met. Eng. 1923, **28**, 510; Chem. Zentr. 1923, IV, 342; Kunst. 1925, **15**, 26. See U. S. P. 1188376.

4. U. S. P. 1408423; abst. J. S. C. I. 1922, **41**, 290-A; Chem. Ztg. 1922, **46**, 506; Caout. et Gutta. 1922, **19**, 11653; Mon. Sci. 1923, (5), **13**, 15.

solution of propylene chlorhydrin and water is an energetic solvent for acetylcellulose. The W. Lindsay process[1] uses this solvent in conjunction with alcohol for cellulose acetate lacquers.

Dichlorhydrin, Glycerol dichlorhydrin, Dichlor-*iso*-propyl alcohol, 1.3-Dichlor-2-hydroxypropane, a colorless, inodorous, slightly viscous liquid, miscible in water to the extent of about 10%, non-inflammable, sp. gr. 1.346 at 15°, b. pt. 174°. The technical compound is usually a mixture of 1.2-dichlorpropanol-3, and 1.3-dichlorpropanol-2, and analogous to the other chlorhydrins, shows a tendency to liberate HCl on standing and in the presence of moisture. It is miscible with linseed, castor and other vegetable oils, and dissolves both cellulose acetate and the cellulose ethers.

L. Lilienfeld[2] employs dichlorhydrin as an ethylcellulose solvent, either alone or in admixture with a large number of other named solvents. R. Schüpphaus[3] combined dichlorhydrin with acetins; G. Kraemer[4] with *p*-toluenesulfochloride; W. Lindsay[5] with tricresyl phophate; A. Eichengruen[6] with acetylmethylaniline and naphthyl acetate;

1. U. S. P. 1027614; abst. J. S. C. I. 1912, **31**, 583; Mon. Sci. 1912, **77**, 163.

2. U. S. P. 1217027. Other solvents used: glycerol, methanol, glacial acetic acid, formic acid, pyridine, quinoline, picoline, dichlorhydrin, epichlorhydrin, nitrobenzene, ethyl acetate, ethyl phthalate, ethyl sebacate, ethyl citrate, ethyl succinate, ethyl tartrate, amyl acetate, butyl acetate, ethyl benzoate, ethyl levulinate, acetylene pentachloride, acetylene tetrachloride, acetylene trichloride, acetylene dichloride, chloroform, carbon tetrachloride, benzene, toluene, xylene, phenol, nitrophenols, *o*-cresol, naphthalene, toluidine, aniline, formanilid, acetanilid, turpentine oil, castor oil, linseed oil, chinese wood oil, olive oil, vaseline, paraffin oil, camphor, petroleum naphtha, vaseline oil, methyl nitrate, triphenyl phosphate, tricresyl phosphate, acetone.

3. U. S. P. 598648.

4. U. S. P. 942395. F. P. 379589; abst. C. A. 1909, **3**, 1092. E. P. 11928, 1907; abst. J. S. C. I. 1907, **26**, 1046. E. P. 26201, 1905. Aust. P. 25770.

5. U. S. P. 1319229. Other solvents used: Triphenyl phosphate, dichlorhydrin, diphenylamine, trichlorphenol, chloroform, acetone, ethyl acetate, acetylene tetrachloride, diacetic ether, benzoic ether, acetodichlorhydrin, urea. See U. S. P. 1386576. W. Lindsay, U. S. P. 1265216; abst. C. A. 1918, **12**, 1699; J. S. C. I. 1918, **37**, 461-A; Chem. Ztg. 1918, **42**, 494.

6. U. S. P. 1015155, 1015156, 1420028. Swiss P. 51952. Can. P. 129265. Aust. P. 47899.

F. Edbrook[1] with benzyl alcohol, and Pathe Cinema[2] with dicresylglyceryl ether. The patented processes of J. Hyde[3], M. Seaton[4], and H. Flemming[5] are similar. The phonograph record of A. Eichengruen[6] combines cellulose acetate with resinous material by harmonious solvent dichlorhydrin.

Epichlorhydrin, Chlorpropylene oxide, is a colorless, mobile liquid resembling that of chloroform, sp. gr. 1.2, b. pt. 117°, practically insoluble in water, but miscible in all proportions with alcohol, ether, ethyl, butyl and amyl acetates, acetone or tetrachlorethane. It dissolves the water-insoluble cellulose ethers, and the acetone-soluble acetylcelluloses. For modifying the process of esterification, both for the preparation of cellulose acetate[7] and cellulose butyrate[8], it is inferior to benzene.

It is also a powerful solvent for coumarone, soft resins, ester gum, benzyl abietate, dammar, elemi and sandarac.

The J. Donohue formula for cellulose ether compositions[9] employs epichlorhydrin with methyl alcohol as supplementary dissolvant, water-insoluble ethylcellulose dissolving to a clear, transparent solution suitable for direct

1. U. S. P. 1607516. E. P. 202154. Epichlorhydrin (U. S. P. 790565. E. P. 14255, 24067, 1906. D. R. P. 200334, 239077); nitrodichlorhydrin (F. P. 395179); ethyleneacetochlorhydrin (U. S. P. 1027615, 1027617, 1027618); and ethylene chloride (U. S. P. 1880513, 1880557), the latter in conjunction with ethyl lactate or tartrate, have been described as useful cellulose acetate gelatinizing bodies.
2. F. P. 597132. See E. P. 237900.
3. U. S. P. 1165179; abst. C. A. 1916, **10**, 393; Kunst. 1916, **6**, 150. See U. S. P. 673955.
4. U. S. P. 1480016; abst. C. A. 1924, **18**, 904.
5. D. R. P. 91819. See D. R. P. 84146.
6. U. S. P. 1175728; abst. C. A. 1916, **10**, 1415. E. P. 17574, 1912. See Farbenfabr. vorm F. Bayer, F. P. 417250.
7. C. Weber and C. Cross, U. S. P. 627031. E. P. 18283, 1898; abst. J. S. C. I. 1899, **18**, 756. Can. P. 62188. F. P. 282320. Russ. P. 3378. Dan. P. 2636. Luxem. P. 3302, 3361, 7610. Port. P. 2899. Belg. P. 138462, Addn. to Belg. P. 137577. Norw. P. 7610. Hung. P. Aug. 31, 1898; Nov. 8, 1898.
8. *Ibid.* U. S. P. 632605. E. P. 22029, 1898; abst. J. S. C. I. 1899, **18**, 756. Can. P. 63101, 1899. D. R. P. 112817. Russ. P. 3264. Belg. P. 137577. Dan. P. 2558. Port. P. 2930.
9. U. S. P. 1473218; abst. C. A. 1924, **18**, 469; J. S. C. I. 1924, **43**, 12-B; Chem. Zentr. 1924, I, 525; Kunst. 1925, **15**, 43. See U. S. P. 1188376.

film casting. Epichlorhydrin with *p*-toluenesulfonamide[1] or triphenyl phosphate[2] forms the basis of the W. Lindsay cellulose acetate compositions, aided by other solvents. A. Eichengruen[3] and H. Richter[4] have also submitted epichlorhydrin-containing formulas with the cellulose esters.

1. W. Lindsay, U. S. P. 1226340; abst. C. A. 1917, **11**, 2153; Kunst. 1918, **8**, 9.

2. W. Lindsay, U. S. P. 1226343. U. S. P. 1244107, Toluene sulfonamid, benzene sulfonamid, ethyl acetanilid, methyl acetanilid, ethyl alcohol, chloroform, epichlorhydrin, acetodichlorhydrin, dichlorethylene, ethylene chloride, trichlorhydrin, pentachlorethane, acetochlorhydrin, acetylene tetrachloride, ethyl chloracetate, acetone, ethyl acetate, di-acetochlorhydrin, triphenyl phosphate, tricresyl phosphate, naphthalene, camphor, tetrachlorethyl acetanilid, trichlormethyl acetanilid. U. S. P. 1244108, Ethyl alcohol, epichlorhydrin, acetodichlorhydrin, dichlorethylene, ethylene chloride, trichlorhydrin, pentachlorethane, acetochlorhydrin, acetylene tetrachloride, ethyl chloracetate, acetone, ethyl acetate, diacetochlorhydrin, toluenesulfonamid, benzenesulfonamid, paraethyltoluolsulfonamid, methyl acetanilid, triphenylphosphate, tricresylphosphate, naphthalene, camphor, tetrachlorethyl acetanilid, trichlormethyl acetanilid, ethyl acetanilid, methyl acetanilid. U. S. P. 1244347, Ethyl alcohol, tricresyl phosphate, naphthalene, camphor, tetrachlorethylacetanilid, trichlormethylacetanilid, toluol sulfonamid, paraethyltoluolsulfonamid, benzene sulfonamid, ethyl acetanilid, methyl acetanilid, chloroform, epichlorhydrin, acetodichlorhydrin, dichlorethylene, ethylene chloride, trichlorhydrin, pentachlorethane, acetochlorhydrin, acetylene tetrachloride, ethyl chloracetate, acetone, ethyl acetate, di-acetochlorhydrin. U. S. P. 1244348, Ethyl alcohol, tricresyl phosphate, naphthalene, camphor, tetrachlorethyl acetanilid, trichlormethylacetanilid, toluol sulfonamid, paraethyltoluenesulfonamid, benzenesulfonamid, ethylacetanilid, methylacetanilid, chloroform, epichlorhydrin, acetodichlorhydrin, dichlorethylene, ethylene chloride, trichlorhydrin, pentachlorethane, acetochlorhydrin, acetylene tetrachloride, ethyl chloracetate, acetone, ethyl acetate, diacetochlorhydrin. U. S. P. 1244349, Ethyl alcohol, tricresyl phosphate, naphthalene, camphor, toluenesulfonamid, epichlorhydrin, acetodichlorhydrin, dichlorethylene, ethylene chloride, trichlorhydrin, pentachlorethane, acetochlorhydrin, acetylene tetrachloride, ethyl chloracetate, acetone, ethyl acetate, diacetochlorhydrin.

3. U. S. P. 1015155. Other solvents used: Methyl alcohol, toluene, acetone, acetic ether, acetic acid, dichlorhydrin, glyceryl acetate, ether of lactic acid, acetochlorhydrin, camphor, primary aromatic amines, aromatic nitro compounds, phenol derivatives. U. S. P. 1015156. Other solvents used: Benzene, trichloraniline, phenol derivatives, acetone, acetic ether, acetic acid, dichlorhydrin, glyceryl acetate, ether of lactic acid, camphor, primary aromatic amines, secondary aromatic amines, aromatic sulfo compounds, aromatic nitro compounds. See F. P. 412797. Can. P. 129265. Aust. P. 47899. Swiss P. 51952, 52115.

4. D. R. P. 125392. For mfr. chlorhydrins, see H. Walker, U. S. P. 972953. K. McElroy, U. S. P. 1253615, 1253616, 1315229. W. Kirst, U. S. P. 1386118; abst. C. A. 1921, **15**, 3851. G. Curme, Jr., and C. Young, U. S. P. 1456916; abst. C. A. 1923, **17**, 2423; Chem. Age, 1923, **31**, 331. C. Young, U. S. P. 1456959; abst. C. A.

Propylene Chlorhydrin has been called to the attention of investigators by M. Seaton[1] as a desirable lacquer component, his preferred formula being cellulose acetate 8, propylene chlorhydrin and alcohol each 20, benzene 60. Butylene chlorhydrin and the acetate and benzoate have been described as cellulose acetate dissolvants[2]. Amylene chlorhydrin, amylenechlorhydrin acetate and amylenechlorhydrin benzoate also are claimed as efficient cellulose ester solvents.

Acetochlorhydrins. As a cellulose acetate solvent[3] or plasticizer[4], in celluloid substitute manufacture[5] and for paint and varnish removers[6], acetochlorhydrin (ethylene acetochlorhydrin), b. pt. 145°, has been found an excellent solvent with the cellulose esters, being insoluble in water. The R. Schüpphaus[7] and W. Lindsay[8] processes both utilize it. In the former method addressed to the nitrocelluloses, glyceryl benzoate, benzochlorhydrin, dichloracetin, benzomonoacetin, benzodiacetin, oleoacetin, oleodiacetin, dinitroacetin and mononitrodiacetin are specified as useful adjuncts. Acetodichlorhydrin, diacetochlorhydrin and monoacetomonochlorhydrin have been recommended as softeners and plastifying bodies for nitrocellulose[9]. Dinitromonochlorhydrin, mononitromonochlorhydrin, nitrodichlorhydrin

1923, **17**, 2423. B. Brooks, U. S. P. 1465595; abst. J. S. C. I. 1923, **42**, 998-A. B. Eldred and B. Brooks, U. S. P. 1465601; abst. J. S. C. I. 1923, **42**, 999-A. See E. P. 126311.

1. U. S. P. 1480016; abst. J. S. C. I. 1924, **43**, 213-B.
2. K. McElroy, U. S. P. 1315229. B. Eldred, U. S. P. 1408423.
3. W. Lindsay, U. S. P. 1244107, 1244108, 1244347, 1244348, 1244349, 1245476, 1386576.
4. *Ibid.* U. S. P. 1388472.
5. *Ibid.* U. S. P. 1245476, 1386576.
6. C. Ellis, U. S. P. 1172773; abst. C. A. 1916, **10**, 1104.
7. U. S. P. 598648. See U. S. P. 410208.
8. U. S. P. 1027618.
9. J. Goldsmith and British Xylonite Co., Ltd.; abst. Mon. Sci. 1902, (4), **58**, 163; J. S. C. I. 1901, **20**, 741. See U. S. P. 1015155, 1027486, 1199800, 1244107, 1244108, 1244347, 1244348, 1244349, 1245476, 1319229, 1386576, 1388472. See D. R. P. 125315.

in conjunction with aluminum stearate may be incorporated with nitrocellulose in explosive mixtures[1].

Ethylenethiohydrin and its esters have been recommended for incorporation with nitrocellulose and acetylcellulose on account of the unusual pliability of films produced therefrom[2], from 2-5 parts being used per weight of cellulose ester employed, auxiliary solvents as paraldehyde, amyl acetate and acetone being added. Ethylenethiohydrin from rapeseed oil has been specified.

Glycol Derivatives. *Glycol Ethers.* Whereas the glycols are but weak solvents of some of the cellulose esters and ethers except in conjunction with lower boiling solvents, the monoalkyl ethers have definite solvent properties. While they are in general, sluggish solvents of the cellulose ethers, their solvent capacity may be materially augmented by the inclusion of relatively small amounts of methyl and ethyl alcohols and acetates. As a class they appear to be permanent additions to the category of cellulose ether and cellulose ester solvents and colloidants. The monoether of ethylene glycol was the first member prepared of this ether-alcohol type, its boiling point (134.8°) being within the desired range, and it has proven such a powerful solvent for the nitrocelluloses that its permanency in the art seems assured. Diethylene oxide is the second ether of glycol, and is decomposed into acetaldehyde and glycol when heated with sulfuric acid. Ethylmethylene ether is obtained from trioxymethylene, ethylene glycol and ferric chloride.

The following data, taken from the work of J. Davidson[3] indicates the principal physical constants and solvent deportment of this class of bodies:

1. Westfälisch Anhaltische Sprengstoff A. G., F. P. 352750, 370132.
2. Farbwerke vorm. Meister Lucius & Brüning, D. R. P. 366115; abst. J. S. C. I. 1923, **42**, 348-A; Ann. Rep. S. C. I. 1923, **8**, 151; Kunst. 1923, **13**, 34, 70; Chem. Zentr. 1923, II, 539. See U. S. P. 1460097, 1460690.
3. Ind. Eng. Chem. 1926, **18**, 669.

Table XXIII. Physical Properties of Monoalkyl Ethers of Ethylene and Propylene Glycols

Monoalkyl Ether	Boiling point[a] °C.	Specific gravity 15°/15° C.	Refractive index (n_D) at 26° C.
Ethylene Glycol			
Methyl	124.5	0.9748	1.4004
Ethyl	134.8	0.9360	1.4042 (24° C.)
iso-Propyl	144.0	0.9139	1.4080
n-Propyl	150.0	0.9110	1.4125
iso-Butyl	158.8	0.9130	1.4135
n-Butyl	170.6	0.9188	1.4177
iso-Amyl	181.0	0.9000	1.4198
Propylene Glycol			
Methyl	122.8	0.9335	1.4035
Ethyl	133.0	0.9090	1.4061
iso-Propyl	141.5	0.8900	1.4062
n-Propyl	150.0	0.8970	1.4102
iso-Butyl	161.3	0.8810	1.4112
n-Butyl	170.6	0.8890	1.4151
iso-Amyl	183.3	0.8835	1.4182

[a] Boiling point of monoalkyl ethers of ethylene glycol at 743 mm. pressure, of propylene glycol at 736 mm.

Table XXIV. Dilution Ratios

Solvent	Toluene	Gasolene	Water
For Cellulose Nitrate			
Ethylene glycol monoethyl ether	6.25	1.50	0.35
Ethyl lactate	5.25	0.75	0.27
Propylene glycol monoethyl ether	5.00	1.00	0.30
Ethylene glycol monomethyl ether	4.75	0.50	0.25
Ethylene glycol monopropyl ether	4.25	1.75	0.35
Ethylene glycol mono*iso*propyl ether	4.25	1.50	0.32
Ethylene glycol monobutyl ether	4.00	2.25	0.375
Methyl lactate	4.00	0.25	0.25
Mesityl oxide	3.75	0.75	0.05
Diacetone alcohol	3.25	0.50	0.22
Ethylene glycol mono*iso*amyl ether	3.00	2.25	0.10
Ethylene glycol mono*iso*butyl ether	2.75	1.75	0.20
Butyl acetate	2.75	1.00	0.00
Propylene oxide	2.50	0.75	0.15
Butyl propionate	2.50	0.75	0.00
Secondary butyl acetate	2.00	1.00	0.00
Secondary amyl acetate	2.00	1.00	0.00
Secondary hexyl acetate	1.75	0.75	0.07
Glycol diacetate	1.75	0.25	0.10
Diethylene oxide	0.25	0.25	0.27
For Cellulose Acetate			
Ethylene glycol monomethyl ether	1.25	0.25	0.15
Ethyl lactate	1.25	0.25	0.15
Glycol diacetate	0.75	0.25	0.00

Several of the glycol ether-esters, as the acetates, have been found more powerful solvents for both cellulose acetate and the cellulose ethers, than have the simple glycol esters or ethers, or physical admixtures of glycol ether with glycol ester, a notable example being that of ethyleneglycol monoethyl ether over the corresponding acetic ester. The activity of the glycol esters as a rule is considerably increased by the addition thereto of alkyl alcohols or esters of comparatively low boiling point.

Dimethyl and diethyl ethers of ethylene and propylene glycols have been prepared and their comparative solvent efficiency studied. Diethylene glycol (*sym*-dihydroxydiethyl ether) is extremely hygroscopic, and therefore finds main application as a softener and conditioning agent, either in oil emulsion or in aqueous solution or suspension in connection with the treatment of artificial silk (see Chapter XIII), being an excellent solvent for leuco-compounds of vat dyestuffs. It is more viscous than ethylene glycol as determined by W. Rinkenbach[1].

A summation of the physical properties of the more commonly employed polyglycols and their ethyl ethers is indicated in Table XXV.

J. Davidson[2] has described polyolefine glycol ethers as *b*-hydroxy-*b*-ethoxyethyl ether, b. pt. 190° as desirable cellulose ester and ether solvents, including ethyleneglycol monoethyl and monobutyl ethers[3]. J. Kessler and O. Helfrich[4] have described a series of plasticizing agents for cellulose ethers and esters, embracing the methyl, ethyl, propyl, butyl and amyl ethers of diethyleneglycol, triethyleneglycol, dipropyleneglycol and ethylenepropylene diglycol, these twenty compounds being used either in the original state or esters prepared therefrom by coupling with capric,

1. Ind. Eng. Chem. 1927, **19**, 474.
2. U. S. P. 1633927; abst. J. S. C. I. 1927, **46**, 859-B.
3. J. Davidson, U. S. P. 1644417, 1644418, 1644419, 1644420; abst. C. A. 1927, **21**, 4068; J. S. C. I. 1927, **46**, 852-B; Plastics, 1927, **3**, 674. E. P. 238485; J. S. C. I. 1925, **44**, 857-B.
4. U. S. P. 1739315; abst. C. A. 1930, **24**, 862.

caproic, lauric, palmitic, stearic, oleic, linoleic or ricinoleic acids, thus constituting a group of 160 ester-ether bodies with an almost unlimited range of boiling points and speeds of evaporation.

Table XXV. Physical Properties of Some Polyglycols and Their Ethyl Ether Derivatives

Compound	Boiling point (760 mm.) ° C.	Specific gravity 15°/15° C.	Refractive index (n_D) at 26°C.
Diethylene glycol	245	1.132 (0° C.)	
Triethylene glycol	276	1.138	
Tetraethylene glycol	230 (25 mm.)		
Diethylene glycol monoethyl ether	198	0.9996	1.4240
Triethylene glycol monoethyl ether	248	1.0566	1.4389
Tetraethylene glycol monoethyl ether (approx.)	284	1.4389	1.4499

The coating composition of W. Jenkins and Imperial Chemical Industries, Ltd.[1], comprehends the methyl, ethyl, propyl, butyl and amyl ethers of butylene glycols, especially of *iso*butylene glycol as nitrocellulose dissolvants, particularly for coating lacquers and enamels, while S. Shipley and G. Given[2] include the methyl, *n*- and *iso*-propyl and the butyl and amyl ethers of ethylene glycol.

The I. G. Farbenindustrie have evolved a series of processes for cellulose ether solvent compositions, including the use of ethyleneglycol monoethyl ether with tetrahydrofurfuryl alcohol[3]; dimethyl, diethyl and dipropyl ethers of ethylene or propylene or butylene glycol[4]; methyl, ethyl, propyl or butyl monoalkyl ethers of ethyleneglycol, pro-

1. E. P. 307085; abst. C. A. 1929, **23**, 5317; J. S. C. I. 1929, **48**, 366-B.
2. E. P. 250894; abst. C. A. 1927, **21**, 1364.
3. E. I. du Pont de Nemours, E. P. 312309; abst. C. A. 1930, **24**, 960; J. S. C. I. 1931, **50**, 16-B; Chem. Zentr. 1929, II, 3199; Brit. Plastics, 1931, **2**, #21, 432. Can. P. 308108; abst. C. A. 1931, **25**, 1379.
4. I. G. Farbenindustrie A.-G., E. P. 256229; abst. J. S. C. I. 1928, **47**, 237-B.

Table XXVI. Solubility of Various Solvents on Cellulose Nitrate and Acetate, Resins, Gums, and Common Diluents

	Water	Cellulose nitrate	Cellulose acetate	Linseed oil	Gasoline	Kerosene	Toluene	Benzene	Shellac	Gum kauri	Gum copal	Gum sanderac	Gum mastic	Gum guaiac	Gum dammar	Gum camphor	Gum cumarone	Gum zanzibar	Gum elemi	Japan wax	Rosin "G"	Ester gum
Amyl acetate	i	s	i	s	s	s	s	ss	ss	s	s	s	s	ss	p	s	s	s	s	i	s	s
Amyl alcohol	ss	i	i	s	s	s	s	s	i	s	s	s	s	i	p	s	s	s	ss	i	s	s
Butyl acetate	i	s	i	s	s	s	s	s	i	ss	ss	i	s	i	s	s	s	s	s	i	s	s
Butyl alcohol	ss	i	i	s	s	s	s	s	i	s	s	s	s	i	p	s	s	s	ss	i	s	s
Butyl butyrate	i	s	i	s	s	s	s	s	i	ss	s	i	s	i	s	s	s	s	s	i	s	s
Glycol ether acetate	ss	s	i	s	s	s	s	s	s	s	s	ss	s	ss	p	s	s	s	ss	i	s	s
Diacetone alcohol	s	s	i	s	i	i	s	s	s	s	s	s	s	ss	i	s	ss	ss	ss	i	s	ss
Dichloroethyl ether	i	i	s	s	s	s	s	s	i	i	s	s	s	ss	i	s	s	s	ss	i	s	s
Ethyl acetate	ss	s	s	s	s	s	s	s	s	s	s	s	s	ss	ss	s	s	s	s	i	s	s
Ethyl alcohol	s	i	i	i	i	i	s	s	s	ss	ss	s	s	i	p	s	s	i	ss	i	i	i
Ether	i	s	i	s	s	s	s	s	ss	ss	s	s	s	ss	s	s	s	ss	s	i	s	s
Ethers of ethylene glycol:																						
Methyl	s	s	s	i	s	i	s	s	s	s	g	s	s	s	p	s	i	ss	s	s	s	ss
Ethyl	s	s	i	s	s	s	s	s	s	s	g	s	s	ss	p	s	s	ss	s	i	s	ss
Diethyl	ss	s	i	s	s	s	s	s	s	s	g	i	s	s	s	s	s	s	s	i	s	s
Propyl	s	s	i	i	s	s	s	s	s	s	g	s	s	s	p	s	s	ss	s	i	s	s
Isopropyl	s	s	i	s	s	s	s	s	s	s	g	s	s	s	p	s	s	ss	s	i	s	s
Butyl	ss	s	i	s	s	s	s	s	s	s	g	s	s	s	p	s	s	ss	s	i	s	s
Isobutyl	ss	s	i	s	s	s	s	s	ss	s	g	s	s	s	p	s	s	ss	s	i	s	s
Isoamyl	ss	s	i	s	s	s	s	s	ss	s	g	s	s	s	p	s	s	ss	s	i	s	s
Ethers of propylene glycol:																						
Ethyl	s	s	i	s	s	s	s	s	s	s	g	s	s	ss	p	s	s	ss	s	i	s	s
Methyl	s	s	i	s	s	s	s	s	s	s	g	s	s	ss	p	s	s	ss	s	i	s	s
Isopropyl	s	s	i	s	s	s	s	s	s	s	g	s	s	ss	p	s	s	ss	s	i	s	s
Glycol diacetate	i	s	s	i	i	i	s	s	i	i	i	i	s	i	i	s	i	i	s	i	s	i
Diethylene oxide	s	s	i	s	s	s	s	s	s	s	g	s	s	s	p	s	s	ss				
Isopropyl acetate	ss	s	i	s	s	s	s	ss	s	s	g	s	s	s	p	s	s	ss	s	ss	s	s
Propylene oxide	s	s	s	s	s	s	s	s	s	s	ss	s	s	s	p	s	s	ss	s	i	s	s
Ethylene oxide	s	s	s	s	s	s	s	s	s	s	i	s	s	s	p	s	s	ss	s	i	s	s
Butyl propionate	i	s	i	s	s	s	s	s	i	ss	i	i	s	ss	s	s	s	i	s	i	s	s
Glycol monoacetate	s	s	s	i	i	i	s	s	i	i	i	i	ss	ss	i	s	s	i	s	i	s	i
Diethylene glycol monoacetate	s	s	s	i	i	i	s	s	i	ss	i	i	ss	ss	p	s	ss	i	ss	i	s	i
Diethylene glycol	s	s	i	i	i	i	ss	s	i	i	i	i	ss	ss	i	s	i	i	i	i	ss	i
Triethylene glycol	s	s	i	i	i	i	s	s	i	i	i	i	ss	ss	i	s	i	i	i	i	ss	i
Tetraethylene glycol	s	s	i	i	i	i	s	s	i	i	i	i	ss	ss	i	s	i	i	i	i	ss	i
Ethyl ether of:																						
Diethylene glycol	s	s	i	s	s	s	s	s	s	s	g	s	s	ss	p	s	s	ss	s	i	s	ss
Triethylene glycol	s	s	i	i	i	i	s	s	ss	s	g	s	s	ss	p	s	s	ss	s	i	s	ss
Tetraethylene glycol	s	s	i	i	i	i	s	s	i	ss	g	s	s	ss	p	s	ss	i	s	i	s	i
Butyl ether of diethylene glycol	s	s	i	s	s	s	s	s	ss	s	g	s	s	ss	p	s	s	ss	s	i	s	s

Key s — Soluble ss — Slightly soluble p — Partially soluble g — Swells i — Insoluble

pyleneglycol and butyleneglycol[1]; or hexyl ethers in combination with methyl, ethyl, *iso*propyl, butyl or amyl ethers of ethylene, propylene or butylene glycols[2]. In the production of colored lacquers[3], cellulose ethers or esters are dissolved in glycol monoalkyl or glycol dialkyl ethers in association with benzene, toluene, xylene or tetrahydronaphthalene. Nitrocellulose with butyl alcohol, a glycol ether and butyl phthalate[4]; or with methyl, ethyl and propyl ethers of monopropylene glycol and dipropylene glycol forms the essence of another described process[5].

Ethyleneglycol Monomethyl Ether. Methylglycol[6] is a stable, colorless, limpid liquid, possessing a bland odor. Miscible both with water and paraffins, benzene, toluene and xylene. Methyl, ethyl, propyl, butyl and amyl glycols in conjunction with gasolene, benzene, toluene, xylene, ethyl lactate and ethyl carbonate[7]; methylglycol with benzene and/or ethyl alcohol[8] and methylglycol or ethylglycol with methyl alcohol or acetate, comprise the ethylcellulose sol-

1. I. G. Farbenindustrie, E. P. 252203; abst. J. S. C. I. 1927, **46**, 340-B. Can. P. 285360.

2. *Ibid.* E. P. 245129; abst. C. A. 1927, **21**, 292. E. P. 251303; abst. J. S. C. I. 1928, **47**, 155-B; Chem. Zentr. 1928, I, 1824; Kunst. 1929, **19**, 90. E. P. 252203; abst. C. A. 1927, **21**, 1556; J. S. C. I. 1927, **46**, 340-B. Can. P. 285360; abst. C. A. 1929, **23**, 704; Plastics, 1929, **5**, 638.

3. *Ibid.* E. P. 294158; abst. C. A. 1929, **23**, 2050. See E. P. 293485; abst. C. A. 1929, **23**, 1749. E. P. 247288; abst. C. A. 1927, **21**, 649.

4. *Ibid.* E. P. 333304; abst. C. A. 1931, **25**, 566.

5. Carbide & Carbon Chemicals Corp., E. P. 255406; abst. J. S. C. I. 1927, **46**, 428-B.

6. There appears considerable confusion in the patent literature as to the designation of methyl glycol, ethyl glycol and propyl glycol, i.e., as to whether "methyl glycol," for instance, should be properly applied to ethyleneglycol monomethyl ether, $CH_2.CH.CH_2.O.CH_3 = C_3H_8O_2$, or propylene glycol, $CH_3.CH(OH).CH_2OH = C_3H_8O_2$, the former being an ether, and the latter an alcohol. The patent context is non-explanatory.

7. S. Shipley and G. Given, U. S. P. 1618481, 1618482, 1618483, 1618484; abst. C. A. 1927, **21**, 1194; Plastics, 1927, **3**, #6, 278, 279. See U. S. P. 1533616. E. P. 236190.

8. I. G. Farbenindustrie, A.-G., E. P. 251303; abst. C. A. 1927, **21**, 1320; J. S. C. I. 1928, **47**, 155-B. E. P. 278735; abst. C. A. 1928, **22**, 2663; J. S. C. I. 1928, **47**, 155-B; Chem. Zentr. 1928, I, 1824; Kunst. 1929, **19**, 113; Plastics, 1928, **4**, 509.

vent mixture of S. Carroll[1]. As cellulose ester solvents in the presence of auxiliary dissolving bodies, have been detailed the applicability of the monomethyl, dimethyl, monoethyl, diethyl, monopropyl, dipropyl, monoallyl and di*iso*-butyl ethers of ethylene glycol[2], the solvent avidity being augmented by the presence of relatively smaller amounts of ethylenechlorhydrin, diacetone alcohol, ethylene dichloride or tetrachlorethane. The H. Finkelstein nitrocellulose brushing lacquer is composed of ethyleneglycol butyl ether with methyl or ethyl alcohols[3].

Ethyleneglycol Monoethyl Ether. Ethylglycol, probably the most important solvent of this class, is a colorless, nearly odorless liquid, b. pt. 135°, sp. gr. 0.934-0.938, miscible with water and hydrocarbons in all proportions, a solvent of cellulose nitrate in the cold, of cellulose acetate by heating or with the addition of small amounts of active solvents, and dissolves methyl-, ethyl- and benzyl-cellulose of higher etherification. Probably innocuous, dissolving benzyl abietate, dammar, elemi, sandarac and mastic. Known commercially as "Solvulose" and "Cellosolve." It has been used to increase the softness and pliability of cellulose ester and ether masses[4]; in combination with nitrocellulose[5]; as a pyroxylin solvent with petroleum hydrocarbons[6]; in combination with cresyl phosphate and benzene[7] and with propyl glycol; and in inks for printing upon nitrocellulose picture films[8]. A solution of celluloid

1. U. S. P. 1735157; abst. C. A. 1930, **24**, 723.
2. J. Davidson, U. S. P. 1644417, 1644418, 1644419, 1644420; abst. C. A. 1927, **21**, 4068; J. S. C. I. 1927, **46**, 852-B; Plastics, 1927, **3**, 674. See E. P. 238485; abst. C. A. 1926, **20**, 2073; J. S. C. I. 1925, **44**, 857-B; Chem. Zentr. 1926, I, 1076. F. P. 605085; abst. Caout. et Gutta. 1927, **24**, 13242. Can. P. 260464.
3. H. Finkelstein, U. S. P. 1818547; abst. C. A. 1931, **25**, 5584.
4. Farbwerke vorm. Meister Lucius & Brüning, D. R. P. 372545, Addn. to 369445. D. R. P. 372546, Addn. to D. R. P. 366115; abst. Kunst. 1923, **13**, 70; Chem. Ztg. 1923, **47**, 218.
5. J. Davidson, U. S. P. 1644420; abst. C. A. 1927, **21**, 4068.
6. S. Shipley, U. S. P. 1692584; abst. British Plastics, 1929, **1**, #3, 114.
7. I. G. Farbenindustrie A.-G., Swiss P. 133200. See Swiss P. 113741.
8. E. Middleton, U. S. P. 1833086; abst. Chem. Zentr. 1932, I, 1044.

in ethylglycol has been patented as a preservative coating for eggs[1], and in conjunction with nitrocellulose, acetone and benzene[2] as a lacquer. Lacquers have been described combining the cellulose ethers with ethylglycol, ethyl lactate and methyl acetate[3], or cellulose ethers with ethylglycol, and butyl or amyl acetates for the production of colored plastics and solutions[4]. For the W. Mendel marking paper[5] a mixture of ethylglycol and carbon tetrachloride has been recommended; and the J. Davidson pyroxylin lacquer vehicle combines ethylglycol or ethylglycol acetate with ethyl alcohol and acetate, to which toluene and xylene may be added[6].

H. Hopkins and J. Segur[7] prepare cellulose ether compositions by combining a solvent of limited dissolving power with one of ordinary dissolving function to either lower the viscosity of the cellulose ether solution or to maintain the viscosity at a relatively low standard. For instance, an ethylcellulose soluble in butyl alcohol but insoluble in gasolene, is prepared of 8% strength in butyl alcohol. To this solution 33% gasolene is added, when the viscosity falls from 2.75 to 1.44 poises. If an 8% ethylcellulose in butyl alcohol 33, benzine 67 be made, it is found that the alcohol-benzine has combined solvent power in excess of the sum of the separate solvent powers. In a composition of ethylcellulose 25, ethylglycol and gasolene 50 each, the alcohol and gasolene solvents have a distinctly higher dispersing power than the sum total of the dispersing powers of the

1. A. Stewart and Farma Cream Product Co., Ltd., E. P. 311877; abst. C. A. 1930, **24**, 901; British Plastics, 1929, **1**, #3, 113.
2. J. Davidson and Carbide & Carbon Chemicals Corp., E. P. 238485; abst. J. S. C. I. 1925, **44**, 857-B. E. P. 289373; abst. C. A. 1929, **23**, 722; J. S. C. I. 1929, **48**, 530-B. Can. P. 281640; abst. C. A. 1928, **22**, 3056.
3. Imperial Chemical Industries, Ltd., and B. Foster, E. P. 331837; abst. C. A. 1931, **25**, 223.
4. C. Immerheiser and E. Knebel, U. S. P. 1830944; abst. Plastics, 1932, **8**, #2, 88. M. Hagedorn, Can. P. 304220.
5. U. S. P. 1769592; abst. C. A. 1930, **24**, 4636.
6. J. Davidson, E. P. 289373; abst. C. A. 1929, **23**, 722; J. S. C. I. 1929, **48**, 530-B.
7. U. S. P. 1855744.

solvents taken individually. In a heavy lacquer composed of ethylcellulose 10, rosin ester 5, blown linseed oil 10, butyl lactate 2, drier 1, butyl alcohol 18.5 and gasolene 55.5, the alcohol and gasolene have a combined solvent power greatly in excess of the sum of the dissolving power of the two liquids, gasolene being substantially a non-solvent.

Ethylene Glycol Diethyl Ether is a colorless, limpid liquid of faint and not disagreeable odor, b. pt. 121°, sp. gr. 0.853. It readily dissolves nitrocellulose, is a feeble solvent for acetated cellulose, and dissolves the cellulose ethers, especially in the presence of a small amount of methyl alcohol and/or ethyl acetate. Partially miscible with water.

The Carbide & Carbon Chemical Corp.[1] prepare cellulose esters with the aid of monomethyl, dimethyl, ethyl and propyl glycol ethers, monoallyl ether or di*iso*butyl ether of ethylene glycol conjointly with glycol monoacetate or diacetate, diacetone alcohol, benzene or acetone. On the other hand, the I. G. Farbenindustrie[2] employ ethylene, propylene or butylene glycol without the addition of other bodies, as cellulose ester solvents. The S. Shipley formula[3] involves the use of ethyleneglycol diethyl ether.

Propylene Glycol Ethers. J. Davidson[4] has described cellulose ether solvents of this class embodying monomethyl, diethyl and monophenyl ethers of propylene glycol, the b. pts. of the monoethers of propylene glycol being, methyl, 122.8°; ethyl, 133°; *iso*propyl, 141.5°; *n*-propyl, 150°; *iso*-butyl, 161.3°; *n*-butyl, 170.6° and *iso*amyl propylene glycol, 183.3°. Di-, tri-, tetra- and penta-propylene glycols are also included. They are used preferably in conjunction with aromatic hydrocarbons. In another patented process[5],

1. U. S. P. 1644417. E. P. 238485. F. P. 596838. Can. P. 260463.
2. E. P. 245129, 256229.
3. U. S. P. 1533616, 1618481. E. P. 250894. F. P. 600178. Can. P. 262784.
4. U. S. P. 1730061; abst. C. A. 1929, **23**, 5474. E. P. 255406; abst. C. A. 1927, **21**, 2798; J. S. C. I. 1927, **46**, 428-B; Chem. Zentr. 1927, I, 381. Belg. P. 325254. Can. P. 260463, 260464, 260466, 268571; abst. C. A. 1926, **20**, 3567; 1927, **21**, 2384, 2798.
5. H. Finkelstein, U. S. P. 1812145; abst. Chem. Zentr. 1932, I, 3506. D. R. P. 545172; abst. C. A. 1932, **26**, 3125.

methyl, ethyl, propyl, *iso*propyl, butyl, *iso*butyl, amyl or *iso*amyl ethers of propylene glycol are combined with cellulose esters in the presence of such diluents as benzene, toluene, xylene and benzine.

Ethylene Glycol Mono-n-butyl Ether, Hydroxyethyl-mono-*n*-butyl ether, Butylcellosolve, boils at about 171°, sp. gr. 0.92, a good solvent for cellulose nitrate and some types of cellulose ethers, but sluggish in its action due to the high boiling point and relatively low volatality. It reduces the viscosity of lacquers in which it is incorporated.

Diethylene Glycol Monoethyl Ether, is an excellent plasticizer for cellulose ester compositions[1]. E. I. du Pont de Nemours Co.[2] have described acetals of the ethyl (or butyl) ether of diethylene glycol as cellulose ether plasticizing bodies, their invention being indicated in scope by the following examples:

1. Benzylcellulose 10 parts by weight, acetal of the ethyl ether of diethylene glycol 2, toluene-butyl alcohol 1:1, 88, this combination producing a composition yielding a clear and pellucid film.

2. Ethylcellulose 10, acetal of the ethyl ether of diethylene glycol 3, benzene-toluene 1:1, 87, the results being similar to the example preceding. This acetal has b. pt. 140-145° at 14 mm.

The I. G. Farbenindustrie[3] have discussed the advantages of the use of methylglycol, ethylglycol, *iso*propylglycol, butylglycol and amylglycol as a solvent for fats and waxes. A. Sulzer[4] has described as desirable cellulose ether and ester gelatinants, phosphoric acid esters of diethyleneglycol monomethyl (ethyl, propyl, butyl or amyl) ether, tri-

1. J. Davidson, U. S. P. 1633927. U. S. P. 1770153; abst. Chem. Zentr. 1930, II, 2332; British Plastics, 1931, **3**, #25, 37.

2. E. P. 318980; abst. C. A. 1930, **24**, 2599; J. S. C. I. 1931, **50**, 685-B; Brit. Plastics, 1931, **3**, #30, 268. W. Lawson and Imperial Chemical Industries, Ltd., U. S. P. 1824961; abst. C. A. 1932, **26**, 304; J. S. C. I. 1932, **51**, 614-B. Can. P. 312570; abst. C. A. 1931, **25**, 4403. See E. P. 316325.

3. E. P. 245129; abst. C. A. 1927, **21**, 292; Chem. Zentr. 1928, II, 190. F. P. 606763.

4. U. S. P. 1826681.

ethyleneglycol monomethyl(ethyl, propyl, butyl or amyl) ether, and tetraethyleneglycol monomethyl(ethyl, propyl, butyl or amyl) ether, monoethyl ether of tetraethyleneglycol dihydrogen phosphate being designated as especially useful.

Polyethyleneglycol monoethyl ether acetates and benzoates, b. pt. 315-355° and 290-340° respectively, have been patented by O. Loehr as cellulose acetate solvents, preferably in conjunction with butyl acetate, alcohol and benzene. Diethyleneglycol benzoate and acetate and diethyleneglycol monoethyl ether benzoate and acetate have been particularly specified[1]. As a pyroxylin spraying lacquer, methyl, ethyl, propyl and butyl ethers of ethyleneglycol are recommended[2].

Diethyleneglycol monoethyl ether, Carbitol, Hydroxyethoxydiethyl ether, is miscible with water in all proportions and, like glycerol, is hygroscopic.

Hydroxyethoxydiethyl ether acetate is a good solvent for cellulose acetate, and the corresponding salicylate and phthalate an excellent nitrocellulose plasticizer.

Diethylene Glycol Mono-n-butyl Ether, Hydroxybutyloxyethyl Ether, Butyl Carbitol, is a colorless liquid of bland odor, b. pt. 170-220° for the commercial product, sp. gr. 0.97 at 20°, and dissolves both the cellulose acetates and certain types of the cellulose ethers. Although miscible with water, it combines with castor and linseed oils and the aromatic hydrocarbons. The lacquer composition of O. Jordan[3] utilizes dialkyl ethers of propylene glycol, such as propyleneglycol mono*iso*propyl ether, propyleneglycol diethyl ether and ethyleneglycol diethyl ether with low boiling solvents.

Trimethyleneglycol monomethyl ether, b. pt. 160-161°,

1. O. Loehr, U. S. P. 1865196; abst. C. A. 1932, **26**, 4487.
2. I. G. Farbenindustrie, A.-G., Can. P. 294724.
3. U. S. P. 1589700, 1865191. For mfr. of glycol ethers, see: J. Davidson, U. S. P. 1614883, 1633927. J. Nieuwland, U. S. P. 1824963. I. G. Farbenindustrie, A.-G., E. P. 256229, 354357. J. Davidson, Belg. P. 329319. I. G. Farbenindustrie, A.-G., Belg. P. 377429. Chemische Fabriken vorm. Weiler-ter-Meer, Can. P. 262404. Carbide and Carbon Chemicals Corporation, Can. P. 267104.

which may be made by the action of sodium ethylate on monochlorpropyl alcohol, although relatively high in boiling point, should prove a useful addition to the cellulose ether compositions in conjunction with low boiling solvents, where high speed of evaporation is not required.

Pinacone diacetate (tetramethylethyleneglycol diacetate)[1], and diethyleneglycol[2] have also been put forward.

Polyhydric Aliphatic Alcohols. Glycerol, Glycerine, is a weak solvent for the cellulose esters and ethers, and is soluble in water, but has been used to a limited extent on account of its emollient properties. It is distinctly hygroscopic. In printing pastes with nitro- and acetyl-cellulose it has been used to some extent[3]. The P. Hewitt varnish is formed of 70% acetylcellulose, 10% glycerol and 20% acetic acid[4], while the American Cellulose & Chemical Manufacturing Co.[5] heat the cellulose acetate with glycerol and then remove excess by washing with water. In the production of photographic films glycerol has been used extensively[6], usually as a softening agent or to minimize curling of the film. A plastic of cellulose acetate and glycerol has been patented[7].

Compounds of polyatomic alcohols as glycerol, erythrite, pentaerythrite and sorbite when heated with ethylene oxide in the presence of boric acid, give rise to ether-alcohols[8], said to be useful cellulose ether and ester solvents

1. F. Bayer & Co., D. R. P. 327128; abst. Kunst. 1921, **11**, 13.
2. D. Keyes, Ind. Eng. Chem. 1925, **17**, 1120.
3. U. S. P. 102798, 112370, 417284, 461272, 587211, 651364, 893987, 904269, 928235, 952724, 1011181, 1140174. E. P. 1208, 1871; 2484, 1878; 959, 1866, 1879; 5974, 1883; 2694, 1887; 17747, 1894; 17717, 24790, 1896; 7676, 1900; 12277, 1905; 4577, 1906; 1715, 1908; 4154, 26657, 1909; 14293, 1910; 13239, 16271, 25449, 27969, 1911; 1378, 23728, 1912; 12091, 1915. F. P. 319926, 339081, 351555, 354942, 364690, 377039, 402028.
4. U. S. P. 1188776, 1188777; abst. C. A. 1916, **10**, 2157; J. S. C. I. 1916, **35**, 898; Mon. Sci. 1917, **84**, 60. See U. S. P. 907598.
5. E. P. 190269; abst. Chem. Ztg. 1923, **47**, 73.
6. U. S. P. 1184772, 1415059, 1431900, 1432368, 1434453, 1434454, 1441185, 1494479.
7. T. Cathelineau and A. Fleury, D. R. P. 185240, 185241.
8. I. G. Farbenindustrie, A.-G., F. P. 650973; abst. Chem. Zentr. 1929, I, 2580. F. P. 698392.

and softeners. Glycolmethyl, glycoldimethyl and glycoltrimethyl ethers in the presence of camphor, urea and nitrocellulose, constitute the embodiment of the G. Rocker and E. Middleton[1] invention for a highly elastic varnish. Alkyl ethers of glycerolchlorhydrin as methyl- or ethyl-glyceryl chlorhydrins or methylene chlorhydrin also exercise a dissolving effect upon cellulose ethers[2]. G. Racky[3] has drawn attention to the desirability of using monobenzoyldiacetylglycerol which is colorless and insoluble in water, as an acetylcellulose gelatinizer. Glyceryl benzoate, glyceryl acetate, glycerylacetobenzoate and glyceryl diacetomonophenylacetate produce an analogous effect.

Glycerol with denatured alcohol forms the starch acetate solvent of E. Pitman[4]. Nitro*iso*butylglycerol trinitrate as a softener[5], and small amounts of nitroglycerol (glyceryl trinitrate) as a solvent have also been put forward as desirable adjuncts in cellulose ester solutions[6]. Methyleneglycerol, cineol, pinol, glycid, glycid acetate, ethylglycid ether, methylene-ethylene ether, glycerylmonochlorhydrinformol, erythritediformal, adonitediformal, rhamnitediformal, mannitetriformal, ethylideneglycol ether, ethylidenepropylene ether, ethylidenetrimethylene ether, acetoneglycerol, diacetone erythrite, diacetone arabite, diacetone mannite, triacetone mannite and benzylideneglycerol[7] are some of the organic cyclic oxide bodies which have been described

1. U. S. P. 1868851. E. I. du Pont de Nemours Co. (E. P. 287940; abst. C. A. 1929, **23**, 532) have described methods of coating metallic surfaces and the preparation of lacquers, a preliminary coating of glycerol and phthalic acid with vegetable oils is first formed, upon which is applied a cellulose ether or ester composition, and W. Moss (U. S. P. 1878249) the manufacture of synthetic resins for incorporation with the cellulose ethers from condensing diphenylolpropane (acetone phenol) with acetone.

2. Chemische Fabrik von Heyden Akt.-Ges., D. R. P. 288267; abst. J. S. C. I. 1916, **35**, 356. A. Verley, Bull. Soc. Chim. 1899, (3), **21**, 275.

3. D. R. P. 402752; abst. J. S. C. I. 1925, **44**, 68-B.

4. U. S. P. 1570079.

5. F. Matthews, E. P. 6447, 1914; abst. J. S. C. I. 1915, **34**, 453.

6. H. Lüttke, E. P. 24955, 1902; abst. J. S. C. I. 1903, **22**, 318. See F. P. 325548; abst. J. S. C. I. 1903, **22**, 760.

7. L. Ach, U. S. P. 996191. C. F. Boehringer and Soehne, D. R. P. 214962.

as desirable colloidants for nitrocellulose. Glyceryl ether oxide[1], *iso*propylideneglycerol[2], trichlorethylidene glycerol[3], acetone glycerol[4] and glycidol and diethylglyceryl ether[5] have been described.

The I. G. Farbenindustrie[6] have described a series of compounds obtained from sorbitol and mannitol by the splitting therefrom of one or two molecules of water, which are stated to be excellent gelatinizing and plasticizing bodies for cellulose ethers and esters. Mono- and dianhydro-sorbitol and -mannitol are formed.

Phenol, Carbolic Acid, has been used in comparatively small amounts for a number of years as a solvent for pyroxylin[7], alone or in combination with creosote[8], as a softener[9] and solvent for acetylcellulose[10], and as a solvent in combination with acetone[11], trichlorethylene[12], or for the production of plastic cellulose bodies[13]. Casein and nitrocellulose may be combined by the interposition of the mutually harmonious solvent phenol[14], but there are acetone-soluble cellulose acetates which dissolve but partially or

1. Compagnie Generale Phonographie Cinematographic Appareils de Precision, Swiss P. 61929; abst. C. A. 1914, **8**, 2124; Kunst. 1914, **4**, 98.
2. H. Hibbert and J. Morazain, Can. J. Research, 1930, **2**, 214.
3. H. Hibbert, J. Morazain and A. Paquet, Can. J. Research, 1930, **2**, 131.
4. H. Hibbert and J. Morazain, Can. J. Research, 1930, **2**, 35.
5. D. Keyes, Ind. Eng. Chem. 1925, **17**, 1120.
6. E. P. 301655; abst. C. A. 1929, **23**, 4282; J. S. C. I. 1929, **48**, 123-B; Chem. Zentr. 1929, I, 1506.
7. N. Hart and R. Bacon, U. S. P. 233851. E. P. 4874, 1880.
8. C. Jacob, U. S. P. 234675.
9. H. Mork, A. Little and W. Walker, U. S. P. 712200; abst. Mon. Sci. 1903, **60**, 165.
10. E. Knoevenagel, U. S. P. 979966; abst. J. S. C. I. 1911, **30**, 206. F. P. 383636; abst. J. S. C. I. 1908, **27**, 332.
11. L. Lederer, U. S. P. 774677; abst. J. S. C. I. 1904, **23**, 1159. E. P. 7088, 1902; abst. J. S. C. I. 1903, **22**, 563. F. P. 319724.
12. G. Koller, U. S. P. 1079773; abst. J. S. C. I. 1913, **32**, 1153. E. P. 4744, 1911; abst. C. A. 1912, **6**, 2315. F. P. 440133; abst. J. S. C. I. 1912, **31**, 680.
13. R. Balston and J. Briggs, E. P. 10243, 1903; abst. J. S. C. I. 1904, **23**, 557. L. Lederer, E. P. 8945, 1909; abst. J. S. C. I. 1909, **28**, 1271. H. Reeser, E. P. 12976, 1909; abst. J. S. C. I. 1910, **29**, 147. A. Eichengrün, E. P. 27258, 1910; abst. J. S. C. I. 1911, **30**, 1112.
14. H. Cathelineau and A. Fleury, D. R. P. 185240, 185241; abst. Chem. Zentr. 1907, II, 1819; Mon. Sci. 1910, (4), **72**, 76.

completely in phenol, usually with the application of a moderate degree of heat[1].

The cellulose ether composition of S. Carroll[2] may be prepared by mixing phenol with methyl or ethyl alcohols, water-insoluble ethylcellulose dissolving therein to transparent flowable solutions. L. Lederer has described corneous products obtained by plasticizing acetylcellulose by phenol aided by heat and pressure[3], and L. Wilson[4] detailed methods for forming a cement composition known as "plastic enamel," in which cellulose ethers are combined with phenol, aniline, nitrobenzene and low boiling solvents. The C. Mijnssen film process[5] involves the use of phenol as a cellulose acetate softening agent[6]. Celluloid is readily dissolvable in phenol[7]. Trichlorphenol with tricresyl phosphate has been advocated as an efficient acetylcellulose solvent[8]. The toxicity and escharotic nature of phenol has minimized the use of what otherwise is an excellent solvent.

Polyhydric Phenols. Cresol and the cresols[9] have been advocated as cellulose acetate plastifiants, and hexahydro-*o*-cresol for gelatinizing pyroxylin[10]. Creosote from Norway tar or beech tar[11], creosote with aliphatic alcohols[12], and hexahydrophenol with diacetone alcohol and ethyl acetate are combinations which dissolve highly

1. Societe Anonyme d'Explosifs et de Produits Chimiques, F. P. 385179; abst. C. A. 1909, **3**, 2383; Mon. Sci. 1909, (4), **70**, 105.
2. U. S. P. 1434426; abst. C. A. 1923, **17**, 467; Chem. Zentr. 1923, II, 643; Caout. et Gutta. 1923, **20**, 11931.
3. L. Lederer, D. R. P. 151918; abst. Chem. Zentr. 1904, II, 1180.
4. U. S. P. 1389084; abst. C. A. 1922, **16**, 150; Chem. Zentr. 1921, IV, 1261.
5. F. P. 411298; abst. J. S. C. I. 1910, **29**, 978.
6. E. Thomson and J. Callan, U. S. P. 695127. W. Walker, U. S. P. 774713; abst. J. S. C. I. 1904, **23**, 1159.
7. L. Wilson, U. S. P. 1389084; abst. C. A. 1922, **16**, 145.
8. W. Lindsay, E. P. 10794, 1910; abst. J. S. C. I. 1911, **30**, 679.
9. W. Walker, U. S. P. 774713, 774714; abst. J. S. C. I. 1904, **23**, 1159. H. Mork, W. Walker and A. Little, U. S. P. 792149; abst. J. S. C. I. 1905, **24**, 799. Societe Anonyme D'Explosifs et de Produits Chimiques, F. P. 385179; abst. C. A. 1909, **3**, 2383. H. Dreyfus, F. P. 432264; abst. J. S. C. I. 1912, **31**, 24.
10. F. Raschig, U. S. P. 900204; abst. J. S. C. I. 1908, **27**, 1082.
11. C. Jacob, U. S. P. 234675. See U. S. P. 190865.
12. H. Cathelineau and A. Fleury, D. R. P. 185240; abst. Chem. Zentr. 1907, II, 1037.

etherified ethylcellulose[1]. *p-ter*-Butylphenol, a crystalline solid of distinctive odor, m. pt. 98°, b. pt. 236-238°, readily plasticizes acetyl-, ethyl- and benzylcellulose. Abracol is *ter*-butylcresol.

The di-hydric alcohol resorcinol[2] as a solvent for cellulose formate or nitrocellulose[3], in connection with pyrogallol, naphthol, amidophenol or saligenin. Ethylidenediphenol[4] has a high solvent power for both nitrocellulose and cellulose acetate, and phloroglucinol when dissolved in alcohol or acetone, dissolves celluloid and the cellulose ethers in the cold[5]. Resorcinol with alcohol as an acetylcellulose dissolvant, and for preparing cellulose ether compositions has been described[6]. In the latter process, 20 parts of ethylcellulose, 2 parts resorcinol and 140 parts of mixed methyl alcohol and acetate is submitted as a representative formula.

Anisol, phenetol, the chloranisols[7]; dimethylhydroquinone, thymoquinone, thymol and benzosol (benzoylguaia-

1. C. Bogin, U. S. P. 1651578; abst. Chem. Zentr. 1928, I, 1237.
2. Intern. Celluloseester-Ges., D. R. P. 265852; abst. C. A. 1914, **8**, 573; J. S. C. I. 1913, **32**, 1104; Chem. Zentr. 1913, II, 1635; Chem. Ind. 1913, **36**, 690; Chem. Ztg. Rep. 1913, **37**, 645; Chem. Zts. 1914, **13**, 3348; Wag. Jahr. 1913, **59**, II, 447; Zts. ang. Chem. 1913, **26**, 700.
3. L. Lederer, D. R. P. 145106; abst. Chem. Zentr. 1903, II, 1155.
4. A. Voss, D. R. P. 367560; abst. J. S. C. I. 1923, **42**, 397-A.
5. U. S. P. 1134527, 1157705, 1174466, 1205957, 1381564, 1426678, 1444469.
6. S. Carroll, U. S. P. 1552793; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Caout. et Gutta. 1926, **23**, 13316; Chem. Zentr. 1926, I, 542. Catechol has been patented as a gasolene stabilizer, in the proportion of less than 75 mgm. per liter of gasolene, Can. P. 317886.
7. H. Dreyfus, F. P. 432264; abst. C. A. 1913, **7**, 3414; J. S. C. I. 1912, **31**, 24; Mon. Sci. 1913, **78**, 392, 393; Chem. Ztg. 1912, **36**, 185; Chem. Ztg. Rep. 1913, **37**, 425; Kunst. 1912, **2**, 77; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 139. E. P. 20975, 1911; abst. C. A. 1913, **7**, 890; J. S. C. I. 1913, **32**, 19; Chem. Ztg. 1913, **37**, 122; Chem. Ztg. Rep. 1913, **37**, 287; Kunst. 1913, **3**, 215; 1914, **4**, 360. U. S. P. 1181859, 1181860, 1916; abst. C. A. 1916, **10**, 1789; J. S. C. I. 1916, **35**, 687; Mon. Sci. 1917, **84**, 29; Chem. Ztg. 1916, **40**, 659. Belg. P. 241251, 1911; abst. Mon. Sci. 1913, **78**, 392, 393; Chem. Ztg. 1912, **36**, 338, 975. Swiss P. 65051, 1911 (Addn. to Swiss P. 63585); Swiss P. 63585; abst. C. A. 1914, **8**, 2252; Chem. Ztg. 1914, **38**, 106; Kunst. 1914, **4**, 216. Swiss P. 65057, 1911; abst. Chem. Ztg. 1914, **38**, 501.

col)[1]; carvacrol (2-methyl-5-*iso*propylphenol) isomeric with thymol (3-methyl-6-*iso*propylphenol) also called cymophenol, m. pt. 0°, b. pt. 236°, eugenol and isoeugenol[2], are polyphenolic compounds which dissolve both cellulose ethers and cellulose esters. The W. Walker acetylcellulose lacquer utilizes thymol, with castor oil to induce softness[3].

Guaiacol, Monomethylcatechol, Pyrocatechin Monomethyl Ester, is an excellent pyroxylin solvent, although the product has a distinctive and to some disagreeable odor[4]. The Dispersions Process, Inc., use wood creosote and guaiacol as both nitrocellulose and acetylcellulose dissolvant[5], while H. Smith has disclosed the usefulness of guaiacol acetate for the same purpose[6].

Naphthol. Both *a*- and *b*-naphthol have been patented for use as camphor substitutes in the manufacture of pyroxylin plastics[7], the object being to reduce the melting point of the mixture in order to plasticize at a lower temperature. Not used at the present time although for a time were employed quite entensively. The three points lacking in camphor, which otherwise would make it an ideal solvent, are odor, high melting point and cost. In artificial leather manufacture with a nitrocellulose base, *b*-naphthol has been tried[8], and *a*- or *b*-naphthol in ethyl alcohol for solid pyroxylin compounds[9]. For fabric waterproofing, naphthol and pyroxylin are used to a limited degree at the present time, where an anti-mildewing effect is desired due to the antiseptic action of the naphthol.

1. J. Stevens, U. S. P. 607554. See U. S. P. 517987, 542692, 543197.
2. T. Tesse, U. S. P. 1521056; abst. C. A. 1925, **19**, 739; J. S. C. I. 1925, **44**, 95-B.
3. U. S. P. 774714; abst. J. S. C. I. 1904, **23**, 1159; J. A. C. S. 1905, **27**R, 434; Mon. Sci. 1905, **63**, 50; Chem. Ztg. 1904, **28**, 1157.
4. G. Walker, U. S. P. 604181. H. Cathelineau and A. Fleury, D. R. P. 185240; abst. Chem. Zentr. 1907, II, 1037.
5. Dispersions Process, Inc., Can. P. 311079.
6. U. S. P. 1858285; abst. C. A. 1932, **26**, 3919; Plastics, 1932, **8**, #7, 280. See U. S. P. 1858286, 1858287.
7. J. Stevens, U. S. P. 543197. See U. S. P. 269340, 269341, 269344, 269345, 517987.
8. *Ibid.* U. S. P. 622727. See U. S. P. 615319.
9. *Ibid.* U. S. P. 615319. C. Schüpphaus, U. S. P. 410207.

Benzyl Alcohol, Phenmethylol, is widely used as a solvent and plastifier, although the plasticizing effect is not permanent due to the volatility of the alcohol. It dissolves methyl, ethyl and benzyl cellulose, especially the latter, in fact in the normal process of cellulose benzylation, the formation of benzyl alcohol by interaction of alkali upon benzyl chloride benzylating agent, causes the benzylcellulose as formed to pass into solution in the benzylating mixture, analogous to the solubility of acetylcellulose in acetic acid in the acetating bath. It is an excellent solvent-evaporation retardant.

The commercial article assays 95-97% benzyl alcohol, boils 200-210°. Soluble in water to the amount of about 3.5%, and is miscible with the usual cellulose ether solvents. The usual impurities are chlortoluene, dibenzyl ether, dibenzyl, benzaldehyde, and small amounts of benzyl chloride. Benzyl alcohol is one of comparatively few chemicals which will freely dissolve all three classes of cellulose dereviatives, the nitrate, acetate and ethers, and hence allows of admixture in any proportion of these cellulose bodies one with the other. It is miscible with the aromatic hydrocarbons and with linseed, castor and other oils, and dissolves benzyl abietate, ester gum, copal ester, mastic, elemi, sandarac, shellac and coumarone resin.

Benzyl alcohol alone[1], with ethyl acetoacetate, eugenol or isoeugenol[2]; with triacetin or methyl phthalate[3]; with benzene and acetone; or a mixture of benzyl alcohol and acetone[4] are some of the combinations which have been put forward as especially useful. H. Dreyfus[5], F. Edbrook[6],

1. D. Sutherland and Wall Paper Manufacturers, Ltd., E. P. 131082. F. P. 499868.
2. T. Tesse, U. S. P. 1426521. E. P. 158521. F. P. 495000. U. S. P. 1521055, 1521056. Soc. Nauton Freres et de Marsac and T. Tesse, E. P. 131369.
3. H. Dreyfus, E. P. 131669; abst. C. A. 1920, **14**, 346.
4. F. Edbrook, E. P. 202154; abst. C. A. 1924, **18**, 335.
5. U. S. P. 1181860; abst. C. A. 1916, **10**, 1789. Swiss P. 65057.
6. U. S. P. 1607516; abst. C. A. 1927, **21**, 333. Can. P. 238217.

D. Sutherland[1], H. Ross[2], W. Stevenson[3], P. Campion[4], and Exceloid Co. and B. Baker[5] have all published formulas for the use of benzyl alcohol as solvents for cellulose esters and ethers. T. Tesse[6] combines benzyl alcohol with glyceryl benzoate, carvol, safrol or chavibetol (allyl-3.4-guaiacol, 1-hydroxy-2-methoxy-2-methoxy-4-allylbenzene). The latter is a colorless liquid, b. pt. 254°. *iso*Chavibetol (betelphenol, 1-hydroxy-2-methoxy-4-propenylbenzene) is a constituent of essential oils.

A mixture of *o*- and *p*-benzyl alcohols[7] forms an excellent solvent for ethyl- and benzyl-cellulose in the presence of a small amount of ethyl alcohol, and W. Webb[8] has described the preparation of cellulose ether compositions in which benzyl alcohol or phenylethyl alcohol constitute the solvent in association with methyl alcohol, a representative lacquer comprising ethylcellulose 1, benzyl alcohol 2-3, and the same amount of ethyl alcohol. Carbon tetrachloride with benzyl alcohol[9], diphenylamine or dicresyline and benzyl alcohol[10], or benzyl alcohol with acetanilid and terpineol[11], or with acetnaphthalid, methyl acetone or triacetin[12] are indicative of the range of supplementary bodies used in conjunction with benzyl alcohol in lacquer formulas. The H. Dreyfus acetylcellulose varnishes utilize benzyl alcohol, cyclohexanone, methyl- and dimethyl-cyclohexanone, diphenyl carbinol, acetophenone, methylacetophenone, benzophenone, methoxyphenone or ethoxyphenone[13]. Whereas Plastoform I is benzyl alcohol, Plastoform II is phenylethyl

1. U. S. P. 1320290; abst. C. A. 1920, **14**, 131. Can. P. 195559.
2. U. S. P. 1440178; abst. C. A. 1923, **17**, 1157. Can. P. 198265.
3. U. S. P. 1458505. E. P. 138379; abst. C. A. 1920, **14**, 1879.
4. U. S. P. 1626113; abst. C. A. 1927, **21**, 2054.
5. E. P. 209633; abst. C. A. 1924, **18**, 1758.
6. E. P. 124763; abst. J. S. C. I. 1919, **38**, 319-A.
7. J. Dupont, U. S. P. 1317276; abst. C. A. 1919, **13**, 3316.
8. U. S. P. 1460690; abst. C. A. 1923, **17**, 2957.
9. Etablissements Poulenc Freres and M. Pechiney, F. P. 494300; abst. Chim. et Ind. 1920, **4**, 228.
10. J. See, U. S. P. 1431845; abst. C. A. 1922, **16**, 4308.
11. C. Dreyfus, E. P. 127615; abst. C. A. 1919, **13**, 2444.
12. *Ibid.* E. P. 127678; abst. C. A. 1919, **13**, 2444.
13. E. P. 128215; abst. C. A. 1919, **13**, 2444. F. P. 432264. British Cellulose & Chemical Mfg. Co., E. P. 177268.

alcohol. In the use of benzyl alcohol, it should be borne in mind that it is readily oxidized to benzaldehyde by atmospheric oxygen.

The A. Piestrak lacquer[1], the C. Ellis varnish[2] and the photographic film of F. Renwick[3] all combine a cellulose ester with benzyl alcohol. In the preparation of airplane dope[4], as a cellulose acetate solvent[5] and plasticizer[6], and as a finish[7] and varnish remover[8], benzyl alcohol has been extensively used.

Aliphatic Aldehydes. F. Pollak[9] treats cellulose acetate with a mixed solvent of formaldehyde and alcohols, and R. Strehlenert[10] has described an improved solution of nitrocellulose containing formaldehyde, acetaldehyde, paraldehyde or benzaldehyde up to about 15% on the weight of the cellulose ester, the object of the aldehyde addition being to reduce tendency of the cellulose ester to take up water. An amine aldehyde condensate composition with ethylcellulose has been described[11]. C. Whitby[12] reports that

1. F. P. 501236; abst. Chim. et Ind. 1921, **5**, 330; Kunst. 1921, **11**, 38.
2. U. S. P. 1172773; abst. C. A. 1916, **11**, 1104.
3. U. S. P. 1680635, 1680636; abst. C. A. 1928, **22**, 3595.
4. U. S. P. 1320290, 1339728, 1426521, 1440178, 1521055, 1521056.
5. U. S. P. 1199800, 1394890, 1458505.
6. U. S. P. 1388472, 1431845, 1465994.
7. U. S. P. 1140449, 1160394, 1169783, 1172773, 1185641.
8. U. S. P. 1130499, 1185641, 1328080, 1406175, 1499101.
9. D. R. P. 375640, 375641; abst. J. S. C. I. 1924, **43**, 52-B; Chem. Zentr. 1923, IV, 961. Aust. P. 87713, 87720; abst. Chem. Zentr. 1922, IV, 907. See A. Eichengruen, Ital. P. 140664. F. Lehmann, Ital. P. 141905. V. Pauthonier, Ital. P. 144105.
10. E. P. 22540, 1896; abst. J. S. C. I. 1896, **15**, 764; 1897, **16**, 782, 907; Chem. Ztg. 1898, **22**, 212; Mon. Sci. 1905, **63**, 323.
11. L. Lilienfeld, U. S. P. 1217028; abst. J. S. C. I. 1917, **36**, 383; Mon. Sci. 1918, **85**, 4. E. P. 6387, 1913; abst. C. A. 1914, **8**, 2947; J. S. C. I. 1914, **33**, 417; Kunst. 1914, **4**, 236, 256. F. P. 459972; abst. C. A. 1914, **8**, 3373; J. S. C. I. 1913, **32**, 1153; Chem. Ztg. 1913, **37**, 1293; Chem. Ztg. Rep. 1914, **38**, 394; Kunst. 1914, **4**, 75. Aust. P. 73001; abst. Kunst. 1917, **7**, 222. Aust. P. 62809; abst. Chem. Ztg. 1913, **37**, 1499. Hung. P. Appl. L-3294; abst. Chem. Ztg. 1913, **37**, 11. Ital. P. 173413, 183582.
12. Canadian Chem. Met. 1925, **9**, 265; abst. C. A. 1926, **20**, 687.

acetaldehyde is a solvent for acetylcellulose but not for rubber, while the reverse is true of heptaldehyde, the solvent combination of R. Gilmour and W. Dunville & Co.[1] being acetaldehyde, ethyl acetate and benzene. The nitrocellulose composition of G. Zeller[2] containing mixed aldehydes is understood to have been commercialized. It consisted in subjecting aldehydes to the action of organic acids and simultaneously to the action of an oxidizing agent. A combination of methyl aldehyde, casein and acetylcellulose has been advocated as a suitable thermoplastic combination[3]. Metaldehyde, paraldehyde, dialdan are polymers of acetaldehyde. Mixtures of paraldehyde and ethyl alcohol form an efficient nitrocellulose solvent mixture[4], and paraldehyde and a ketone[5] dissolve cellulose esters. Aldol (*b*-hydroxybutyraldehyde) is also an efficient pyroxylin solvent[6], while paraldehyde dissolves natural and synthetic resins[7]. The preparation of chloracetaldehyde has been described[8].

Trichloraldehyde, Chloral, Trichloracetaldehyde, especially when combined with a molecule of water to form chloral hydrate, has been used to some extent as a solvent, the soporific odor being a point against its extended use.

1. E. P. 131647; abst. C. A. 1920, **14**, 346; J. S. C. I. 1919, **38**, 896-A; Chem. Age, London, 1919, **1**, 453; Chem. Ztg. 1919, **43**, 733; Kunst. 1920, **10**, 79; 1921, **11**, 61; Caout. et Gutta. 1920, **17**, 10659.
2. U. S. P. 518386, 518387. According to the R. Eisemann formula for a dipping fluid for incandescent mantles (D. R. P. 195312; abst. Wag. Jahr. 1908, II, 96), camphor is replaced by an aldehyde or mixture of aldehydes.
3. H. Peters, E. P. 14293, 1910; abst. C. A. 1911, **5**, 3347; J. S. C. I. 1911, **30**, 1171.
4. Chem. Fabr. vorm. Weiler-ter Meer, D. R. P. 343162; abst. J. S. C. I. 1922, **41**, 138-A; Kunst. 1922, **12**, 8; Chem. Zentr. 1922, II, 92.
5. H. Langwell and Distillers Co., Ltd., E. P. 367390; abst. J. S. C. I. 1932, **51**, 475-B.
6. E. I. du Pont de Nemours Powder Co., U. S. P. 1234921; abst. Kunst. 1918, **8**, 70.
7. Farbw. vorm. Meister, Lucius und Bruening, D. R. P. 364347; abst. J. S. C. I. 1923, **42**, 279-A.
8. I. G. Farbenind. A.-G., H. Lange and O. Ernst, D. R. P. 521723; abst. C. A. 1931, **25**, 3363. See D. R. P. 496062; abst. C. A. 1930, **24**, 3251.

L. Lederer[1], J. Stevens[2], C. Ellis[3] and J. Zdanowich[4] have described cellulose ester compositions containing chloral hydrate or chloral alcoholate (chloral alkoxide) as solvents. H. Dreyfus[5], W. Parkin and A. Williams[6], Farbenfabriken vorm. F. Bayer & Co.[7] and A. Eichengruen[8] combine

1. U. S. P. 1195040; abst. J. S. C. I. 1916, **35**, 961. F. P. 377010; abst. J. S. C. I. 1907, **26**, 1027. Aust. P. 16377, 34908; abst. Zts. ang. Chem. 1909, **22**, 505. D. R. P. 189703, Addn. to D. R. P. 152111. E. P. 9537, 1907; abst. J. S. C. I. 1908, **27**, 589. D. R. P. 220228; abst. Wag. Jahr. 1910, II, 589.

2. U. S. P. 1508483, 1508484; abst. C. A. 1924, **18**, 3720; J. S. C. I. 1924, **43**, 905-B.

3. U. S. P. 999490; abst. C. A. 1911, **5**, 3156; J. S. C. I. 1911, **30**, 1051; J. Soc. Dyers, 1911, **27**, 223; Mon. Sci. 1912, **77**, 163; Kunst. 1911, **1**, 458.

4. Can. P. 261525.

5. F. P. 432264; abst. C. A. 1913, **7**, 3414; J. S. C. I. 1912, **31**, 24; Mon. Sci. 1913, **78**, 392, 393; Chem. Ztg. 1912, **36**, 185; Chem. Ztg. Rep. 1913, **37**, 425; Kunst. 1912, **2**, 77; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 139. E. P. 20975, 1911; abst. C. A. 1913, **7**, 890; J. S. C. I. 1913, **32**, 19; Chem. Ztg. 1913, **37**, 122; Chem. Ztg. Rep. 1913, **37**, 287; Kunst. 1913, **3**, 215; 1914, **4**, 360. U. S. P. 1181859, 1181860; abst. C. A. 1916, **10**, 1789; J. S. C. I. 1916, **35**, 687; Mon. Sci. 1917, **84**, 29; Chem. Ztg. 1916, **40**, 659. Belg. P. 241251; abst. Mon. Sci. 1913, **78**, 392, 393; Chem. Ztg. 1912, **36**, 338, 975. Swiss P. 65051 (Addn. to Swiss P. 63585); Swiss P. 63585; abst. C. A. 1914, **8**, 2252; Chem. Ztg. 1914, **38**, 106; Kunst. 1914, **4**, 216. Swiss P. 65057; abst. Chem. Ztg. 1914, **38**, 501. See also E. P. 7088, 1902.

6. E. P. 26657, 1909; abst. J. S. C. I. 1910, **29**, 1152; Mon. Sci. 1913, **78**, 392; 1916, **83**, 47; Kunst. 1911, **1**, 36. F. P. 421010; abst. J. S. C. I. 1911, **30**, 416; Mon. Sci. 1913, **79**, 30, 392.

7. E. P. 13100, 1910; abst. C. A. 1911, **5**, 3165; J. S. C. I. 1911, **30**, 533; J. Soc. Dyers Col. 1911, **27**, 161. First Addn. 12469 to F. P. 408370; abst. J. S. C. I. 1910, **29**, 1299. Second Addn. 12755 to F. P. 408370; abst. J. S. C. I. 1910, **29**, 1371. Cf. F. P. 408370; abst. J. S. C. I. 1910, **29**, 624, 752; 1911, **30**, 533; J. Soc. Dyers Col. 1910, **26**, 96, 226, 242; Mon. Sci. 1913, **79**, 392. For producing pressed and shaped cellulose acetate compounds, consult Farbenfabriken vorm. F. Bayer & Co., E. P. 14364, 1910; abst. J. S. C. I. 1910, **29**, 1152; J. Soc. Dyers Col. 1910, **26**, 255; Mon. Sci. 1913, **78**, 392; Chem. Ztg. 1910, **34**, 914; Kunst. 1911, **1**, 57, 136. F. P. 417250; abst. J. S. C. I. 1911, **30**, 19; Mon. Sci. 1913, **79**, 30; Chem. Ztg. 1910, **34**, 1026. D. R. P. Anm. F. 28111, Aug. 25, 1909 (Refused Feb. 20, 1911); abst. Chem. Ztg. 1911, **35**, 233. Belg. P. 226582; abst. Chem. Ztg. 1910, **34**, 1042. Swiss P. 52273; abst. Chem. Ztg. 1911, **35**, 1122. Swiss P. 52438, 1910; abst. Chem. Ztg. 1911, **35**, 1205; Kunst. 1912, **2**, 135. Aust. P. 46991, 1910; abst. Kunst. 1911, **1**, 216.

8. E. P. 27258, 1910; abst. C. A. 1912, **6**, 1526; Kunst. 1912, **2**, 34; Chem. Ztg. 1911, **35**, 982. F. P. 419530; abst. J. S. C. I. 1911, **30**, 205; Mon. Sci. 1913, **78**, 392; Chem. Ztg. 1910, **34**, 1311. First Addn. 13237, 1911, to F. P. 419530; abst. J. S. C. I. 1911, **30**, 415; Chem. Ztg. 1911, **35**, 185; Kunst. 1911, **1**, 156. Australian P. 46, 1911. Can. P. 129983. Swiss P. 51952; abst. Chem. Ztg. 1911, **35**, 965.

chloral compounds with acetylcellulose in flowable compositions. Both chloral hydrate and alcoholate are formylcellulose solvents[1]. Like chloral hydrate, butyl chloral hydrate dissolves acetylcellulose. Butyraldehyde (butaldehyde) may be made by the processes of C. Pigg[2], C. Bogin[3] or D. Legg[4]. Isovaleric aldehyde (isovaleraldehyde) and its derivatives amylidenedimethyl ether and amylidenediethyl ether have been brought forward as desirable pyroxylin colloiding agents[5].

Propaldehyde, present in wood tar, has a solvent effect upon the nitrocelluloses, and heptaldehyde, oenanthol (enanthol) dissolves pyroxylin feebly, more so in the presence of a small amount of alcohol or acetone. Trichloracetal with ethyl alcohol readily gelatinizes triethylcellulose, best by warming. Chloral formamide (chloralamide) and dormiol (a condensation product of chloral and *ter*-amyl alcohol) both dissolve ethyl -and benzyl-cellulose in the presence of alcohol. *ter*-Trichlorbutyl alcohol (chloretone) readily gelatinizes ethylcellulose in the cold and dissolves the same in the presence of methyl or ethyl alcohols or acetates, best with the application of moderate heat.

Aromatic Aldehydes. Benzaldehyde in conjunction with methyl acetate[6] forms the cellulose ether composition of S. Carroll. Water-insoluble ethylcellulose will dissolve directly in 4-6 parts benzaldehyde. Or[7], *p*-brombenzaldehyde or methyl *m*-brombenzoate added thereto are particularly compatible with cellulose derivatives, especially cellulose acetate. Benzaldehyde is also a cellulose acetate sol-

1. Internationale Celluloseester-Ges. m. b. H., D. R. P. 265852, 265911; abst. C. A. 1914, **8**, 573; J. S. C. I. 1913, **32**, 1104.
2. U. S. P. 1576544; abst. J. S. C. I. 1926, **45**, 463-B.
3. U. S. P. 1576503; abst. C. A. 1926, **20**, 1631. U. S. P. 1556067; abst. 1925, **19**, 3490; J. S. C. I. 1926, **45**, 28-B. Re-issue 17157; abst. C. A. 1929, **23**, 610; J. S. C. I. 1929, **48**, 89-B.
4. U. S. P. 1418448; abst. C. A. 1922, **16**, 2695; Chem. Met. Eng. 1922, **27**, 322.
5. R. Schüpphaus, U. S. P. 410206; abst. J. Soc. Dyers Col. 1889, **5**, 167.
6. U. S. P. 1467104; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A. See U. S. P. 1188376.
7. S. Carroll, U. S. P. 1826688.

vent[1]. The composition of H. Smith[2] comprises cellulose acetate and approximately an equal amount of salicylaldehyde. Anisaldehyde (anisic aldehyde) is an acetylcellulose dissolvant[3], and has been used as a component of photographic films[4]. The celluloid and nitrocellulose formulas of R. Strehlenert[5], J. Goldsmith[6], R. Eisenmann[7] and P. Breteau and H. Leroux[8] all employ benzaldehyde. Cinnamic aldehyde (cinnamylaldehyde) with alcohol dissolves hydrated acetylcellulose and ethylcellulose.

Aldol, Acetaldol, 3-Butanolal, *b*-Oxybutyraldehyde, an aldehyde alcohol, being a colorless liquid soluble in water, and having about the viscosity of a 50% glycerol solution, sp. gr. 1.1208 at 0°, b. pt. about 82° at 20 mm., has been described by W. Weedon and E. I. du Pont de Nemours Co.[9] as a direct solvent of pyroxylin upon application of heat, and W. Masland[10] has patented a mixture of aldol and castor oil as a pyroxylin composition aided by ethyl alcohol, ethyl acetate and benzene. The cellulose acetate composi-

1. W. Nebel, U. S. P. 1478137; abst. C. A. 1924, **18**, 752; J. S. C. I. 1924, **43**, 129-B.
2. U. S. P. 1858286.
3. W. Lindsay, U. S. P. 1199800; abst. C. A. 1916, **10**, 3159; J. S. C. I. 1916, **35**, 1215.
4. *Ibid.* U. S. P. 1388472; abst. C. A. 1921, **15**, 3950; J. S. C. I. 1921, **40**, 732-A.
5. E. P. 22540, 1896.
6. E. P. 13131, 1900.
7. E. P. 15536, 1907.
8. F. P. 409557.
9. U. S. P. 1082573; abst. C. A. 1914, **8**, 822; J. S. C. I. 1914, **33**, 132. E. P. 24033, 1914; abst. J. S. C. I. 1915, **34**, 956. U. S. P. 1135026; abst. J. S. C. I. 1915, **34**, 606. D. R. P. 292951. Aust. P. 72493. E. P. 22623, 1912, is also cited. U. S. P. 1008333, 1086048, 1086381, 1151113, 1234921. E. P. 17259, 1911; 22622, 29964, 1912; 879, 1913. F. P. 449605, 449606, 449607, 453406. Can. P. 147423. Belg. P. 250115, 250116, 250117, 250118. Swiss P. 63136, 63137; abst. C. A. 1913, **7**, 2096, 3196; 1914, **8**, 210, 992, 1190; J. S. C. I. 1913, **32**, 507, 1129; 1914, **33**, 278, 374, 375; 1917, **36**, 1044; Kunst. 1914, **4**, 35, 154, 174. See also Consortium f. Elektrochem. Ind., E. P. 19463, 26825, 1913. F. P. 461734; abst. J. S. C. I. 1914, **33**, 219, 221. Belg. P. 262208. R. Earle and L. Kyriakides, U. S. P. 1094314; abst. Kunst. 1914, **4**, 318. N. Grünstein, U. S. P. 1234156. E. P. 101636; abst. J. S. C. I. 1917, **36**, 1064. H. Hibbert, U. S. P. 1261811; abst. C. A. 1918, **12**, 1558.
10. U. S. P. 1267785; abst. J. S. C. I. 1919, **38**, 319-A. See also U. S. P. 1234921.

tion of J. Kessler[1] is acetylcellulose 6-8, acetaldol 10-20%, dissolved in 72-82% of a solvent mixture composed of acetone 40, ethyl acetate 30, benzene 20 and denatured alcohol 10. E. Robinson provides a fireproofed composition[2] of cellulose acetate and magnesium ammonium phosphate each 7, aldol 20, acetone 56.

Aldol may be prepared from acetic acid by condensation in the presence of aqueous sodium hydroxide[3]. H. Hibbert[4] has described the use of acetaldol as a nitrocellulose adjunct.

Ethers, Aliphatic Oxides. L. Paget has been granted a series of patents covering the preparation of the simple and compound ethers and their use as nitrocellulose solvents[5], and J. Stevens[6] has described for the same purpose, butyric ether (dibutyl oxide), valeric ether, benzoic ether, sebacic ether (sebacylic ether), amyl ether and oxalic ether, either alone or admixed with a large number of essential oils specified in the specification.

R. Schüpphaus[7] has dilated on the advantages of the aliphatic mixed ethers as cellulose ester solvents, especially methyl*iso*butyl ether (b. pt. 60°), ethyl*iso*butyl ether (b. pt. 78-80°), methyl*iso*amyl ether (b. pt. 92°), and ethyl*iso*amyl ether (b. pt. 112°). *bb'*-Dichlorethyl ether (b. pt. 177-

1. U. S. P. 1303563; abst. C. A. 1919, **13**, 1938; J. S. C. I. 1919, **38**, 531-A; Chim. et Ind. 1921, **5**, 578.
2. U. S. P. 1310841; abst. C. A. 1919, **13**, 2443.
3. N. Gruenstein, U. S. P. 1437139; abst. C. A. 1923, **17**, 563; J. S. C. I. 1923, **42**, 73-A. E. P. 147119; abst. J. S. C. I. 1922, **41**, 78-A.
4. H. Hibbert and E. I. du Pont de Nemours Powder Co., U. S. P. 994841, 994842. U. S. P. 1158217; abst. C. A. 1915, **9**, 3363. U. S. P. 1164647; abst. J. S. C. I. 1916, **35**, 198. U. S. P. 1213367; abst. C. A. 1917, **11**, 888. U. S. P. 1313661; abst. J. S. C. I. 1919, **38**, 794-A. E. P. 4099, 1911; 22621, 22622, 22623, 22626, 22964, 1912; 5408, 1914; abst. J. S. C. I. 1911, **30**, 836; 1914, **33**, 161; 1913, **32**, 1105; 1914, **33**, 984; C. A. 1914, **8**, 992, 1010, 984; Kunst. 1914, **4**, 155. F. P. 449604, 449605, 449606; abst. J. S. C. I. 1913, **32**, 507, 508; C. A. 1913, **7**, 2683; Mon. Sci. 1914, **81**, 5; Chem. Ztg. 1913, **37**, 228. D. R. P. 292951; abst. Chem. Zentr. 1916, II, 246. Swiss P. 63136, 63137, 64932; abst. C. A. 1914, **8**, 3490. Belg. P. 250118, 252722; abst. Chem. Ztg. 1913, **37**, 76. Aust. P. 72493; abst. C. A. 1917, **11**, 1041.
5. U. S. P. 494790, 494791, 494792, 494793. E. P. 7784, 1893.
6. U. S. P. 269340.
7. U. S. P. 741554.

178°) dissolves both methylcellulose and ethylcellulose, and may be used with or without such high boilers as benzyl acetate or ethyl benzoate[1]. Diethyl, dipropyl, di*iso*propyl, dibutyl and di*iso*butyl ethers may be made by heating the aliphatic alcohol under pressure in the presence of a dehydrating catalyst as aluminum or thorium oxides or sulfates[2]. *iso*Propyl ether is prepared by heating *iso*propyl alcohol with 70-85% sulfuric acid at 100-125°[3], being purified by the addition of water and the ether separated from the diluted solution by stratification and distillation[4]. Glycerylbenzyl ether (b. pt. 123-124° at 3.5 mm.)[5]; *b*-naphthylethyl ether, anisol (methylphenyl ether), phenetol (ethylphenyl ether), propyl ether, butyl ether and amyl ether, all dissolve nitrocellulose and some types of cellulose ethers[6]. Guaiacol (b. pt. 200°), diphenylglyceryl ether, phenylglycide, chlorphenylglyceryl ether and dicresylglyceryl ethers[7] dissolve the cellulose ethers and acetylcellulose.

Amyl ether has been used as a paint remover[8] and in liquid fuels[9]; dibenzyl ether dissolves cellulose esters. Methylcresyl and ethylcresyl ethers dissolve cellulose ethers and cellulose chloracetate. Phenylglycol ether and cresylglycol ether are both solvents of the cellulose ethers. For instance, 50 parts water-insoluble ethylcellulose are dissolved in a mixture of *iso*butyl acetate 500, toluene 250, ethyl alcohol 180 and 10-20 parts phenylglycol ether (ethyleneglycol monophenyl ether)[10]. Acetolethyl ether (ethoxy

1. W. Lindsay, U. S. P. 1620977; abst. C. A. 1927, **21**, 1548.
2. N. V. de Bataafsche Petroleum Maatschapij, E. P. 332756; abst. C. A. 1931, **25**, 302. F. P. 711085; abst. C. A. 1932, **26**, 1616.
3. M. Mann, U. S. P. 1482804; abst. C. A. 1924, **18**, 988.
4. H. Buc, U. S. P. 1442520; abst. C. A. 1923, **17**, 1029.
5. C. F. Boehringer, D. R. P. 403050; abst. Chem. Zentr. 1925, I, 293.
6. R. Schuepphaus, U. S. P. 600556.
7. H. Danzer, E. P. 13239, 1912; abst. J. S. C. I. 1912, **31**, 1120.
8. C. Ellis, U. S. P. 1143110.
9. E. Chasbonneaup, U. S. P. 1480372.
10. G. Steimmig, U. S. P. 1788781; abst. C. A. 1931, **25**, 1083.

acetone) has been mentioned[1] as to its solvent possibilities for cellulose esters and ethers.

As efficient cellulose ether solvents[2], there has been described phenetol, anisol, *n*-butylcresyl ether, benzylethyl ether, diphenyl ether, *n*-butylphenyl ether, *n*-butylbenzyl ether and methyl-*o*-cresyl ether, from 50-90 parts of one of the above being mixed with 10-50 parts by weight of methyl or ethyl alcohols as an ethylcellulose dissolvant. Pentaerythritol-mono-, di or tri-ethyl ether, all pale yellow oils, dissolve the etherified celluloses[3].

C. Burke[4] prepares pentaerythrite ethers by heating them with the ester of an inorganic acid (ethyl chloride, methyl chloride, butyl chloride or benzyl chloride) in the presence of a solvent and an alkali. In this manner pentaerythritemethyl, pentaerythrite ethyl, pentaerythrite butyl, and pentaerythritebenzyl ethers result. In the stabilization of gelatinous explosives diphenyl, phenylbenzyl, ethylnaphthyl, and phenanthryl ethers have been recommended[5], and as a substitute for camphor in nitro- and acetyl-cellulose[6], phenetol, anisol, methylnaphthyl and ethylnaphthyl ethers, resorcinol methyl, resorcinol ethyl, pyrocatecholmethyl, pyrocatecholethyl, methylbenzyl and benzylethyl ethers have been described, including the usefulness of safrol and isosafrol in this connection. Diphenyl ether may be prepared by heating chlorbenzene and potassium phenolate in phenol to 200 under pressure[7], or by heating sodium phenolsulfonate to about 420°[8]. Methyl- and ethyl-benzyl ether[9], methyl- or ethyl-brombenzyl ether and methyl- and ethyl-chlorbenzyl ether are covered by the

1. D. Keyes, Ind. Eng. Chem. 1925, **17**, 1120.
2. S. Carroll, U. S. P. 1479955; abst. C. A. 1924, **18**, 904.
3. Imperial Chemical Industries, Ltd., E. P. 358393; abst. J. S. C. I. 1931, **50**, 1135-B.
4. C. Burke, U. S. P. 1774500; abst. J. S. C. I. 1931, **50**, 621-B. Can. P. 319949.
5. Nobel's Explosive Co., Ltd., Swiss P. 65549.
6. H. Dreyfus, U. S. P. 1181859, 1181860.
7. L. Ostermann, U. S. P. 1099761; abst. C. A. 1914, **8**, 2779.
8. J. Johlin, U. S. P. 1372434; abst. C. A. 1921, **15**, 1905.
9. C. Mettler, U. S. P. 815548. E. P. 14316, 1905. D. R. P. 166181.

process of C. Mettler, and glyceryldibenzyl ether with butyl stearate by the formula of W. Lawson[1].

Amylidenedimethyl and amylidenediethyl ethers with acetyldiphenylamine or tricresyl phosphate comprise the E. Franquet camphor substitutes, and have the advantage of being odorless[2]. Benzyl ether (dibenzyl oxide)[3], methylbenzyl, ethylbenzyl, *n*-butylbenzyl and tolylbenzyl ethers are all dissolvants of the cellulose ethers[4]. *b*-Naphtholamyl ether is a direct solvent of ethyl-, propyl- and benzyl-cellulose[5], 10 parts cellulose ether, 100 parts acetone and 5-10 parts *b*-naphtholamyl ether being a recommended proportion. This ether boils at 325°. Ethylbornyl ether[6] has been used in a paint and varnish remover formula.

Anisol (methylphenyl ether) except for its high price, would be extensively used in the cellulose ether industry. In the coating of metal surfaces in conjunction with indene, glycol diacetate, diethyl phthalate or triacetin[7]; anisol with phenetol or veratrol (pyrocatecholdiethyl ether), methylal, safrol, isosafrol, methylacetanilid (manol) have been described as efficient plasticizing agents[8].

Anisol has been proposed for use in a binder composi-

1. U. S. P. 1792102; abst. C. A. 1931, **25**, 2012.
2. E. Franquet, F. P. 312817; abst. J. S. C. I. 1902, **21**, 134.
3. U. S. P. 1130499, 1199800, 1388472, 1483738, 1504437.
4. S. Carroll, U. S. P. 1479955.
5. Farbenfabrik. vorm. F. Bayer & Co., D. R. P. 307125; abst. J. S. C. I. 1920, **39**, 400-A. D. R. P. 322648; abst. Kunst. 1920, **10**, 205. E. P. 115855.
6. C. Ellis, U. S. P. 1169783.
7. Compagnie Francaise pour l'Exploitation des Procedes Thomson-Houston, F. P. 649384; abst. C. A. 1929, **23**, 2841.
8. H. Dreyfus, F. P. 432264; abst. C. A. 1913, **7**, 3414; J. S. C. I. 1912, **32**, 24; Mon. Sci. 1913, **78**, 392, 393; Chem. Ztg. 1912, **36**, 185; Chem. Ztg. Rep. 1913, **37**, 425; Kunst. 1912, **2**, 77; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 139. E. P. 20975, 1911; abst. C. A. 1913, **7**, 890; J. S. C. I. 1913, **32**, 19; Chem. Ztg. 1913, **37**, 122; Chem. Ztg. Rep. 1913, **37**, 287; Kunst. 1913, **3**, 215; 1914, **4**, 360. U. S. P. 1181859, 1181860; abst. C. A. 1916, **10**, 1789; J. S. C. I. 1916, **35**, 687; Mon. Sci. 1917, **84**, 29; Chem. Ztg. 1916, **40**, 659. Belg. P. 241251; abst. Mon. Sci. 1913, **78**, 392, 393; Chem. Ztg. 1912, **36**, 338, 975. Swiss P. 65051 (Addn. to Swiss P. 63585). Swiss P. 63585; abst. C. A. 1914, **8**, 2252; Chem. Ztg. 1914, **38**, 106; Kunst. 1914, **4**, 216. Swiss P. 65057; abst. Chem. Ztg. 1914, **38**, 501; Kunst. 1914, **4**, 370.

tion[1], celluloid substitute[2], fire-extinguisher component[3] and paint remover[4]; and *n*-butylphenyl and *n*-butylcresyl ethers as direct ethylcellulose dissolvants[5]. Bibenzyl ether (benzyl ether, dibenzyl oxide) is a colorless liquid of almond-like odor, insoluble in water but soluble in the usual cellulose ether solvents. B. pt. 298-300° with decomposition, sp. gr. 1.035. Erganol is stated to be benzyl ether. H. Dreyfus has described pyrocatecholdiethyl ether, and D. Keyes[6] has mentioned acetinylmethylethyl ether (methylethoxyethyl ether).

Guaiacol (pyrocatechinmethyl ether), occurring in the creosote from beech-wood tar, has been advocated on account of its solvency for cellulose esters, as a useful addition to lacquers[7]. The heterocyclic compounds, *a*-propylene oxide, a colorless liquid, b. pt. 35°, sp. gr. 0.859, soluble in water, alcohol and ether, is now available in the United States in commercial quantities.

Acetal, Ethylidene diethyl ether, Acetaldehyde diethylacetal, *aa*-diethoxyethane, sp. gr. 0.8314, b. pt. 104°, is produced normally in the process of brandy distillation.

In the pyroxylin industry, acetal was first used in 1882 by J. Stevens[8]. The Industrial Alcohol Co.[9] combine anhydrous ethyl alcohol with diethyl acetal as a nitrocellulose dissolving composition, while lacquers have been described containing a hydroxyacetal as aldoldimethylacetal in the presence of urea. The cyclic acetals (condensation products from ketone or aldehyde with polyvalent alcohols) have in a large degree the characteristic of dissolving nitro-

1. L. Redman, U. S. P. 1209333.
2. H. Dreyfus, U. S. P. 1181860.
3. G. Ferguson, U. S. P. 1270393.
4. C. Ellis, U. S. P. 1499101.
5. S. Carroll, U. S. P. 1479955.
6. Ind. Eng. Chem. 1925, **17**, 1120.
7. C. Mijnssen, U. S. P. 1005454; abst. J. S. C. I. 1911, **30**, 1249. F. P. 421166; abst. J. S. C. I. 1911, **30**, 484.
8. U. S. P. 269344, 269345.
9. E. P. 357227; abst. J. S. C. I. 1931, **50**, 1106-B. A. Stevens, U. S. P. 1860822.

cellulose. Under this heading C. F. Boehringer & Sohne[1] include methylene-ethylenic ether, ethylideneglycollic ether, methyleneglycerol, benzylideneglycerol, erythridiformal, diacetonearabite, triacetonemannite, and produced by the general process of condensing benzaldehyde and glycol, trimethyleneglycol, glycerol, erythrite, adonite, arabite, mannite and dulcite.

The softness and elasticity of artificial fabrics containing nitrocellulose[2] may be enhanced by the addition of acetals of fatty-aromatic alcohols, as benzylacetal, an oil boiling at 198° at 20 mm., and xylylacetals boiling about 12° higher, especially on account of their great stability. Polyhydric alcoholic aromatic ethers may be incorporated, such as dibenzylglycol, dixylylglycol, dichlorbenzylglycol, tribenzylglyceryl or dibenzylglyceryl ethers. R. Calvert[3] combines dimethylacetal, a liquid boiling at 73° at 13 mm. as a direct nitrocellulose solvent, with ethyl and butyl acetates, and J. Stevens[4] mixes acetal with benzine, methyl alcohol and ether for the same purpose. L. Paget[5], G. Zeller[6] and R. Leopold and A. Michael all employ acetal as a subsidiary solvent for nitrocellulose in combination with light boiling solvents[7].

In the technical applications of the acetylcelluloses, cycloacetals prepared from aldehydes and *a*- and *b*-glycols have been detailed, such as ethylene ethylidene ether (b. pt. 80-82°), ethylenebutylidene ether (b. pt. 130°), and the acetal of 1.3-butyleneglycol (b. pt. 115-120°). Cellulose

1. D. R. P. 214962; abst. Chem. Zentr. 1909, II, 1607; Rev. de Chim. Ind. 1910, **21**, 156. See U. S. P. 996191.
2. Chem. Fabr. vorm. Weiler-ter Meer, D. R. P. 353233, 353234; abst. J. S. C. I. 1922, **41**, 704-A; Phot. Abst. 1922, **2**, 137.
3. U. S. P. 1848105; abst. C. A. 1932, **26**, 2879; Chem. Zentr. 1932, I, 3354.
4. U. S. P. 478543; abst. J. Soc. Dyers Col. 1892, **8**, 160; J. A. C. S. 1892, **14**, 289. See U. S. P. 559823.
5. U. S. P. 507749. E. P. 22137, 1893; abst. J. S. C. I. 1894, **13**, 263.
6. U. S. P. 518386, 518387.
7. See Farben Zeitung, 1926, **31**, 519.

ethers may be dissolved in the absence of water[1] in compounds of the acetal type of polyhydric alcohols, and ethylcellulose and benzylcellulose[2] in the methyl acetal of diethyleneglycolethyl ether, supplemented by diacetone alcohol, acetone oils and ethyleneglycolmethyl ether. The acetal of diethyleneglycol monomethyl ether[3] is a direct solvent of acetated cellulose. An excellent solvent and softener for cellulose esters is obtained by combining cycloacetals with ethyleneethylidene ether, ethylenebutylidene ether or the acetal of 1.3-butyleneglycol[4], while glyceryl monoformal[5] constitutes an acceptable emollient for cellulose ethers.

Acetal may be made by the processes of H. Guinot[6], Consortium f. Elektrochem. Industrie[7], K. Baur[8], A. King and F. Mason[9], and M. Marshall and G. Shaw[10].

1.4-Dioxane, *Dioxan, Dioxyethylene Ether, Diethylene Oxide, Diethylene Ether, Diethylene Dioxide,* is the second ether of glycol, and is obtained by the loss of 2 mols. water from 2 mols. glycol, and therefore is a di-ether. It was first described by A. Lourenco[11] and A. Würtz[12], and may be prepared from the action of mercury upon the bromide of ethylene oxide, or by distilling ethylene glycol in pres-

1. I. G. Farbenind. A.-G., E. P. 289523, Addn. to E. P. 286789; abst. J. S. C. I. 1928, **47**, 492-B.
2. Imperial Chemical Industries, Ltd., and W. Lawson, E. P. 318980; abst. Chem. Zentr. 1930, I, 3490.
3. Canadian Industries, Ltd., and W. Lawson, Can. P. 312570.
4. R. Leopold and A. Michael, D. R. P. 419223; abst. J. S. C. I. 1926, **45**, 248-B; Chem. Zentr. 1926, I, 1057.
5. I. G. Farbenind. A.-G., E. P. 286789; abst. J. S. C. I. 1928, **47**, 376-B; Plastics, 1929, **5**, 334.
6. U. S. P. 1850836. E. P. 283112; abst. J. S. C. I. 1929, **48**, 315-B. F. P. 646666; abst. C. A. 1929, **23**, 2191.
7. E. P. 257622; abst. J. S. C. I. 1927, **46**, 379-B. H. Deutsch and W. Herrmann, D. R. P. 502431; abst. C. A. 1930, **24**, 4793.
8. D. R. P. 525836; abst. C. A. 1931, **25**, 4556. F. P. 703509; abst. C. A. 1931, **25**, 4284.
9. U. S. P. 1312186; abst. C. A. 1919, **13**, 2536.
10. U. S. P. 1450982; abst. C. A. 1923, **17**, 1969.
11. Ann. Chim. Phys. 1863, (3), **67**, 288.
12. Ann. Chim. Phys. 1863, (3), **69**, 323. See A. Faworski, Chem. Zentr. 1907, I, 15.

ence of a dehydrating agent[1]. Miscible in all proportions with water and organic solvents, and forms a constant boiling point mixture of 80% dioxane, 20% water of 86.8° at 742 mm.[2]. M. pt. 11°, b. pt. 101.1°, density at 20°, 1.0338, viscosity 0.01215 at 25°, refractive index (Abbe refractometer) 18°, 1.4238; 20°, 1.4232; 25°, 1.4203; 50°, 1.4181. The odor resembles butyl alcohol.

In addition to being a solvent for cellulose acetate and methyl, ethyl and benzyl-cellulose, dioxane dissolves glyceryl phthalate, ester gum, cumarone, dammar, shellac, elemi, kauri, sandarac, mastic and guaiac. To produce a clear lacquer of difficult inflammability[3], it is recommended to dissolve ethylcellulose 50 in a mixture of dioxane 60, benzene and butanol 20 each. Another lacquer formula is ethylcellulose (47% ethoxyl) 19, dioxane 81[4]. Or[5], cellulose ether dissolved in dioxane and thinned with benzene or toluene, or other miscible solvents[6]. As a general solvent for nitrocellulose, cellulose acetate, cellulose laurate and ethylcellulose, A. Knorr[7] recommends dioxane with dibutyl phthalate, methylcyclohexanone, methylglycol acetate and similar bodies. For the stretching of cellulose ether or cellulose acetate yarn[8], it is recommended to immerse in dioxane, when the extensibility increases 200-1000%. On account of its broad solvent capacity, dioxane has been advocated as a wetting-out agent in the dyebath[9],

1. A. Knorr and K. Steimmig, U. S. P. 1681861. Belg. P. 377434. G. Reid (U. S. P. 1879637) prepares 1.4-dioxane by reacting upon *bb'*-dichlordiethyl ether with hot, aqueous 5% NaOH.
2. E. Reid and H. Hoffmann, Ind. Eng. Chem. 1929, **21**, 695.
3. A. Knorr and I. G. Farbenindustrie, U. S. P. 1780883. E. P. 275653. F. P. 688315. See E. P. 245098.
4. I. G. Farbenindustrie, D. R. P. 542814; abst. Chem. Zentr. 1932, I, 2258.
5. Akt. Ges. fuer Anilin Fabrikation, E. P. 245098.
6. I. G. Farbenindustrie, E. P. 326824; abst. Brit. Plastics, 1930, **2**, 75.
7. U. S. P. 1599569; abst. C. A. 1926, **20**, 3567; J. S. C. I. 1926, **45**, 1010-B.
8. K. Weissenberg and B. Rabinowitsch, E. P. 352445. See U. S. P. 1523459.
9. I. G. Farbenindustrie, E. P. 245098. D. R. P. 431249.

for the production of laminated glass[1], and as a non-solvent in cellulose benzopyruvate mixtures[2].

On account of the fact that dioxane is a solvent both of the chloroform-soluble and acetone-soluble cellulose acetate, it has been proposed to utilize it in the hydrolysis of acetylcellulose, preferably diluted with glacial acetic acid which aids in the more rapid solution of the ester[3]. Brush and other heavier lacquers are formed by dissolving a cellulose ether in dioxane, cyclohexanone or dimethylacetal and adding thereto a synthetic resin of urea or methylurea with formaldehyde[4]. A. Noll[5] in 1927 reviewed the newer cellulose ether solvents and their properties, including dioxane. 1.4-Dioxane should not be confused with *p*-dioxane (tetrahydro-*p*-dioxin) or *m*-dioxane (dihydro-*m*-dioxin). (See p. 119, n. 4; 124, n. 3; 283, n. 3; 301, n. 2; 698, n. 2; 938, n. 3; 1020, n. 1).

Aliphatic Ketones. In 1892 A. Seher[6] disclosed the use with pyroxylin of propione, butyrone, valerone, caprone, methylethyl ketone, methylpropyl ketone, methylbutyl ketone, methylvaleral, ethylbutyl ketone and methylamyl ketone. This was followed by the J. Stevens disclosures five years later[7], covering the use with cellulose nitrates of methylethyl, methylpropyl, methylbutyl, methylpentyl (methylamyl), methylhexyl, ethylpropyl, ethylbutyl, ethylpentyl (ethylamyl), ethylhexyl, propylbutyl, propylpentyl (propylamyl), propylhexyl and butylpentyl (butylamyl) ketones. In connection with polymerized vinyl esters[8], and cellulose derivative lacquers, the solvent properties of

1. Brit. Celanese, Ltd., E. P. 347777, 347972.
2. C. Webber and C. Staud, U. S. P. 1861200.
3. *Ibid.* U. S. P. 1826335; abst. C. A. 1932, **26**, 598. See U. S. P. 1823359.
4. I. G. Farbenindustrie, E. P. 344626; abst. C. A. 1931, **25**, 4725.
5. Papierfabr. 1927, **25**, 65; abst. C. A. 1928, **22**, 4795.
6. U. S. P. 470451.
7. J. Stevens, U. S. P. 595355.
8. Chemische Fabrik Griesheim-Elektron, D. R. P. 291299, Addn. to D. R. P. 290544; abst. J. S. C. I. 1916, **35**, 698. D. R. P. 474086.

methylethyl ketone, acetophenone, benzaldehyde, salicylaldehyde and chlorbenzene have been described.

As cellulose ether dissolvants, S. Carroll[1] has advocated methylethyl, methylpropyl, methylbutyl, diethyl, dipropyl, di*iso*propyl, dibutyl and diamyl ketones, including acetone oil. As auxiliary solvent methyl or ethyl alcohols may be added to the ketones, an acceptable combination being 1 part water-insoluble ethylcellulose to 5 parts of one of the above compound solvents to obtain a thick, flowable solution. The I. G. Farbenindustrie[2] recommend preparing cellulose ether or ester lacquers by the use of *iso*propylethyl ketone or *iso*-butylethyl ketone.

Acetone, Dimethyl ketone, is one of the most widely used general solvents for the cellulose derivatives, dissolving alike the nitrocelluloses, cellulose acetates and the cellulose ethers, especially those of higher etherification. The earlier patent literature of the United States[3], England[4], Germany[5], France[6] and Canada[7] indicate the wide range

1. U. S. P. 1469812; abst. C. A. 1923, **17**, 3919; J. S. C. I. 1923, **42**, 1172-A; Faser. 1924, **6**, 11.
2. E. P. 330735; abst. C. A. 1930, **24**, 6041.
3. U. S. P. 269343, 381354, 463039, 470451, 471422, 507749, 510617, 517987, 542692, 543108, 551456, 552934, 552935, 553270, 559823, 561624, 566349, 578714, 596662, 598649, 621360, 783828, 797373, 855556, 881827, 884475, 888516, 894108, 927674, 942395, 972464, 974285, 974900, 979431, 988965, 999490, 1005454, 1015155, 1015156, 1021569, 1025217, 1027614, 1027615, 1027616, 1027617, 1027618, 1027619, 1035108, 1039782, 1050065, 1067785.
4. E. P. 6542, 6543, 1892; 21455, 1893; 6389, 12693, 1896; 7975, 27534, 1897; 13560, 1898; 20092, 1899; 7088, 9992, 1902; 4863, 15696, 1903; 5280, 22245, 26072, 28376, 1904; 26201, 1905; 11397, 11928, 1907; 19735, 1908; 1799, 11625, 24006, 1909; 1441, 1779, 6519, 8646, 10794, 12406, 14586, 21719, 1910; 2064, 2145, 4253, 6798, 10708, 16271, 16810, 20976, 21426, 1911; 18822, 23728, 28210, 1912; 2425, 7086, 8880, 17953, 25182, 26079, 28490, 1913; 714, 1262, 4668, 8126, 12895, 13100, 14042, 18268, 1914; 15428, 1915; 122679, 123628, 124515, 124763, 124807, 127027, 127615, 127678, 128215, 128274, 128659, 128974, 131369, 131647, 131669, 132996, 134228, 145510, 146212, 149319, 156752, 157126, 158521, 161564, 176367, 177268, 179234, 184671.
5. D. R. P. 80776, 103726, 151918, 185808, 189703, 202720, 210519, 211520, 238361, 240751, 242467, 242786, 244566, 246657, 253984, 267992, 276661, 279127, 281265, 284672, 295764, 314317, 331285, 352905, 364347, 397919.
6. F. P. 184548, 320452, 322457, 324121, 333824, 336970, 340622, 342469, 344501, 351555, 368004, 374395, 379589, 387179, 379979, 387791, 393963, 397429, 402072, 412797, 413657, 415517, 415945, 418347, 420212,

of compounds in which acetone has been found suitable. Its low boiling point and miscibility with water in all proportions are its main drawbacks. The J. Donohue[1] cellulose ether composition combines acetone and benzene in the ratio of about 3 parts acetone to 11 parts benzene, dissolving alike ethylcellulose, propylcellulose and benzylcellulose, and is an unusually inexpensive solvent combination. A 12-20% solution of water-insoluble ethylcellulose may be made with the above mixture, which is transparent, flowable and from which films may be cast. Acetone has been extensively used as an airplane dope solvent[2], to dissolve celluloid[3], celluloid substitutes[4], cellulose acetate[5], cellulose

421843, 422763, 425900, 427804, 429788, 432264, 435417, 436538, 440955, 441146, 422819, 432483, 445638, 447645, 447664, 448808, 452432, 454379, 456261, 461034, 461544, 463156, 463622, 464617, 464646, 467800, 469872, 470092, 472423, 477294, 491490, 495000, 498949, 499868, 501700, 508975, 521370, 562056, 580882, 580883, 596838, 601547, 601662, 611899.

7. Can. P. 238217, 259662, 260927, 260463, 261371, 268571.

1. U. S. P. 1552797; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, I, 540; Caout. et Gutta. 1926, **23**, 13316.

2. See G. Kita, I. Sakurada and T. Nakashima, Cellulosechemie, 1928, **9**, 13. E. Desparmet, Cuir Tech. 1928, **21**, 56. C. Gabriel, Paint, Oil and Chem. Rev. 1925, **80**, #6, 10. R. Remler, J. Ind. Eng. Chem. 1923, **15**, 717.

3. U. S. P. 1128094, 1140174, 1141224, 1150047, 1153574, 1160041, 1181758, 1202495, 1205822, 1210987, 1221457, 1223538, 1287793, 1294355, 1300550, 1322631, 1326639, 1331127, 1342767, 1352216, 1366256, 1370853, 1377677, 1389574, 1389575, 1393290, 1408816, 1419998, 1425510, 1443012, 1446049, 1446050, 1461161, 1467749, 1472165, 1477880, 1477881, 1477882, 1477883.

4. U. S. P. 1153596, 1158961, 1160063, 1181853, 1181860, 1185074, 1188356, 1189841, 1195040, 1199798, 1200886, 1216581, 1217027, 1241738, 1245476, 1331127, 1353384, 1353385, 1363763, 1386576, 1420028, 1440006, 1488294, 1501206, 1508928, 1510779, 1512751.

5. U. S. P. 1128468, 1132384, 1133385, 1136248, 1142619, 1143877, 1143878, 1143979, 1156894, 1160979, 1165179, 1175791, 1181758, 1181857, Re-14338, 1181860, 1184257, 1185514, 1188797, 1188798, 1188799, 1188800, 1195040, 1195673, 1199798, 1199800, 1201260, 1203756, 1216581, 1217722, 1226342, 1236578, 1242783, 1244107, 1244108, 1244347, 1244348, 1244349, 1245476, 1260977, 1275884, 1286172, 1298199, 1303563, 1309980, 1310841, 1316311, 1319229, 1320290, 1338661, 1342601, 1342602, 1342603, 1343135, 1351652, 1353384, 1353385, 1354401, 1354726, 1357447, 1363763, 1370879, 1386576, 1388472, 1392849, 1393355, 1394890, 1395401, 1397103, 1406224, 1408095, 1410790, 1417587, 1418347, 1420028, 1421341, 1426521, 1429295, 1432367, 1434634, 1437828, 1437829, 1440006, 1440178, 1441185, 1449157, 1453764, 1454959, 1454960,

esters[1], cellulose nitrate[2], the cellulose ethers[3], ethylcellulose[4], in the coating of fabrics[5], film manufacture[6] especially photographic film[7], as component in finish removers[8], liquid fuels[9], electric insulation[10], lacquer production[11], artificial leather fabrication[12], in producing

1454961, 1463864, 1465937, 1465994, 1467493, 1469815, 1476392, 1478137, 1484004, 1488294, 1494479, 1494816, 1494830, 1501206, 1508928, 1516225.

1. U. S. P. 1295533, 1316311, 1345354, 1351652, 1370853, 1389084, 1397986, 1408095, 1408423, 1429153, 1437952, 1454959, 1454960, 1454961.

2. U. S. P. 1135026, 1139112, 1141224, 1142619, 1143877, 1143878, 1147850, 1158961, 1160041, 1160979, 1173628, 1181758, 1194095, 1195040, 1197304, 1204709, 1208358, 1256240, 1260977, 1269339, 1290794, 1309981, 1316311, 1320458, 1321611, 1321633, 1321634, 1323624, 1323792, 1324227, 1327197, 1329386, 1329525, 1342601, 1342602, 1351652, 1354401, 1356440, 1360759, 1370853, 1370878, 1370922, 1377761, 1379596, 1380258, 1382077, 1388546, 1390537, 1393355, 1394890, 1398239, 1398525, 1398939, 1408095, 1410790, 1415059, 1418347, 1421341, 1427941, 1429174, 1429295, 1430020, 1431900, 1432368, 1434453, 1434454, 1437828, 1437829, 1441203, 1441204, 1441205, 1449157, 1453764, 1454961, 1456782, 1463864, 1464012, 1466733, 1469815, 1469839, 1476392, 1480016, 1484004, 1493207, 1493208, 1497137, 1497138, 1503835, 1510739, 1518396.

3. U. S. P. 1217027, 1217028, 1389084, 1429179, 1437952, 1454959, 1454960, 1454961, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105, 1500366.

4. U. S. P. 1188376, 1217027, 1217028, 1429153, 1429179, 1432366, 1432367, 1432368, 1441142, 1454959, 1454960, 1454961, 1467071, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105, 1469816, 1500366.

5. U. S. P. 1141224, 1316782, 1316783, 1395242.

6. U. S. P. 1217027, 1241738, 1347801, 1351652, 1353384, 1353385, 1354401, 1354726, 1363763, 1429153, 1429174, 1440006, 1480016, 1484004, 1488608, 1501206, 1502945, 1508928, 1514283, 1518396.

7. U. S. P. 1199800, 1226342, 1229485, 1229486, 1229487, 1342601, 1342602, 1342603, 1388472, 1415059, 1429179, 1431900, 1432366, 1432367, 1432368, 1434453, 1434454, 1437828, 1437829, 1441142, 1441185, 1444333, 1486245, 1488294, 1493000, 1494479, 1500366, 1512751.

8. U. S. P. 1140449, 1145365, 1145980, 1147851, 1147852, 1160394, 1167462, 1167640, 1167641, 1172773, 1173628, 1185641.

9. U. S. P. 1158367, 1271115, 1360872, 1420006, 1420622, 1438823, 1460767, 1469053, 1480368, 1480372, 1493874, 1496260, 1504837, 1516757.

10. U. S. P. 1156452, 1179357, 1185074, 1194201, 1236460, 1236959, 1241738, 1242592, 1242593, 1245981, 1267883, 1370666, 1392849, 1397144, 1398143, 1413144, 1413145, 1418891, 1439056, 1448556, 1452086, 1493062, 1500844, 1514508.

11. U. S. P. 1137374, 1156969, 1185514, 1187231, 1195673, 1229485, 1229486, 1229487, 1241738, 1242592, 1242593, 1245981,

molded articles[1], paint remover[2], as component in phenol-aldehyde condensate manufacture[3] and as a phenol-aldehyde solvent[4], in phonograph record production[5], plastic fabrication[6], artificial resin synthesis[7], synthetic silk manufacture[8], varnish preparation[9] and in waterproofing formulas[10]. For manufacture of acetone see pp. 462, 509, 869, 1012[11].

1347801, 1354154, 1377677, 1406498, 1437170, 1480016, 1488608, 1502945.

12. U. S. P. 1140174, 1141224, 1179357, 1217123, 1269339, 1308231, 1320458, 1392849, 1493062.

1. U. S. P. 1125906, 1175791, 1185074, 1241738, 1342067, 1354154, 1358394, 1370666, 1383864, 1392849, 1397144, 1398143, 1439056, 1442420, 1443936, 1448556, 1452086, 1500303, 1502945, 1514508, 1514509.

2. U. S. P. 1130499, 1143110, 1143111, 1143130, 1143877, 1143878, 1147848, 1147849, 1147850, 1173628, 1185641, 1189803, 1189804, 1201181, 1273307, 1274430, 1328080, 1381485, 1406175, 1483587, 1499101.

3. U. S. P. 1168626, Re-14087, 1187231, 1225748, 1225749, 1225750, 1242592, 1242593, 1342067, 1354154, 1358394, 1370666, 1414139, 1439056, 1442420, 1500303, 1500844.

4. U. S. P. 1087422, Re-14530, 14531, 1125906, 1133083, 1137374, 1146214, 1146300, 1150642, 1160363, 1160364, 1187231, 1188014, 1188439, 1211227, 1213051, 1213144, 1213726, 1225748, 1225749, 1225750, 1230829, 1236460, 1259472, 1259473, 1261615, 1277904, 1370666, 1377519, 1398143, 1398144, 1401633, 1404792, 1414139, 1418891, 1435721, 1439056, 1440097, 1441133, 1500303.

5. U. S. P. 1158964, 1328371, 1468608, 1468609.

6. U. S. P. 1156969, 1158961, 1175791, 1185074, 1189841, 1194201, 1199800, 1216581, 1229485, 1229486, 1229487, 1241738, 1317721, 1331127, 1367886, 1386576, 1388472, 1389084, 1397144, 1402969, 1440006, 1452086, 1468608, 1468609, 1482929, 1488608, 1502945.

7. U. S. P. 1194201, 1241738, 1397144, 1448556, 1451843, 1489744, 1500844, 1502945.

8. U. S. P. 1156969, 1189841, 1217028, 1347801, 1353384, 1353385, 1440006, 1441203, 1441204, 1441205, 1458542, 1484004, 1497321, 1501206, 1508928.

9. U. S. P. 1137374, 1187231, 1188439, 1195673, 1209333, 1228428, 1229485, 1229486, 1229487, 1242592, 1242593, 1251863, 1347801, 1354154, 1354726, 1392849, 1395242, 1413144, 1413145, 1429174, 1431080, 1437170, 1440006, 1443935, 1444333, 1451843, 1481485, 1482929, 1502945.

10. U. S. P. 1165179, 1241738, 1382077, 1388827, 1388828, 1389084, 1395242, 1453764.

11. For other acetone manufacturing processes, see also, U. S. P. 1129542, 1148104, 1168785, 1169321, 1169322, 1196290, 1197983, 1201850, 1202317, 1250282, 1271591, 1282805, 1315525, 1315544, 1322737, 1365053, 1427595, 1438123, 1470885, 1487456, 1488278, 1497817, 1499363, 1502896, 1510526, 1516701.

Dichloracetone has been described as a desirable acetylcellulose solvent[1]. It dissolves acetone-soluble acetylcellulose perfectly, and associated with a small proportion of ethyl alcohol or methyl or ethyl acetates, constitutes an excellent solvent for both ethyl- and benzyl-cellulose. The H. Buc process is for the manufacture of pentachloracetone[2]. Acetylacetone of the ideal b. pt. of 137°, coupled with methyl or ethyl alcohol has been patented as a desirable cellulose ether solvent, especially for dissolving ethylcellulose[3]. Equal parts of acetylacetone and methyl alcohol make an acceptable solvent combination. Not to be confused with acetonyl acetone, which is 2.5-diketohexane, a liquid of pleasant odor boiling at 188°. H. Dreyfus[4] has used acetylacetone in several of his processes as an acetylcellulose direct solvent. Methyleneacetone, b. pt. 80°, and methyl*iso*propenyl ketone, b. pt. 96° have been advocated as methyl-, ethyl- and benzyl-cellulose solvents, especially applicable in those compositions containing a synthetic resin of the diphenylol-propane-formaldehyde, diphenylolbutane-formaldehyde, cresol-formaldehyde and xylenol-formaldehyde types[5].

Methylethylketone, Methyl Acetone, the next higher member of the aliphatic ketone series, has been used extensively in the cellulose derivative art[6], being the lower boiling fraction of light acetone oil. The processes of J. Adler[7], W. Alexander and J. Clegg[8], R. Quait[9], J. Weidig[10],

1. H. Dreyfus, F. P. 432264; abst. J. S. C. I. 1912, **31**, 24.
2. H. Buc, U. S. P. 1391757; abst. J. S. C. I. 1921, **40**, 827-A.
3. J. Donohue, U. S. P. 1552800; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, I, 795; Caout. et Gutta. 1926, **23**, 13316.
4. U. S. P. 1363763. E. P. 131669. F. P. 432264, 501700.
5. Brit. Celanese, Ltd., E. P. 359387.
6. U. S. P. 470451, 595355, 999490, 1021569, 1200886, 1298199, 1303563, 1315216, 1320458, 1358914, 1408035, 1469812, 1521859, 1529056, 1538861. E. P. 124515. F. P. 498949.
7. U. S. P. 1147066; abst. C. A. 1915, **9**, 2460.
8. U. S. P. 1358914; abst. C. A. 1921, **15**, 442; J. S. C. I. 1921, **40**, 399-A.
9. U. S. P. 1635862; abst. Plastics, 1927, **3**, 540.
10. U. S. P. 1775179; abst. C. A. 1930, **24**, 5157; Cellulose 1930, **1**, #9, 246.

D. Clark[1], F. Bohan[2], and the paint remover formula of C. Ellis[3], all employ methylethyl ketone—the latter process in association with ethylbutyl ketone. M. Ow-Eschingen[4] has described a cellulose ether and ester solvent composition embracing methylethyl ketone, dimethyl acetate, pyroxanthine, trimethylacetaldehyde, *iso*valeraldehyde and cyclopentanone, components of commercial wood oil. Ethylcellulose is said to dissolve quickly in wood oil. If methylethyl ketone were obtainable in unlimited quantities, it would probably be used to as large extent as acetone, being the equal of the latter in solvent power, less soluble in water, less hygroscopic and having a higher boiling point. Commercial methyl acetone usually contains 20-30% methyl acetate and 10% or more of methyl alcohol.

Diethyl Ketone has been advocated as a motor fuel[5] and for use in internal combustion engines[6].

Butyrone, Di-*n*-propyl Ketone, known commercially as Amyl ketol, is really a purified light acetone oil, in which butyrone predominates. It dissolves the cellulose ethers and the acetylcelluloses, but not the pyroxylins of lower nitrogen content[7], and has been used quite extensively in paint and varnish removers[8] on account of its slow evaporative capacity. Butylmethyl ketone dissolves celluloid[9] and the cellulose ethers[10]. Butylethyl ketone acts analogously.

Acetone Oils are an aggregation of high boiling ke-

1. U. S. P. 1495547; abst. C. A. 1924, **18**, 2258.
2. U. S. P. 1521859; abst. C. A. 1925, **19**, 739.
3. U. S. P. 985405.
4. U. S. P. 1794066; abst. C. A. 1931, **25**, 2289. E. P. 231161; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1926, **45**, 739-B; Ann. Rep. S. C. I. 1926, **11**, 131; Chem. Zentr. 1925, II, 872. See E. P. 28613, 1896. Aust. P. 99665. H. Pringsheim and A. Gorgas, Ber. 1923, **56**, 2035; 1924, **57**, 1561.
5. W. Schreiber, U. S. P. 1469053; abst. J. S. C. I. 1923, **42**, 1061-A.
6. M. Whitaker, U. S. P. 1420006.
7. U. S. P. 1283183.
8. U. S. P. 1130499, 1143110, 1143111, 1147851, 1147848, 1147849, 1172773, 1189803, 1189804.
9. H. Hibbert, U. S. P. 1158217; abst. C. A. 1915, **9**, 3363.
10. S. Carroll, U. S. P. 1469812; abst. C. A. 1923, **17**, 3919.

tones with (probably) many other materials, possessing a pungent and acrolein-like odor, very difficult to remove in purification. Roughly the distillation from the pyrogenetic decomposition of wood and its neutralization with lime, being the calcium salts of a series of aliphatic monocarboxylic acids, when dry distilled yield acetone oils after the acetone has been removed. This higher fraction is conveniently divided into "light acetone oil" and "heavy acetone oil." But little use has commercially been made of the latter, primarily on account of its disagreeable and penetrating smell. G. de Briailles combined acetone oil with nitrocellulose and gelatin as a celluloid substitute[1]; W. Scheele[2] has described an enamel of copal, cellulose nitrate and acetone oil, b. pt. 80-227°; and the Zapon-Lack Ges.[3] have detailed varnish formulas combining pyroxylin, coumarone resin and acetone oil.

Stearone, a homologue of acetone[4], either alone or associated with palmitin, has been patented by R. Schüpphaus as a desirable softener for nitrocellulose in varnish and enamel manufacture.

Diacetone Alcohol, 4-Hydroxy-2-keto-4-methylpentan, Alco Deo, Dial, Diacetonyl Alcohol, Pyranton A, may be prepared by the methods of W. Heintz[5], A. Hoffmann[6], C. Crockett[7] and W. Doerflinger[8], the latter[9] being the first to point out the advantages of this solvent in the cellulose ester

1. E. P. 8542, 1908; abst. J. S. C. I. 1908, **27**, 877.
2. U. S. P. 1408035.
3. U. S. P. 1185514. F. P. 471104. D. R. P. 281265.
4. U. S. P. 410209. Stearone is insoluble in water, soluble in hot alcohol or ether, melts at 88° and has a density of 0.80.
5. Ann. 1875, **178**, 342; abst. Chem. Zentr. 1875, 805; Jahr. Chem. 1875, 281; Bull. Soc. Chim. 1876, (2), **26**, 412; J. C. S. 1876, **30**, i, 375. Ann. 1873, **169**, 114; abst. Chem. Zentr. 1874, **21**, 452; J. C. S. 1874, **27**, 145.
6. D. R. P. 229678; abst. C. A. 1911, **5**, 2535. U. S. P. 1082424; abst. C. A. 1914, **8**, 788.
7. U. S. P. 1075284; abst. C. A. 1913, **7**, 4046. D. R. P. 295822.
8. U. S. P. 1066474; abst. C. A. 1913, **7**, 2994.
9. W. Doerflinger, U. S. P. 1003438; abst. C. A. 1911, **5**, 3922. E. P. 11728, 1911; abst. C. A. 1912, **6**, 3183. F. P. 429754. D. R. P. 246967; abst. C. A. 1912, **6**, 2529. Can. P. 136538; abst. C. A. 1912, **6**, 303.

and ether art. A satisfactory solvent combination[1] is diacetone alcohol, *n*-butyl alcohol, benzene and a ketone, or[2] acetone 400, diacetone alcohol 25-40, the latter being recommended in cellulose acetate silk formation. The published processes of W. Edmonds[3], P. Sawyer[4], G. Trumpler[5], A. Jones[6], and the I. G. Farbenindustrie[7] indicate the range of methods of application. The latter prepare lacquers of cellulose acetate and soluble resinous products obtained by the condensation of dibasic organic acids with hydroxylalkyl ethers of the polyhydric alcohols, using diacetone alcohol, glycol monoalkyl ether and its lower fatty acid esters or methyl acetate.

Diacetone alcohol may be used alone or admixed with tetrachlorethane, trichlorethylene, methylcyclohexanone or cyclohexanone[8]. Airplane dope[9], acetylcellulose direct solvent[10], imitation gold leaf production[11] and artificial leather coating are some of its indicated spheres of usefulness.

This solvent boils at 163.5-164.5°, sp. gr. 0.93 at 25°. The commercial article has a sp. gr. of 0.91-0.925, depending upon the amount of mesityl oxide and unchanged acetone therein. The higher the sp. gr. of diacetone alcohol, the less acetone does it contain. It is miscible with water, alcohol, acetone, chloroform, acetylene tetrachloride and butyl and amyl acetates without turbidity, and is a poor solvent of castor and other vegetable and animal oils. It dissolves colophony, mastic, sandarac, elemi, shellac, glyceryl phthalate resin, benzyl abietate, coumarone and guaiac.

1. W. Doerflinger, U. S. P. 1320458; abst. Kunst. 1921, **11**, 14.
2. H. Dreyfus, E. P. 182166; abst. J. S. C. I. 1922, **41**, 627-A.
3. U. S. P. 1550792; abst. C. A. 1926, **20**, 51.
4. U. S. P. 1575940.
5. E. P. 294261; abst. C. A. 1929, **23**, 2050. F. P. 668125; abst. C. A. 1930, **24**, 1528.
6. E. P. 275949; abst. C. A. 1928, **22**, 2476.
7. E. P. 322541, 322542, 322543.
8. P. Head, E. P. 299900.
9. W. Doerflinger, U. S. P. 1345354. W. Ross, U. S. P. 1440178.
10. U. S. P. 1160979, 1345354, 1434634, 1440178, 1467493.
11. J. Fichtmueller, U. S. P. 1160979.

A series of cyclic oxides have been brought to the attention of workers in this field as substitutes for camphor in both the cellulose nitrate and acetate fields[1], comprising diacetone arabite, diacetone adonite, triacetone mannite, benzylidene glycerol, cineol, pinol, paraldehyde, glycid, glycid acetate, ethylglycid ether, methylene ethylene ether, glycerol monochlorhydrineformal, erythritediformal, adonitediformal, rhamnitediformal, mannitetriformal, ethylideneglycol ether, ethylidenepropylene ether, acetoglycerol, triethylidenemannite, acetoneglycerol and diacetonerybite. Apparently but little is as yet known as to their specific advantages.

Mesityl Oxide, *4-Methyl-3-pentanone, isoPropylidene Acetone, 2-Methylpentan-(2)-on-4,* is an unsaturated ketone obtained by boiling acetone with 0.05-0.1 part of aniline hydrochloride with reflux cooling[2]; from diacetone alcohol by treatment with an equal amount of concentrated sulfuric acid or zinc chloride at high temperature[3]; by action of silicon tetrachloride on acetone[4]; or by heating diacetone alcohol with a small amount of HCl[5]. It occurs in acetone oils with phorone, has a rather powerful odor, boils at 129.5°[6], and sp. gr. 20°/4°, 0.857[7]. Insoluble in water, miscible in all proportions with alcohol and ether[8].

It is an excellent solvent for cellulose nitrate and acetate, and for methyl-, ethyl- and benzyl-cellulose. C. Crockett described a nitrocellulose solvent of mesityl oxide, ethyl acetate and benzene[9]; V. Sease dissolves acetate in mesityl

1. A. Lorenz, U. S. P. 996191.
2. E. Knoevenagel, D. R. P. 162281, Addn. to D. R. P. 161171; abst. Chem. Zentr. 1905, II, 726.
3. M. Kohn, D. R. P. 208635; abst. Chem. Zentr. 1909, I, 1282. See pp. 95, 513, 574, 801.
4. J. Currie, J. A. C. S. 1913, **35**, 1061; abst. J. C. S. 1913, **104**, i, 1043.
5. A. Hoffmann, U. S. P. 1474035. See J. Hertkorn, D. R. P. 258057. F. P. 440445. U. S. P. 1030177.
6. W. Perkin, J. C. S. 1888, **53**, 587.
7. J. Bruehl, Ann. 1885, **235**, 7.
8. R. Fittig, Ann. 1859, **110**, 34.
9. U. S. P. 1437170.

oxide or diacetone alcohol[1]; P. Seel[2] has described mesityl oxide as a cellulose ether solvent, and L. Clement and C. Riviere[3] a dissolving mixture for cellulose ether composed of mesityl oxide, phorone or diacetone alcohol. H. Hibbert[4] prepares mesityl oxide by distilling diacetone alcohol with 0.01% iodine, and C. Simms[5] methyldiacetone ether by acting on mesityl oxide with methyl alcohol.

This solvent has also been employed in the flotation of ores[6], as a vulcanization accelerator, and as a paint remover with phorone, xylitone and *iso*xylitone[7]. (See p. 95, n. 2; 513, n. 4; 574, n. 4; 801, n. 1.)

Phorone, obtained with mesityl oxide by saturating acetone with HCl gas[8], forms yellowish-green prisms, m. pt. 28°, boils at 197.2° at 743 mm., and has been patented for the manufacture of di- and tri-acetoneamine[9].

Acetoxime, Propanoxime, Acetonoxime, *b*-Oximinopropane, *b-iso*Nitrosopropane, Acetone oxime, a ketoxime smelling like chloral, m. pt. 59-60°, b. pt. 135°, dissolves readily in water, alcohol and ether, from which it crystallizes well[10]. It forms a methylethyl ketoxime, b. pt. 152-153°; methyl-*n*-propyl ketoxime, b. pt. 168°; methyl-*n*-butyl ketoxime, b. pt. 185°; methyl*iso*propyl ketoxime, b. pt. 157°; and methyl-*ter*-butyl ketoxime (pinacoline oxime), m. pt.

1. U. S. P. 1434634, 1488294.
2. U. S. P. 1469826. It is recommended to dissolve the cellulose ether, as water-insoluble ethylcellulose, in mesityl oxide until a strong, viscous solution is obtained, using 1 part of the ether to 5-7 parts mesityl oxide. As indicated by its boiling point, mesityl oxide has a relatively low volatility and speed of evaporation, and hence film formed therefrom cures rather slowly. A more rapid setting and satisfactory solvent combination is cellulose ether 100, mesityl oxide 20, methyl acetate 450, methyl alcohol 50. Optional solvents are triphenyl and tricresyl phosphate, camphor and monochlornaphthalene.
3. F. P. 505073.
4. E. P. 5408, 1914; abst. J. S. C. I. 1914, **33**, 984. For other methods for producing mesityl oxide, see U. S. P. 1164647, 1370843, 1473285, 1474035.
5. U. S. P. 1823704.
6. R. Sayre, U. S. P. 1415899.
7. C. Ellis, U. S. P. 985405.
8. A. Baeyer, Ann. 1866, **140**, 297, 301.
9. H. Fisher, U. S. P. 1473285; abst. J. S. C. I. 1924, **43**, 25-B. For manufacture of phorone, see U. S. P. 1370843.
10. H. Wege, Ber. 1891, **24**, 3537.

75°. Acetoxime in the presence of acetone has been described by S. Carroll[1] as a cellulose ether solvent, and a process for *iso*propylamine manufacture has been evolved[2], using acetoxime.

Aromatic Ketones. In 1898, J. Stevens[3] obtained patent protection for the use as pyroxylin plasticity-inducing bodies of dimethylhydrochinone (dimethylhydroquinone), thymochinone (thymoquinone, thymoil), thymol, and benzoylguaiacol (benzosol). R. Schüpphaus[4] followed with anthraquinone (diphenyl ketone) and alcohol, while E. Zühl[5] called attention to the advantage of replacing camphor in nitrocellulose plastics by methylnaphthyl ketone, dinaphthyl ketone, methyloxynaphthyl ketone and dioxydinaphthyl ketone. H. Dreyfus[6] disclosed the advantages of associating acetylcellulose with benzophenone, *o*- and *p*-methylacetophenone, ditolyl ketone, methoxy- or ethoxy-acetophenone, in combination with methyl- or dimethyl-cyclohexanone or cyclonaphthanone. He also described[7] the uses of methoxy- and ethoxy-acetophenone, especially in conjunction with benzyl alcohol, chlorbenzyl alcohol and diphenyl carbinol. P. Breteau and H. Leroux added tetra- and hexa-hydrobenzyl ketones and hydronaphthyl ketone[8], and R. Ortmann[9] methylethyl, methylnaphthyl, dinaphthyl, methoxynaphthyl and dinaphthyl ketones. Acetophenone, m. pt. 20.5°; benzylidene acetone, m. pt. 41-42°; benzophenone, m. pt. 48°; phenylbenzyl ketone; oxyacetophenone, m. pt. 86°; benzil, m. pt. 95°; dibenzylideneacetone, m. pt. 112°; trioxybenzophenone, m. pt. 133-134°; *p*-oxybenzophenone, m. pt. 134°; oxyphenylbenzyl ketone (benzoïn),

1. U. S. P. 1813660; abst. C. A. 1931, **25**, 5287.
2. J. Blagden, U. S. P. 1239867; abst. C. A. 1917, **11**, 3277.
3. U. S. P. 607554. 4. U. S. P. 410205.
5. E. P. 20733, 1900; abst. J. S. C. I. 1901, **20**, 273. F. P. 305481. Zuehl & Eisemann, D. R. P. 122166; abst. J. S. C. I. 1901, **20**, 926.
6. E. P. 20975, 1911. F. P. 19680, Addn. to F. P. 432264.
7. U. S. P. 1181680. E. P. 128215.
8. F. P. 409557; abst. J. S. C. I. 1910, **29**, 752.
9. E. P. 5280, 1904. F. P. 342464; abst. J. S. C. I. 1904, **23**, 949; 1905, **24**, 344.

m. pt. 137°; and trioxyacetophenone (gallacetophenone), m. pt. 168° were described as plasticizing elements in 1898[1].

m-Styrene (styrol, phenyl-ethylene, vinylbenzene), and methyl-, ethyl- and chlor-styrene have been described by W. Lawson for coating compositions with dibutyl phthalate, dixylylethane, glyceryldibenzyl ether or butyl stearate as associate solvents and softening bodies[2].

Acetophenone, Methylphenyl Ketone, Hypnone, Acetylbenzene, Methylbenzoyl, Agent AHN, b. pt. 200°, sp. gr. 1.031 at 15°, has been patented by S. Carroll[3] as a cellulose ether dissolving body, preferably associated with methyl or ethyl alcohols or acetates or with acetone. A preferred formula is to dissolve 1 part triethylcellulose in a mixture of 5 parts of a mixed solvent containing acetophenone 1 to methyl acetate 3. L. Lederer[4] combines acetophenone with phenol, chloral hydrate, acetamide and aniline; C. Mijnssen[5] with chlorhydrin, guaiacol, acetin and aniline; the Chemische Fabrik Griesheim Elektron[6] with nitromethane, benzaldehyde and salicylaldehyde; while D. Spence and A. Clark[7] prepare an artificial rubber using methylstyryl ketone.

1. R. Schuepphaus, U. S. P. 598649.
2. E. P. 311700; abst. C. A. 1930, **24**, 980.
3. U. S. P. 1467098; abst. Chem. Met. Eng. 1923, **29**, 679.
4. U. S. P. 774677; abst. J. S. C. I. 1904, **23**, 1159. E. P. 7088, 1902; abst. J. S. C. I. 1903, **22**, 563. F. P. 319724; abst. J. S. C. I. 1902, **21**, 1550; Mon. Sci. 1903, (4), **59**, 123. Addn. 811 dated Mar. 18, 1902, to F. P. 319724; abst. J. S. C. I. 1903, **22**, 563. D. R. P. 145106; abst. Jahr. Chem. 1904, 1168; Mon. Sci. 1904, (4), **60**, 93; Zts. ang. Chem. 1903, **16**, 1090; Chem. Zentr. 1903, II, 1155. D. R. P. 151918, Addn. to D. R. P. 145106; abst. Chem. Zentr. 1904, II, 1180; Jahr. Chem. 1904, 1168. D. R. P. 152111.
5. U. S. P. 1005454; abst. C. A. 1912, **6**, 153; J. S. C. I. 1911, **30**, 1249. E. P. 476, 1910; abst. J. S. C. I. 1910, **29**, 1082; Mon. Sci. 1913, **78**, 392. F. P. 411298; abst. J. S. C. I. 1910, **29**, 978; Phot. Ind. 1910, 1221; Eder's Jahr. Phot. 1911, 526; Mon. Sci. 1913, **78**, 392. Aust. P. 50656; abst. Kunst. 1912, **2**, 77. Belg. P. 222106; abst. Chem. Ztg. 1910, **34**, 450; Mon. Sci. 1913, **78**, 392. Hung. P. Appl. M-3691, 1909. Ital. P. 115776; abst. Chem. Ztg. 1912, **36**, 817. Swiss P. 51839; abst. Chem. Ztg. 1911, **35**, 930; Kunst. 1912, **2**, 77; Mon. Sci. 1913, **78**, 392.
6. D. R. P. 291229, Addn. to D. R. P. 290544; abst. J. S. C. I. 1910, **35**, 698. See also D. R. P. 281877.
7. U. S. P. 1161904; abst. C. A. 1916, **10**, 295.

The brom- and nitro-derivatives of acetophenone, methylstyryl ketone, benzophenone, phenylbenzyl ketone, oxyacetophenone, benzil, dibenzylidene acetone, trioxybenzophenone, *p*-oxybenzophenone, oxyphenylbenzyl ketone, trioxyacetophenone[1] have also been advanced as peculiarly advantageous camphor substitutes. Acetophenone has also been used in the production of abrasives in a binder[2], as a paint remover[3] and for artificial rubber synthesis[4]. Chloracetophenone[5] has been recommended as an irritating gas suitable for use in shells, and dihydroxybenzophenone[6] with acetone as a cellulose acetate plastifiant. Benzylacetone (methylphenylethyl ketone) added in small amounts to a mixture of ethylcellulose in methyl alcohol and methyl acetate materially lowers the viscosity of the solution. An amount of benzylacetone equivalent to one-seventieth of the combined weight of methyl alcohol and acetate, will lower the viscosity of a thick solution of cellulose ether in such a mixture by 15-20%[7].

The solid aromatic ketone tetrahydromethylpropylbenzene has been put forth as a pyroxylin solvent by H. Blackmore[8]. It melts at 210°, and has an aromatic, camphoraceous odor. Benzyldihydrocarvone, methane-2-on, found in caraway oil, and benzylidenedihydrocarvone; *a*-naphthyldihydrocarvone, and benzyldihydropulegone, the benzyl derivative of pulegone, methene-3-ketone, have been described as plastifiers for acetylcellulose[9].

Aliphatic Acids. Formic acid is a solvent of cellulose

1. R. Schuepphaus, U. S. P. 598649. See also U. S. P. 410205, 410206, 528812.
2. L. Redman, U. S. P. 1209333; abst. C. A. 1917, **11**, 710.
3. C. Ellis, U. S. P. 985405; abst. C. A. 1911, **5**, 1527.
4. H. Stern, U. S. P. 1218332; abst. C. A. 1917, **11**, 1574.
5. N. Oglesby and D. Ehrenfeld, U. S. P. 1864754; abst. C. A. 1932, **26**, 4393.
6. W. Moss, Can. P. 319733; abst. C. A. 1932, **26**, 2593.
7. E. Farrow, U. S. P. 1494474; abst. C. A. 1924, **18**, 2249; J. S. C. I. 1924, **43**, 593-B.
8. U. S. P. 830044.
9. B. Zelinski, D. R. P. 202720; abst. Chem. Zentr. 1908, II, 1837.

acetate[1], formylcellulose[2], ethylcellulose[3], and cellulose ethers[4]. Formic and acetic acids have been used to toughen acetylcellulose films[5] and to increase the pliability of pyroxylin films[6]. To increase adhesion of pyroxylin lacquers to a leather surface, it is advised to apply acetic acid to the surface of the leather, and then spread on the lacquer[7]. Formic, lactic, tartaric or oxalic acids are considered as equivalents. Furfural with formic or acetic acid[8] has been patented as an energetic nitrocellulose solvent, and also[9] as a useful addition to celluloid plastics to prevent crystallization of the camphor substitutes (as ethylacetanilid) which may be used therein. In the preparation of celluloid substitutes using pyroxylin[10], in the dyeing of acetylcellulose[11], and as a solvent for the same[12], formic acid has but a limited use on account of the effects of its vapors on the eyes and mucous membranes when in the concentrated condition.

Acetic Acid has been employed in the production of celluloid substitutes[13], as a celluloid solvent[14], to dissolve[15] and to dye cellulose acetate[16], to dissolve cellulose esters[17],

1. Furst Guido Donnersmarck'sche Kunstseiden und Acetatwerke, U. S. P. 922340. E. P. 6554, 1909. F. P. 400652. D. R. P. 237718. J. Hübner, E. P. 127027.
2. E. Bronnert, U. S. P. 1029341. E. P. 8313, 1911. F. P. 428069. See also R. Woodbridge, J. A. C. S. 1909, **31**, 1067; abst. C. A. 1910, **4**, 667.
3. L. Lilienfeld, U. S. P. 1217027; abst. C. A. 1917, **11**, 1545.
4. *Ibid.* U. S. P. 1563205; abst. C. A. 1926, **20**, 465; Plastics, 1926, **2**, 12; Chem. Zentr. 1926, I, 2397.
5. British Cellulose and Chemical Mfg. Co., E. P. 179234; abst. C. A. 1922, **16**, 3394.
6. A. Ott, E. P. 184495. 7. J. Paisseau, E. P. 255803.
8. G. Meunier, F. P. 472423.
9. Chem. Fabrik vorm. Weiler-ter-Meer, D. R. P. 343182.
10. U. S. P. 1153596, 1217027, 1245976, 1245984, 1280862.
11. U. S. P. 1448432, 1517581, 1517709.
12. U. S. P. 1296847, 1445382, 1457131, 1467493.
13. U. S. P. 1245818, 1245976, 1245983, 1245984, 1275324, 1280862, 1360356, 1363763, 1427645.
14. L. Mascart, U. S. P. 1342267. L. Crossman, U. S. P. 1425510.
15. U. S. P. 1275884, 1316311, 1342267, 1363763, 1420028, 1421341, 1457131, 1467493.
16. C. Shook, U. S. P. 1517591. R. Clavel, U. S. P. 1517709.
17. H. Levey, U. S. P. 1316311. L. Mascart, U. S. P. 1342267. L. Wilson, U. S. P. 1389084.

especially nitrocellulose[1], on airplane mending compositions[2] and wing dope[3]. The apparatus[4] and methods[5] of more modern acetic acid manufacture are listed below. The light-transforming composition of P. Hewitt[6] employs nitrocellulose in acetic acid as solvent.

Propionic Acid dissolves hydrated (acetone-soluble) acetylcellulose even in the cold in the presence of a small amount of alcohol, as likewise does it dissolve ethyl- and benzyl-cellulose. Neither propionic or butyric acids have been used commercially as cellulose ether solvents insofar as aware.

Butyric Acid, like propionic acid, dissolves acetyl-, ethyl- and benzyl-cellulose in the presence of a small proportion of ethyl alcohol, but not ethyl alcohol alone. Butyric acid has been mentioned as a celluloid solvent[7].

Higher Fatty Acids. Oleic acid[8] has been claimed as a cellulose acetate softening body possessing weak solvent powers, and the complex of fatty acids extractable from cocoanut oil, taken as an integer[9] has been specified and claimed as an efficient direct solvent for acetylcellulose, aided by the customary volatile solvents. Fluor(or chlor or brom)-stearic, -palmitic and -myristic acids form the

1. U. S. P. 1147850, 1148258, 1202712, 1299479, 1316311, 1321611, 1321633, 1321634, 1323624, 1342267, 1356440, 1421341.
2. L. Wilson, U. S. P. 1389084.
3. H. Dreyfus, U. S. P. 1363763. T. Tesse, U. S. P. 1521055, 1521056.
4. U. S. P. 1129542, 1140502, 1143319, 1157316, 1196329, 1225226, 1250282, 1315543, 1315546, 1327737, 1339489, 1431301, 1440852, 1471058, 1481326, 1485706, 1488278, 1495461, 1504385, 1510730.
5. U. S. P. 1123572, 1128780, 1129542, 1140502, 1143319, 1157316, 1159376, 1174250, 1178223, 1179420, 1193795, 1196329, 1201850, 1214518, 1225226, 1230899, 1241789, 1250282, 1271591, 1282805, 1283183, 1286255, 1286256, 1308173, 1315543, 1315546, 1327737, 1339489, 1359099, 1365053, 1400852, 1431301, 1437483, 1457484, 1463209, 1463212, 1471058, 1481326, 1485706, 1485844, 1488278, 1495461, 1504385, 1510284, 1510730, 1516701, 1521541.
6. U. S. P. 1188665; abst. C. A. 1916, **10**, 2157. U. S. P. 1188775; abst. C. A. 1916, **10**, 2157; J. S. C. I. 1916, **35**, 898.
7. H. Hibbert, U. S. P. 1158217.
8. H. Mork, A. Little and W. Walker, U. S. P. 712200.
9. G. Miles, U. S. P. 1357335; abst. C. A. 1921, **15**, 314. E. P. 146212; abst. C. A. 1920, **14**, 3528.

nitrocellulose solvent of the J. Aylsworth phonograph record base[1].

Lactic Acid as a cellulose formate[2] and nitro- and acetyl-cellulose solvent[3] has been known for some time, its chief drawback in addition to the feebleness of its solvency being a well marked hygroscopicity. E. Worden[4] unsuccessfully endeavored to increase the solubility of the cellulose formates by a partial hydration treatment analogous to that applied to the corresponding acetates. Many of the solvents of cellulose acetate do not dissolve the formic esters, lactic acid being a notable exception.

E. Bronnert and T. Schlumberger[5] found that 95° Trailles ethyl alcohol which does not dissolve certain types of cellulose nitrate may be used as a very good solvent provided about 5% of certain acids in a free state or in the form of their ethers or salts be employed, provided they are alcohol-soluble. These acids include oxalic, citric, tartaric, lactic and levulinic acids, or their potassium, sodium, ammonium, magnesium, calcium, strontium, aluminum or zinc salts.

Glycine, Glycocoll, Amidoacetic acid, Aminoethane acid, and Phenyl glycine (phenylglycocoll, anilidoacetic acid) have been used in their ester form in the cellulose ether and ester industries. Ethylphenylglycine (ethyl anilidoacetate) has been patented as a nitrocellulose plastifier and stabilizer[6], and acetylphenylglycine[7] as a cellulose ether solvent coupled with acetone. Methyl-, ethyl-, butyl- and phenyl-phenylglycine[8] have also been advocated as pyroxylin stabilizing bodies.

1. U. S. P. 855556; abst. C. A. 1907, **1**, 2500. U. S. P. 962877; abst. C. A. 1910, **4**, 2570.
2. E. Bronnert, U. S. P. 1029341.
3. C. Waite, U. S. P. 690211; abst. J. S. C. I. 1902, **21**, 272; J. A. C. S. 1902, **24**, 339.
4. Chem. Eng. 1913, **17**, 26; abst. C. A. 1913, **7**, 2304. See also U. S. P. 690211. E. P. 8313, 1911. F. P. 421854.
5. E. P. 6856, 1896. T. Schlumberger, D. R. P. 93009; abst. Wag. Jahr. 1897, **43**, 1103.
6. Canadian Industries, Ltd., Can. P. 295754.
7. S. Carroll, U. S. P. 1826687.
8. C. Burke, U. S. P. 1626916.

Glycid ether, glycid and glycidic ether[1], and phenyl glycid have been proposed as cellulose acetate softening bodies[2].

Aromatic Acids. Benzoic acid has been proposed as a solvent for celluloid manufacture[3], for nitrocellulose and cellulose acetate[4], and cellulose ethers, but there is a proneness to crystallize when benzoic acid solutions of cellulose derivatives are cast into films or fabricated into plastics and allowed to stand for some time. Cresylic acid as the dissolving medium for acetylcellulose[5], and salicylous acid and alcohol for hydrated acetylcellulose have also been advocated. The E. Farrow[6] cellulose ether solvent consists of benzoic acid with methyl alcohol or acetate, being especially applicable to water-insoluble ethylcellulose, and employed in about the proportion of 10% benzoic acid on the weight of the etherified cellulose. The salicylic acid added to the A. Pearl composition containing nitrocellulose[7] exerts but little solvent action, but does produce beautiful crystalline effects upon evaporation of the volatile solvent and crystallization of the salicylic acid.

Anthranilic acid, *o*-aminobenzoic acid, has been used by E. Farrow[8] for its lowering effect on the viscosity of cellulose ether solutions, and as a plasticizing body for the same in association with methyl acetate and methyl alcohol.

1. L. Ach, U. S. P. 996191. Other solvents mentioned are, cineol, pinol, paraldehyde, glycid, glycid acetate, ethyl glycid ether, methylene ethylene ether, glycerol monochlorhydrineformal, erythritediformal, adonitetriformal, rhamnitediformal, mannitetriformal, ethylideneglycolether, ethylidenepropylene ether, acetoglycerol, triethylidenemannite, diacetonerybite, acetone-glycerol, diacetone arabite, diacetone adonite, triacetone mannite, benzylidene glycerol and camphor.
2. H. Danzer, E. P. 13239, 1912. F. P. 443031. Other solvents are, diphenyl glyceryl ether, phenylglycide, chlorinated diphenylglyceryl ethers and dicresylglyceryl ethers.
3. B. Goldsmith, U. S. P. 1134527. S. Satow, U. S. P. 1245976, 1245984, 1280862.
4. H. Hibbert, U. S. P. 1283183.
5. A. Zimmer, J. Bryce and G. Davies, E. P. 124807; abst. C. A. 1919, **13**, 1771.
6. U. S. P. 1494472; abst. C. A. 1924, **18**, 2249.
7. U. S. P. 1844479; abst. C. A. 1932, **26**, 2057.
8. U. S. P. 1494470; abst. J. S. C. I. 1924, **43**, 593-B; Chem. Zentr. 1924, II, 2112.

An amount of anthranilic acid equal to 1/70th of the weight of the methyl acetate and methyl alcohol used, will lower the viscosity of a thick solution of cellulose acetate by about 15-20%. Methyl anthranilate is an important constituent of oil of orange blossoms, and this oil is a direct solvent of the cellulose ethers.

Dibromcinnamic acid, styrol dibromide, cinnamyl dibromide and cinnamylaldehyde dibromide[1] have been described as compatible additions to methyl-, ethyl and benzyl-cellulose in the ratio of 10-15% of the weight of cellulose derivative, for the double purpose of their gelatinizing effect and reduction of inflammability by virtue of the combined bromine contained therein.

Phosphoric Esters. Phosphoric acid, being tri-basic, allows of the formation of mono-, di- and tri-esters, and in both alkyl, aryl and aralkyl groups have been found derivatives which stand in the unique position of dissolving, either in the cold or by heat, the three classes of cellulose compounds, the nitrates, acetates and cellulose ethers; therefore they are of prime importance.

They may be briefly synopsized in classes as follows:

1. Triphenyl, tricresyl (tritolyl), trinaphthyl phosphates[2] (see page 1900).

2. Haloid substitution products of the above, including dichlor- and tetrachlor-phenyl-, cresyl- and naphthyl-phosphates, and in which fluorine, bromine and iodine may replace chlorine as in the above[3]. As a class they are prone to split off halogen on prolonged exposure to light, and discolor and decompose the compound in which they are incorporated.

3. Triphenyl, tricresyl, trinaphthyl, dichlordiphenyl, monochlortricresyl, dinitrotrinaphthyl, and tetranitrotri-

1. British Celanese, Ltd., E. P. 313535; abst. J. S. C. I. 1930, **49**, 1147-B. Addition to E. P. 313133. Can. P. 323144.
2. Zuehl & Eisemann, D. R. P. 128120, 142452. Russ. P. 7848, 1903. E. P. 8072, 1901. F. P. 309962.
3. *Ibid.* D. R. P. 142832.

naphthyl thiophosphates[1]. Triphenyl thiophosphate melts at 49°, boils at 245° at 11 mm. pressure, and has sp. gr. 1.2341 at 20°/4°.

4. Diphenyl, dicresyl, dinaphthyl phosphoric anilid or phenyl, cresyl or naphthyl dianilids[2]. One objectionable characteristic of these bodies as a class is their odor and proneness upon prolonged exposure to light as in an automobile laminated glass windshield, to yellow and to crystallize out. Excellent solvents and plastifiants of nitrocellulose and cellulose ethers, especially in the presence of a small amount of ethyl alcohol. Used in the proportion of 25-35% on the weight of the cellulose derivative.

5. Esters of phenyl-, cresyl- or naphthyl-phosphoric acid[3], including the methyl, ethyl and amyl diphenyl, dicresyl-, or dinaphthyl-phosphates; dimethyl, diethyl, diamyl phenyl-, cresyl-, naphthyl-phosphates; phenyl, cresyl, naphthyl phosphoric acid dianilids; diphenyl, dicresyl, dinaphthyl phosphoric acid anilid.

6. Tetranitrotrinaphthyl, dichlordiphenyl, monochlortricresyl, tricresyldinitrotrinaphthyl phosphates[4]; tricresyl, dichlordiphenyl, dinitrotrinaphthyl thiophosphates.

7. Tri-*m*-oxyphenyl phosphate (Tris-(3-oxyphenyl)-phosphate)[5], m. pt. 114°, and is soluble in alcohol, acetone and benzene.

8. Chlor(or brom- or iodo-)phenyl (or cresyl or xylenyl) phosphate[6].

9. Tri(*o*-diphenyl) phosphate[7]. M. pt. 114°. Soluble in benzene, alcohol and acetone; insoluble in petroleum ether or water. B. pt. above 300° at 10 mm.

10. Diphenylmonocresyl and monophenyldicresyl

1. Zuehl & Eisemann, D. R. P. 140164. Russ. P. 8893, 1904. F. P. 432264. See F. P. 309962 and Addn. 148 to F. P. 413657.
2. *Ibid.* D. R. P. 144648. E. P. 23445, 1902.
3. *Ibid.* D. R. P. 142971. E. P. 4383, 1902; 23445, 1902.
4. E. Zuehl, U. S. P. 729990, 733110. E. P. 872, 1901; 4383, 1902.
5. M. Theumann, U. S. P. 1870972.
6. British Celanese, Ltd., E. P. 313405.
7. E. Britton, U. S. P. 1858659.

phosphates are used together[1], preferably in the proportion of 55:45, as a mixed solvent for cellulose ethers. In this way, so it is claimed, the reduction of inflammability imparted by triphenyl phosphate, and the pliability induced by tricresyl phosphate may be obtained, without the disadvantages arising from the tendency of the former to crystallize out, and the latter to impart a greasy character to the film.

11. Diphenyl-*b*-naphthyl, phenyl-*m*-tolyl-*b*-naphthyl phosphate[2].

12. Tri*iso*amyl (b. pt. 143-144°, 2.5 mm.), di*iso*amylbutyl (b. pt. 121-122°, 15 mm.), diethyl*iso*amyl (b. pt. 84-85° at 2 mm.), di*iso*amylcyclohexyl phosphates (b. pt. 142° at 5 mm.)[3].

13. Dimethylglycolbutylglycol, dipropylglycolbutylglycol, butyldiethylglycol, benzyldimethylglycol, tributylglycol phosphates[4]. The tertiary phosphates of the uniform or mixed glycolmono-alkyl ethers (or -aryl ethers) are excellent solvents of the cellulose ethers, being colorless substances, of high stability and boiling point and low inflammability.

14. Methyl-, ethyl- or butyl-glycol phosphates; diethylglycolmonobutyl, diethylglycolbutyl, diphenylglycolbutyl phosphates, either alone or in conjunction with methylglycol acetate or glycol monomethyl ether acetate[5].

15. Tribenzyl, chlorbenzyl, hydroxybenzyl, tritolyl, chlortolyl, hydroxytolyl phosphates[6]. They are soluble in acetone, ethyl alcohol, chloroform or benzene, and do not discolor when exposed to light.

1. H. Hands and Spicers, Ltd., E. P. 294008. F. P. 659141. India P. 12998, 13089, 13856. Ital. P. 264194, 271718, 272478. Australia P. 15154. Aust. P. 118246. Belg. P. 353739.
2. H. Hands, E. P. 346339. Spicers, Ltd., D. R. P. 527737. Can. P. 289854. See F. P. 659141.
3. I. G. Farbenind., E. P. 308395. F. P. 674118. D. R. P. 539367.
4. *Ibid.* E. P. 352988. F. P. 693496.
5. C. Schoenburg, G. Wick and I. G. Farbenind., D. R. P. 549220. S. Shipley and G. Given, U. S. P. 1533616. D. Keyes, J. I. E. C. 1925, **17**, 1120.
6. F. Stockelbach, U. S. P. 1370853.

16. Monomethyldichlorphenyl, methylphenylchlorphenyl, dimethylchlorphenyl, dimethylmono(dichlorphenyl, diethylchlorphenyl) phosphates[1]. They are solvents of ethylcellulose and benzylcellulose.

17. Diphenylmonocresyl phosphate[2] (cresyldiphenyl phosphate), liquid at ordinary temperature and boiling with slight decomposition at atmospheric pressure at about 400°.

18. Tri(chlorethyl) phosphate[3] as an ethyl- or benzyl-cellulose solvent, either alone or in conjunction with hexachlorethane, hexachlorbenzene or dicresylglyceryl ether.

19. Di-, tri-, tetra-ethyleneglycol monomethyl (or ethyl, propyl, butyl or amyl) phosphate[4], the esters produced being orthophosphoric esters, solvents of the cellulose ethers to a moderate degree, films prepared therefrom having a high transparency, especially when equal parts of ethyl alcohol and chloroform are used in conjunction. Before use the esters are hydrolyzed to the dihydrogen alkyl ether of the glycol involved.

20. Methyldiphenyl, ethyldiphenyl, dimethylphenyl, diethylphenyl phosphates[5] are direct solvents of ethyl- and benzyl-cellulose, used in the proportion of about 20% on the weight of the cellulose ether.

21. *o*-Tricresyl phosphate[6].

22. Monophenyl-(or monocresyl)di-*b*-naphthyl, Diphenyl-(or dicresyl)mono-*b*-naphthyl, phenyl-*m*-cresyl-*b*-naphthyl phosphates, alone or with heptachlorpropane and/or resorcinol diacetate[7].

23. Triphenyl and tricresyl phosphates physically admixed[8], preferably in the ratio 15:12.

1. G. Zelger, U. S. P. 1685444.
2. A. St. John, U. S. P. 1462306.
3. Soc. Pathe Cinema, Anciens Etab. Pathe Freres, F. P. 612414.
4. A. Sulzer, U. S. P. 1826681.
5. G. Zelger, U. S. P. 1685443. Pathe Cinema, F. P. 606969.
6. L. Lilienfeld, U. S. P. 1140174. See U. S. P. 1037158.
7. H. Hands, E. P. 346339.
8. Pathe Cinema, F. P. 643884. E. P. 237900.

24. Tetrachlor-(or tetrabrom- or tetraiodo-)phenyl (or cresyl or xylenyl) phosphates, preferably the brom. If, for instance, tricresyl phosphate is brominated at room temperature so as to introduce 3 Br atoms, all the Br is substituted in the nucleus[1]. If bromination be carried out at 150° so as to introduce 4 Br atoms, about half the Br is introduced into the nucleus, the remaining half entering the side chain. By brominating at 180° so as to introduce 4 Br atoms, 3 enter the side chain and only one in the nucleus. These compounds are direct solvents of methyl-, ethyl- and benzyl-cellulose, the solvent power being increased by heat and the addition of alcohol, or a mixture of alcohol and benzene. Auxiliary solvents, softeners and plastifiers may be added, as triacetin, xylenemonomethylsulfonamide, diethyl phthalate, dibutyl phthalate or tartrate. With tetrabromtricresyl phosphate, 3-4% on the cellulose ether is sufficient to show a marked diminution in inflammability.

25. Propyl, butyl and amyl phosphates have been recently described as efficient softeners and plasticizers for the cellulose esters and ethers, specifically tripropyl, monoamyldiethyl, tricyclohexanol and diethylamyl phosphates. These bodies are soluble in alcohol, tri-*n*-butyl acetone, benzene, ethyl acetate and chlorinated aliphatic hydrocarbons, and confer emollient properties said to be substantially permanent[2].

26. Triresorcinol phosphate (Tri-*m*-oxyphenyl phosphate) has been described by H. Theumann as a desirable cellulose ether plasticizer, and may be prepared by heating resorcinol with an excess of phosphorous pentachloride and treating the product with water. For instance, a lacquer may be produced by dissolving ethylcellulose 12, and resorcinol phosphate in a mixture of benzene 60 and ethyl alcohol 40. After filtration, if desired, films are producible

1. British Celanese, Ltd., E. P. 313405.
2. I. G. Farbenindustrie, F. P. 700680; abst. Chem. Zentr. 1931, II, 3062. D. R. P. 517538; abst. Chem. Zentr. 1931, I, 3057.

in the usual manner[1]. Instead of ethylcellulose, cellulose acetate, cellulose diacetomonobutyrate or cellulose nitrate may be used.

27. Tricyclohexylamino-*N*-phosphine oxide prepared by treating cyclohexylamine with phosphorous oxychloride in ether solution, and diethyl or dibutyl di-*n*-butylmonoamidophosphate[2], are representative of a series of compounds in which phosphorus is linked to an amido group or a substituted amido group, and in which the remaining valencies of the phosphorus are not all linked to aromatic groups. They are claimed as excellent softening and plasticizing agents for cellulose ethers and esters, synthetic resins and rubber.

Triphenyl Phosphate (Triphenol Phosphate, Orsacoid)[3], Of the various high boiler solvents, swelling agents and plastifiers applicable both in the cellulose ester and cellulose ether arts is triphenyl phosphate, the orthophosphoric acid ester of phenol, a substance crystallizing in white needles, m. pt. 50°, ester no. 515, flash point 220°. Readily soluble in alcohol, ether, chloroform, acetone, and amyl acetate; less soluble in petroleum benzine, practically insoluble in water. It is obtained commercially in a high state of purity, and not an ideal solvent, its low cost combined with its solvent capacity and its wide dissolving range being the main points in its favor. Known commercially as "T. P.

1. U. S. P. 1870972. See M. Secretant, Bull. Soc. Chim. 1896, (3), **15**, 363. He has described the isomeric trihydroquinone phosphate, white crystals, readily soluble in alcohol, glacial acetic acid and ether, but insoluble in petroleum ether, benzene or carbon bisulfide. It melts at 149° and hence differs from triresorcinol phosphate, which melts at 75°.

2. O. Schmidt and E. Meyer, D. R. P. 534235; abst. C. A. 1932, **26**, 844; Chem. Zentr. 1931, II, 3051.

3. A. Bresser, Plastics, 1930, **6**, #8, 460. M. Trimmer, Paint, Oil and Chemical Review, 1925, **80**, #10, 10. See this work, p. 43, n. 4; p. 64, n. 2; p. 65, n. 3; p. 162, n. 4, 5; p. 249, n. 6; p. 251, n. 3; p. 377, n. 1; p. 391, n. 2; p. 407, n. 5; p. 421, n. 6; p. 442, n. 3; p. 443, n. 7; p. 467, n. 5; p. 469, n. 11; p. 470, n. 1; p. 471, n. 7, 8; p. 472, n. 6; p. 487, n. 9; p. 502, n. 1; p. 520, n. 1; p. 531, n. 4; p. 541, n. 4; p. 558, n. 2; p. 559, n. 2; p. 566, n. 2; p. 575, n. 5; p. 580, n. 7; p. 592, n. 2; p. 595, n. 1; p. 645, n. 1, 5; p. 699, n. 1; p. 702, n. 2; p. 703, n. 7; p. 709, n. 3; p. 723, n. 6; p. 740, n. 1; p. 788, n. 4; p. 795, n. 3; p. 862, n. 3; p. 940, n. 2; p. 990, n. 3; p. 1000, n. 6; p. 1027, n. 7.

P.," "Altai" and "Kronilyne." Triphenyl phosphate is a more powerful solvent for cellulose nitrate than is tricresyl phosphate with about an equal reduction in inflammability.

As a cellulose ether solvent and plastifier, C. Dreyfus[1] combines triphenyl phosphate with dibutyl phthalate for ethylcellulose plastics; S. Carroll[2] uses ethyl acetate, alcohol and camphor; and the phosphoric ester is combined[3] with benzene and alcohol to plasticize benzylcellulose.

As a dissolvant and plasticizing medium for the nitrocelluloses, P. Seel adds butyl and amyl alcohols[4]; while a mixture with alcohol and triphenyl borate[5], alcohol and ethyl acetate[6], and for mixed cellulose nitrate and acetylcellulose a mixture of methyl and ethyl alcohols[7] has been proposed. Cellulose phosphoformate is plasticized by triphenyl phosphate[8].

In conjunction with the organic cellulose esters as acetylcellulose, ethyl alcohol and acetate[9], chloroform[10], acetone and dichlorhydrin[11], propyl or butyl alcohols[12], tetrachlorethane[13] with urea as antacid, methyl alcohol[14], higher

1. E. P. 303516; abst. C. A. 1929, **23**, 4571; J. S. C. I. 1930, **49**, 553-B; Chem. Zentr. 1929, I, 2371.
2. U. S. P. 1425173; abst. C. A. 1922, **16**, 3393; J. S. C. I. 1922, **41**, 748-A; Chem. Zentr. 1922, IV, 964; Chem. Age, 1922, **30**, 468; Mon. Sci. 1923, (5), **13**, 15; Chem. Tech. Uebers. 1923, **47**, 38. See U. S. P. 1188376. F. P. 520070.
3. Soc. Anon. Des Laboratories "Odont-Email," F. P. 683418; abst. C. A. 1930, **24**, 4597.
4. U. S. P. 1379596; abst. C. A. 1921, **15**, 3255.
5. P. Rothberg and A. Sachs, U. S. P. 1448869; abst. C. A. 1923, **17**, 1896.
6. W. Lindsay, U. S. P. 1430020.
7. Imperial Chem. Industries, Ltd., E. P. 353589; abst. J. S. C. I. 1931, **50**, 1019-B.
8. E. Bronnert, U. S. P. 1055513.
9. I. G. Farbenind. A.-G., F. P. 700680; abst. C. A. 1931, **25**, 3832; Chem. Zentr. 1931, II, 3062.
10. W. Lindsay, Can. P. 175107; abst. C. A. 1918, **12**, 95.
11. *Ibid.* U. S. P. 1245476; abst. C. A. 1918, **12**, 424; J. S. C. I. 1918, **37**, 27-A. See U. S. P. 1199798.
12. *Ibid.* U. S. P. 1199798; abst. C. A. 1916, **10**, 3159; J. S. C. I. 1916, **35**, 1215. See U. S. P. 1027616.
13. *Ibid.* U. S. P. 1133385; abst. C. A. 1915, **9**, 1282; J. S. C. I. 1915, **34**, 488; Mon. Sci. 1915, **82**, 45. E. P. 10794, 1910; abst. Kunst. 1911, **1**, 356. F. P. 415517; abst. J. S. C. I. 1910, **29**, 1299; 1911, **30**, 679; Mon. Sci. 1913, **79**, 392.
14. W. Lindsay, U. S. P. 1128468; abst. C. A. 1915, **9**, 1114;

aliphatic ketones[1], benzene[2], triacetin[3], benzyl alcohol[4], mesityl oxide[5], diphenylamine or trichlorphenol, benzoic ether or acetodichlorhydrin[6], indicate some of the combinations which have been brought forward to obviate tendency of triphenyl phosphate to crystallization, while still conserving the solvent power and lowering the inflammability point. The Societe Lyonnaise de Soie Artificielle[7] incorporate butyl, amyl or cetyl ethers, while the I. G. Farbenindustrie[8] prefer acetone. The stencil blank of D. Williams[9] combines triphenyl phosphate with alcohol and tetrachlorethane, and Pathe Cinema[10] benzene and alcohol. Triphenyl phosphate plasticizes cellulose formate[11].

Triphenyl phosphate has been and is most extensively used in dope for airplane wing fabrics[12], in celluloid substitutes[13], as a solvent[14] and plasticizer for cellulose ace-

J. S. C. I. 1915, **34**, 349; Mon. Sci. 1915, **82**, 44; Kunst. 1915, **5**, 131. See U. S. P. 1076215; abst. C. A. 1914, **8**, 246.

1. Verein für Chemische Industrie, D. R. P. 303018; abst. J. S. C. I. 1918, **37**, 367-A; Kunst. 1918, **8**, 36.

2. H. Dreyfus, E. P. 179208; abst. C. A. 1922, **16**, 3370; J. S. C. I. 1922, **41**, 542-A; Chem. Zentr. 1922, IV, 646; Chem. Tech. Uebers, 1922, **46**, 311; Caout. et Gutta. 1923, **20**, 11687. F. P. 542740; abst. Caout. et Gutta. 1923, **20**, 11686; Chem. Zentr. 1923, II, 1066; Chem. Ztg. 1922, **44**, 892. For phenyl phosphate, see J. Scheidegger and C. Dreyfus, Can. P. 323143; abst. C. A. 1932, **26**, 4172.

3. A. von Biehler, D. R. P. 358285, Addn. to D. R. P. 357011; abst. C. A. 1923, **17**, 2397; J. S. C. I. 1922, **41**, 998-A; Phot. Abst. 1923, **3**, 15. See D. R. P. 357011; abst. J. S. C. I. 1922, **41**, 917-A.

4. W. Stevenson, U. S. P. 1458505. E. P. 138379; abst. C. A. 1920, **14**, 1879.

5. V. Sease, U. S. P. 1488294; abst. C. A. 1924, **18**, 1750; J. S. C. I. 1924, **43**, 464-B.

6. W. Lindsay, U. S. P. 1386576; abst. C. A. 1921, **15**, 3906; J. S. C. I. 1921, **40**, 689-A.

7. F. P. 705639; abst. C. A. 1932, **26**, 306; Chem. Zentr. 1931, II, 2952.

8. D. R. P. 516716; abst. C. A. 1931, **25**, 3139.

9. U. S. P. 1795461; abst. Plastics, 1931, **7**, #5, 301.

10. F. P. 643884; abst. C. A. 1929, **23**, 1749.

11. Vereinigte Glanzstoff-Fabriken Akt.-Ges., E. P. 29246, 1910.

12. U. S. P. 1315216, 1230290, 1325363, 1363763, 1440178.

13. U. S. P. 1153596, 1181860, 1188356, 1188797, 1188798, 1188799, 1188800, 1199798, 1217027, 1242783, 1245476, 1245983, 1353384, 1353385, 1363763, 1386576, 1440006, 1488294, 1501206, 1508928.

14. U. S. P. 1128468, 1143979, 1226342, 1244107, 1244108, 1244347, 1244348, 1244349, 1265217, 1309980, 1463864, 1488294.

tate[1], for the dissolving[2] and plastifying of the cellulose ethers[3], as a dissolving[4] and softening agent for ethylcellulose[5], in the production of films[6] especially photographic films[7], in general plastics production[8], and in the preparation of varnishes and enamels[9].

1. U. S. P. 1143979, 1188797, 1188798, 1188799, 1188800, 1193178, 1199395, 1199798, 1199799, 1199800, 1203756, 1245476, 1319229, 1325931, 1353384, 1353385, 1363763, 1386576, 1388472, 1394890, 1408095, 1417587, 1440178, 1453764, 1454959, 1454960, 1454961, 1458505, 1468222, 1501206, 1508928.

2. U. S. P. 1188376, 1217027, 1217028, 1405487, 1450714, 1450715, 1450716, 1467091, 1467092, 1467093, 1467094, 1467095, 1467096, 1467097, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105, 1469812, 1469813, 1469816, 1469825, 1469826, 1469862, 1469863.

3. U. S. P. 1217027, 1389084, 1418413, 1425173, 1429188, 1450714, 1450715, 1450716, 1454959, 1454960, 1454961, 1473217, 1473218, 1473219.

4. U. S. P. 1188376, 1217027, 1217028, 1405487, 1450714, 1450715, 1450716, 1467091, 1467092, 1467093, 1467094, 1467095, 1467096, 1467097, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105, 1469812, 1469813, 1469816, 1469825, 1469826, 1469862, 1469863.

5. U. S. P. 1405449, 1425173, 1429169, 1432373, 1432374, 1434426, 1434427, 1434432, 1434465, 1437792, 1441143, 1441181, 1444331, 1444406, 1450714, 1450715, 1450716, 1454959, 1454960, 1454961, 1460097, 1460690, 1464169, 1464170, 1467071, 1467091, 1467092, 1467093, 1467094, 1467095, 1467096, 1467097, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105, 1473217, 1473218, 1473219.

6. U. S. P. 1193178, 1199395, 1217027, 1242783, 1353384, 1353385, 1354725, 1354726, 1363763, 1405487, 1425173, 1429153, 1429169, 1434426, 1434427, 1434432, 1437792, 1440006, 1441181, 1450714, 1450715, 1450716, 1460097, 1473217, 1473218, 1473219, 1479955, 1494469, 1494470, 1494471, 1494472, 1494473, 1494474, 1494475, 1494476, 1501206, 1508928, 1514283.

7. U. S. P. 1188797, 1188798, 1188799, 1188800, 1199799, 1199800, 1203756, 1226340, 1226342, 1226343, 1229485, 1229486, 1229487, 1388472, 1394505, 1405449, 1411708, 1429188, 1431905, 1432373, 1432374, 1434465, 1441143, 1441181, 1450714, 1450715, 1450716, 1467091, 1467092, 1467093, 1467094, 1467095, 1467096, 1467097, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105, 1488294, 1500366, 1518417.

8. U. S. P. 1188797, 1188798, 1188799, 1188800, 1193178, 1199800, 1203756, 1226340, 1226343, 1229485, 1229486, 1229487, 1386576, 1388472, 1389084, 1405487, 1425173, 1437792, 1440006, 1450714, 1450715, 1450716, 1467091, 1467092, 1467093, 1467094, 1467095, 1467096, 1467097, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105.

9. U. S. P. 1188798, 1188799, 1188800, 1193178, 1203756, 1226340, 1226343, 1229485, 1229486, 1229487, 1242783, 1354725, 1354726, 1429169, 1440006, 1441181, 1448869, 1467092, 1467093, 1467094, 1467095, 1467096, 1467097, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105.

Tricresyl Phosphate[1], Tritolyl Phosphate, Lindol, Kronitex. Ranks with triphenyl phosphate, dibutyl phthalate and the sulfonamides as one of the most widely used and usefully applicable plasticizers for cellulose derivatives. It should be completely soluble in acetone, benzene and chloroform, and when pure is colorless and substantially odorless. Miscible with many oils and hydrocarbons, but insoluble in water. The commercial product usually slightly fluoresces and varies considerably in viscosity. The commercial products "T. C. P.," "Plastol X" and "Plastic X" have sp. gr. 1.185-1.19 and boiling range of 430-440°. On heating at 45-50° for days practically no evaporation takes place. Tricresyl phosphate has a moderate solvent action on nitrocellulose, less so with cellulose acetate and dissolves the cellulose ethers with avidity, especially in conjunction with alcohol and by the application of heat[2].

C. F. Boehringer & Sohne[3] improve the elasticity of ethylcellulose by the use of tricresyl phosphate and benzene, and H. Börnstein[4] plasticizes benzylcellulose with tricresyl phosphate and alcohols, although the viscosity becomes somewhat reduced (see p. 224, n. 3). The light permanency of cellulose ethers is conserved by incorporation of tricresyl phosphate therewith (p. 146, n. 3).

The solvent capacity of tricresyl phosphate may be modified and accentuated by combining therewith in connection primarily with the cellulose acetates, methyl salicylate[5], methyl or ethyl alcohol[6], indene, glycol diacetate,

1. See this work, p. 19; p. 92, n. 1, 2, and 3; p. 102, n. 2; p. 107, n. 3; p. 146, n. 3; p. 162, n. 5; p. 124; p. 224, n. 3; p. 407, n. 3 and 5; p. 449, n. 4; p. 468, n. 6; p. 469, n. 1 to 12; p. 563, n. 4; p. 645, n. 1; p. 689, n. 6; p. 702, n. 2; p. 728, n. 6; p. 803, n. 5.
2. M. Trimmer, Paint, Oil and Chem. Rev. 1925, **80**, #10, 10; abst. C. A. 1925, **19**, 3604.
3. F. P. 698321; abst. C. A. 1931, **25**, 3137.
4. E. P. 306140.
5. L. Malone and S. Carroll, U. S. P. 1575778; abst. C. A. 1926, **20**, 1522; J. S. C. I. 1926, **45**, 516-B; Plastics, 1926, **2**, 287.
6. W. Jenkins and Imperial Chemical Industries, Ltd., E. P. 309840; abst. C. A. 1930, **24**, 723.

diethyl phthalate or anisol[1], or benzyl alcohol[2]. In the pyroxylin industry tricresyl phosphate is seldom used alone, usually in conjunction with acetone or methyl alcohol[3], ethyl alcohol and acetate[4], to which calcium tartrate may be added as fire-retardant[5], or butyl acetate[6].

Tricresyl phosphate with a mixture of dibutyl phthalate, camphor and camphor oil[7], chlorbenzene[8], diacetone alcohol[9], benzine[10], toluene, xylene, or butyl propionate[11], or of a mixture of butyl acetate and toluene[12], are solvent combinations which have received patent protection. The Canadian Industries, Ltd., have put forth a formula of tricresyl phosphate, carbon tetrachloride and butyl alcohol[13], and M. Bandli[14] a mixture of acetone, ether and alcohol. The G. Roelandts varnish[15] combines butyl alcohol, the I. G. Farbenindustrie[16] butyl or amyl acetates, while E. de Stubner[17] prefers butyl acetate and tricresyl phosphate. C. Barker[18], G. Peters[19], W. Lindsay[20], C. Berger[21] and J. Hirsh

1. Compagnie Francaise pour L'Exploitation des Procédés Thomson-Houston, F. P. 649384; abst. C. A. 1929, **23**, 2841.
2. M. Morel, Swiss P. 127231; abst. C. A. 1929, **23**, 1231.
3. W. Lindsay, U. S. P. 1523813; abst. C. A. 1925, **19**, 900.
4. *Ibid.* U. S. P. 1493207; abst. C. A. 1924, **18**, 2077.
5. *Ibid.* U. S. P. 1493208; abst. C. A. 1924, **18**, 2077.
6. Farbw. vorm. Meister, Lucius & Brüning, E. P. 248767; abst. J. S. C. I. 1927, **46**, 565-B.
7. Imperial Chemical Industries, Ltd., and B. Foster, E. P. 348156.
8. Chemische Fabrik Griesheim-Elektron., E. P. 223891; abst. C. A. 1926, **20**, 832.
9. A. Randolph, U. S. P. 1820198; abst. J. S. C. I. 1932, **51**, 545-B.
10. I. G. Farbenindustrie, E. P. 287116.
11. G. Peters, E. P. 293434; abst. C. A. 1929, **23**, 1763; J. S. C. I. 1929, **48**, 138-B.
12. Hercules Powder Co. and G. Peters, E. P. 293435; abst. J. S. C. I. 1929, **48**, 138-B.
13. Can. P. 299309.
14. F. P. 706319; abst. C. A. 1932, **26**, 337.
15. F. P. 652410; abst. C. A. 1929, **23**, 3588.
16. F. P. 650814; abst. C. A. 1929, **23**, 3359.
17. F. P. 660877; abst. C. A. 1930, **24**, 252.
18. U. S. P. 1809011; abst. C. A. 1931, **25**, 4329.
19. E. P. 293434; abst. C. A. 1929, **23**, 1763. See Can. P. 283058; abst. C. A. 1928, **22**, 4262.
20. U. S. P. 1508457; abst. C. A. 1924, **18**, 3720.
21. Swiss P. 130137; abst. C. A. 1929, **23**, 3113.

and A. Robson[1] have described other auxiliary solvent combinations to be used with cresyl phosphate[2].

Carbonic and Resorcindicarbonic Esters. E. Zuehl[3] in 1900 described the application of diphenyl carbonate, tricresyl carbonate and trinaphthyl carbonate in conjunction with naphthyl propionate, resorcinol diacetate, chlornaphthyl acetate and nitronaphthyl acetate as nitrocellulose gelatinants, and J. Stevens[4] the uses of methyl, ethyl, propyl, butyl and amyl carbonates for the same purpose. As cellulose ether solvents, especially for water-insoluble ethylcellulose and benzylcellulose, dichlorethyl and dichlorpropyl carbonates have been advocated[5], preferably dissolved in alcohol or acetone. J. Donohue[6] has furnished details of the application of methyl, ethyl, propyl, butyl and amyl carbonates as direct dissolvants for the cellulose ethers, in conjunction with methyl or ethyl alcohol. The uses of diethyl carbonate, alone or with diethyl oxalate forms the subject matter of the M. Fredenburgh disclosure[7].

According to S. Shipley and G. Given[8] diethyl carbonate in conjunction with methyl-, ethyl-, propyl-, butyl- or amyl-glycol produces an excellent solvent mixture for cellulose ethers and esters. Diethyl carbonate with the phthalates of copper, ferric, lead, nickel or butyl; diacetone alcohol, furfural, butyl formate or hexahydrophenol[9] with cel-

1. U. S. P. 1690680; abst. C. A. 1929, **23**, 532; Plastics, 1929, **5**, #5, 264.
2. P. Rothberg and A. Sachs, U. S. P. 1448869; abst. J. S. C. I. 1923, **42**, 940-A. W. Lindsay, U. S. P. 1468820; abst. C. A. 1923, **17**, 3919. U. S. P. 1493207. C. Ellis, U. S. P. 1541693; abst. C. A. 1925, **19**, 2277. W. Doerflinger, U. S. P. 1721295; abst. C. A. 1929, **23**, 4283. C. Gabriel, U. S. P. 1813735; abst. J. S. C. I. 1932, **51**, 518-B. I. G. Farbenindustrie, A.-G., E. P. 280178. Canadian Industries, Ltd., Can. P. 295755. A. Ritschke, U. S. P. 1497028; abst. C. A. 1924, **18**, 2428.
3. U. S. P. 700884. E. P. 17948, 1900. Zuehl & Eisemann, D. R. P. 139589.
4. U. S. P. 610728.
5. I. G. Farbenind., E. P. 257258; abst. J. S. C. I. 1928, **47**, 341-B.
6. U. S. P. 1552805. See D. R. P. 117625, 120864, 120865, 122096, 287601.
7. U. S. P. 1842161.
8. U. S. P. 1618481. E. P. 236190, 250894.
9. B. Brown and C. Bogin, Can. P. 260927.

lulose esters produces lacquers of high viscosity and transparency. Ethyl chlorcarbonate in the presence of a solvent such as acetone[1] readily dissolves ethylcellulose, nitrocellulose or cellulose acetate. The lacquer containing synthetic resins of C. Ellis[2] comprises cellulose ethers, ethyl carbonate, diethyl phthalate, acetanilid, triacetin, methylethyl ketone, diacetone alcohol, furfural and benzene, toluene and xylene.

Diethyl Carbonate, ethyl carbonate (Diatol in 90% strength solution), is a colorless liquid, sp. gr. 0.976-0.988, b. pt. 120-130°, miscible with castor oil and the majority of cellulose ether solvents, insoluble in water, dissolves the cellulose ethers with moderate avidity, the solvency being materially increased by the addition of alcohol or acetone. Comparatively speaking, diethyl carbonate solutions have a low tolerance for hydrocarbons and other cellulose ether and ester non-solvents. Addition of a small amount of ethyl lactate materially increases its solvent powers[3]. For the coating of cathodes, nitrocellulose dissolved by diethyl carbonate has been advocated.

A series of carbonic esters has been described[4], comprising acetylethylamidophenylmethyl (or ethyl) carbonate, acetylmethylamidophenylmethyl (or ethyl) carbonate, acetylamidophenylmethyl (or ethyl, *iso*butyl, *iso*amyl) carbonate, lactylamidophenylmethyl (or ethyl) carbonate, and formylamidophenylmethyl (or ethyl) carbonate. Like santalyl carbonate (Blenal), santalyl allophenate (Allosan), santyl camphorate (Camphoral), santalyl methyl ether (Thyreol) and santalyl salicylate (Santyl) their solvent properties and applicability in the cellulose ether art have been but imperfectly investigated. Santalyl carbonate in conjunction with alcohol dissolves triethylcellulose. Santalyl ben-

1. S. Carroll, U. S. P. 1826690.
2. U. S. P. 1529056; abst. C. A. 1925, **19**, 1502.
3. E. Clayton and C. Clark, Text. Mfr. 1931, **57**, 455. Anon., Chem. Tech. Ind. 1926, **26**, 51, 67, 82.
4. Farbwerke, vorm. Meister, Lucius and Bruening, E. P. 24901, 1894.

zoate[1] and santalyl *iso*valerianate and stearate[2] have weak dissolving powers for cellulose ethers.

Resorcinol Dicarbonate is a direct cellulose ether solvent. 10 parts ethylcellulose dissolved in acetone 100 and resorcinol dicarbonate 5 produce films of high transparency and flexibility. Benzylcellulose also readily dissolves in this ester[3]. It boils at 298-302°. As an adhesive for the cellulose ethers[4], a mixture of resorcinol dicarbonate and *b*-naphthol ether is recommended, benzylcellulose being especially soluble in this solvent combination.

Inorganic Esters. In addition to the phosphoric and carbonic esters described above, there have been advocated from time to time other alkyl, aryl and aralkyl combinations with inorganic acid radicals which have had a more or less limited use for special classes of cellulose ester compositions.

Methyl and amyl nitrite and nitrate have been patented as desirable pyroxylin solvents[5], methyl nitrate[6], ethyl nitrate[7], and either methyl or ethyl nitrite with higher boilers[8] having the same solvent function. The California Explosive Co.[9] combines ethyl nitrate with nitrobenzene. Methyl and ethyl nitrates were used or known as solvents as far back as 1863[10]. The C. Lundholm and J. Sayers pyroxylin composition contained ethyl nitrate[11]. The Chemische Fabrik Kalk and H. Oehme[12] have detailed ethyleneglycol nitrates.

Silicic Esters. H. Peters has described nitrocellulose

1. Knoll & Co., D. R. P. 173240.
2. Chem. Fabrik von Heyden, D. R. P. 182627.
3. Farbenfabriken vorm. F. Bayer & Co., D. R. P. 322619. See D. R. P. 139589.
4. *Ibid.* D. R. P. 322648. F. P. 516900. E. P. 115855.
5. J. Stevens, U. S. P. 269344, 269345, 478543.
6. *Ibid.* U. S. P. 269340.
7. I. and J. Hyatt, U. S. P. 156353, 156354.
8. W. Rintoul and D. Cross, U. S. P. 1303115.
9. E. P. 11326, 11326-A, 1891; abst. J. S. C. I. 1891, **10**, 1029.
10. A. Nobel, E. P. 2359, 1863.
11. D. R. P. 53296.
12. D. R. P. 341720, Addn. to D. R. P. 338056; abst. Chem. Ztg. 1921, **45**, 473.

lacquers of diminished inflammability[1] obtained by dissolving in methyl or amyl silicate, methylated ether and nitrobenzene. Methyl silicate forms the basis for the pyroxylin compositions of D. Bachrach[2], the celluloid mixture of N. Pillion[3], and the linen coating composition of H. Peters[4]. Certain disilicic esters[5] as ethyl monosilicate, diethyl monosilicate, diethyl disilicate and hexaethyl disilicate are examples of the silicic esters claimed as suitable. They are soluble in alcohol, ether and acetone.

Boric Esters. The methyl, ethyl, propyl, butyl and amyl borates in the hands of G. Botrele and G. Fretard[6] are utilized to diminish the inflammability of nitrocellulose. An ether solution of borax has been used for the same purpose[7]. Boric acid[8], borates[9] and borax[10] are useful fire-retardants in the cellulose ester industry and equally applicable when incorporated with the cellulose ethers. Amyl borate is a high-boiling solvent defective in that it liberates boric acid in the presence of moisture. It has a direct but weak solvency for cellulose esters. Sp. gr. 0.85-0.86, b. pt. 255°.

Triphenyl borate[11] is similar in action to the phenyl phosphates and a direct solvent of acidylcelluloses.

Formic Esters. A cellulose ether composition has been disclosed by J. Donohue[12], comprising methyl, ethyl, propyl, butyl and amyl formates, an especially useful mixture being methyl formate with methyl alcohol 5-7 parts, to 1 part

1. E. P. 14293, 1910; abst. C. A. 1911, **5**, 3347.
2. U. S. P. 794581. U. S. Re-13793 to U. S. P. 794581.
3. F. P. 325336.
4. E. P. 870, 1910. F. P. 420127. D. R. P. 140784, 149764.
5. E. Clement, E. P. 10320, 1910. F. P. 402569. Span. P. 47917. Belg. P. 225222.
6. Belg. P. 242735.
7. Soc. Celluloid Uninflammable, Belg. P. 199328.
8. U. S. P. 1358914, 1381440, 1436231, 1472830.
9. S. Satow, U. S. P. 1245975.
10. U. S. P. 1248092, 1271506, 1276742, 1346287, 1414609, 1418730, 1436231, 1501895, 1501944.
11. Farbenfabriken vorm. F. Bayer & Co., E. P. 13100, 1910. See H. Dreyfus, E. P. 21628, 1901.
12. U. S. P. 1552806; abst. C. A. 1925, **19**, 3593.

water-insoluble ethylcellulose. The engine fuel composition of M. Whitaker[1] is a mixture of methyl, ethyl, butyl and amyl formate, acetate, propionate and butyrate, and the pyroxylin mixture of J. Stevens[2] a combination of methyl, ethyl and propyl formates, made by esterifying a mixture of the three alcohols together with formic and sulfuric acids. H. Mork[3] has found that methyl formate is a much more powerful solvent for cellulose acetate than is acetone, and is preferably mixed with a less volatile liquid as tetrachlorethane or carbon tetrachloride. A. Wohl[4] has described methyl formate solutions of acetylcellulose.

Ethyl Formate. Formosol. Whereas methyl formate boils at 32.5°, the ethyl ester boils at 54.4°, about the same temperature as acetone. Still the boiling point is too low to be used alone, and it is best to incorporate in ethyl formate mixtures higher boiling solvents of lower evaporative capacity. In conjunction with acetaldol[5], methylene chloride[6], furfural[7], ethyl lactate[8], and as an acetone substitute, ethyl formate has been used in the arts as a cellulose ester solvent[9]. The C. Ellis[10], J. Duclaux[11], and B. Jaillard processes[12], all employ ethyl formate or the corresponding methyl ester. Although ethyl formate is miscible with benzene, it is soluble in 9 parts water at 18°. The viscosity of ethyl formate solutions of the cellulose esters is unsually low.

Butyl Formate. The nitrocellulose lacquer of R. Gilmour and Dunville & Co.[13] employs butyl formate, while B.

1. U. S. P. 1421879.
2. U. S. P. 561624.
3. U. S. P. 972464; abst. C. A. 1911, **5**, 197. E. P. 20672, 1910.
4. E. P. 3139, 1911. Aust. P. 53099.
5. J. Kessler, U. S. P. 1303563.
6. A. Eichengruen, E. P. 243350.
7. G. Meunier, F. P. 472423.
8. G. Bonwitt, E. P. 138078. F. P. 519536. D. R. P. 331285.
9. Chem. Fabrik. von Heyden, D. R. P. 302460.
10. U. S. P. 1529056.
11. E. P. 2465, 1913. F. P. 439721.
12. F. P. 487350. See also U. S. P. 1127871, 1188376.
13. E. P. 132996; abst. C. A. 1920, **14**, 358.

Brown and C. Bogin[1] combine zinc butyl phthalate therewith. This ester imparts high strength to nitrocellulose films and dissolves some types of cellulose acetate as well as the cellulose ethers, especially benzylcellulose in the presence of an aliphatic alcohol. It is a solvent of copal, coumarone resin, benzyl abietate, dammar, elemi and mastic. Sp. gr. 0.91, b. pt. 106-107°.

Amyl Formate. The photographic film of E. Vogel[2] uses amyl formate in conjunction with amyl nitrite and acetate. This ester has been recommended as a desirable precipitant for cellulose formate and phosphoformate[3], as a useful component in celluloid substitute, and as an acetylcellulose solvent and plasticizer. In many instances amyl formate is preferred to the acetate, being less odoriferous and a more energetic solvent. By virtue of its lower boiling point, its speed of evaporation is greater. In the aliphatic esters of monocarboxylic acids, those of the same or similar weight (as butyl acetate and amyl formate) have substantially the same solvent power. Sp. gr. 0.88-0.885, b. pt. 123°.

Benzyl Formate. A solvent of cellulose acetate, as described in the processes of W. Lindsay[5]. Similar to benzyl acetate but of higher volatility, benzyl formate dissolves cellulose nitrate and some cellulose ethers, especially the water-insoluble modifications. B. pt. 200-201°, sp. gr. 1.08-1.09. A good solvent for benzyl abietate, coumarone, glyceryl phthalate resins and ester gum.

Glycol Formate. There has been detailed by the I. G. Farbenindustrie[6] a process for lacquer manufacture, in which benzylcellulose is dissolved in 2.5 times its weight of glycol mono- or di-formate, which may be combined with a glyceryl formate solution of shellac. Propyleneglycol mono- and di-formates are equally applicable, and have a lower volatility by virtue of their higher boiling points. Glyceryl,

1. Can. P. 260927.
2. D. R. P. 53078.
3. E. Bronnert, U. S. P. 1153596.
4. W. Lindsay, U. S. P. 1388472.
5. U. S. P. 1199800.
6. Swiss P. 127241; abst. C. A. 1929, **23**, 1190. E. P. 311795.

erythritol and sorbitol formates, acetates, benzoates, oxalates, maleates, succinates and phthalates have been proposed as cellulose nitrate flexilizing bodies[1]. Ethyleneglycol mono-methyl formate, acetate and phthalate[2] have also been advocated as acidylcellulose solvents and plastifiants.

W. Schrauth[3] has described the properties of new synthetic alcohols and their esters as cellulose derivative solvents, including hexalin formate (sp. gr. 0.973; b. pt. 150-159°) and acetate (sp. gr. 0.966; b. pt. 164-180°); and heptalin formate (sp. gr. 0.959; b. pt. 173-185°) and acetate (sp. gr. 0.941; b. pt. 176-193°).

Acetic Esters. The acetic esters as a class are probably the most important and widely used of any solvents in connection with the manipulation of nitrocellulose in its transformation from the uncolloided to the dissolved state. They are used much less at the present time as direct and adjuvant solvents with cellulose ethers and acetylcellulose. They are colorless, stable liquids of distinctive but not unpleasant odor, are non-toxic, and depending upon the nature of the alkyl, aryl or aralkyl group introduced, may be had in a wide range of boiling points and a corresponding variation in rapidity of evaporation.

Methyl Acetate. The boiling points and solvent powers of methyl acetate and acetone are substantially the same, however, methyl acetate hydrolyzes in the presence of moisture and splits off acetic acid. Methyl acetate is a good solvent of cellulose acetate and the cellulose ethers, but with increase in molecular weight of alkyl in combination with acetic acid, solvency diminishes both for the cellulose ethers and for acetylcellulose. The cellulose ether composition of P. Seel[4] embraces a mixture of methyl acetate and benzene, this mixture in the latitude 9:1 to 1:9 dissolving

1. I. G. Farbenindustrie, E. P. 313892.
2. *Ibid.* E. P. 279771; abst. C. A. 1928, **22**, 3044. See E. P. 278735. Ital. P. 256719.
3. Farb. Ztg. 1922, **26**, 647; abst. Chem. Tech. Uebers. 1922, **46**, 59.
4. U. S. P. 1405449; abst. C. A. 1922, **16**, 1316.

water-insoluble ethylcellulose and benzylcellulose in the cold. Benzene 2 to methyl acetate 1 gives the best results with nearly all types of cellulose ethers. W. Webb[1] obtains best results by dissolving ethylcellulose in methyl acetate 90, methyl alcohol 10. It is best to use the anhydrous methyl acetate rather than the cheaper commercial grade.

In cellulose acetate and nitrocellulose lacquers, enamels, paints and varnishes, the processes of A. Helbronner[2], H. Chute[3], S. Shipley[4], A. Wohl[5] and L. Seidell and G. Jack[6] are indicative of the general trend of manipulation. Eastman Kodak Co. have published the formula[7] methyl acetate 50, ethyl acetate 40-10, and acetone 10-40. It also dissolves the cellulose ethers[8] when mixed with cyclohexanol, camphor, ethylbenzene, butyl tartrate, acetophenone, dimethyl aniline, dibenzylamine, ethylbenzyl aniline, diphenylmethane and monochlornaphthalene[9].

Methyl chloracetate is a cellulose acetate solvent, but there is a proneness upon prolonged exposure to light and

1. U. S. P. 1432374; abst. C. A. 1923, **17**, 341.
2. E. P. 1262, 1914. A. Helbronner and G. Criquebeuf, U. S. P. 1260977. F. P. 464646 and Addn. 18975.
3. U. S. P. 845616.
4. U. S. P. 1633292; abst. J. S. C. I. 1927, **46**, 774-B.
5. E. P. 3139, 1911. F. P. 425900, 435742. D. R. P. 246651. Belg. P. 232699.
6. U. S. P. 1676362; abst. C. A. 1928, **22**, 3305.
7. E. P. 345505; abst. C. A. 1932, **26**, 304.
8. S. Carroll, U. S. P. 1467091, 1467105.
9. For other applications of methyl acetate in connection with cellulose ethers and esters, see U. S. P. 269343, 428654, 434330, 478543, 552934, 552935, 621360, 1021569, 1181860, 1188799, 1188800, 1226342, 1260977, 1275884, 1303115, 1303563, 1309980, 1310841, 1320458, 1329386, 1353384, 1353385, 1363763, 1370879, 1393355, 1394890, 1395401, 1398239, 1405449, 1406224, 1410790, 1426521, 1429153, 1432365, 1432374, 1434465, 1437170, 1437952, 1439293, 1440006, 1440178, 1449157, 1460097, 1464169, 1464170, 1467071, 1467091, 1467092, 1467093, 1467094, 1467095, 1467096, 1467097, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105, 1469826, 1494469, 1494470, 1494471, 1494472, 1494473, 1494474, 1494475, 1494476, 1494479, 1500366, 1501206, 1508928, 1521055, 1521056, 1529056, 1530987, 1536052, 1548933, 1548938, 1552793, 1552794, 1552803, 1618482, 1618484. E. P. 9315, 12684, 1890; 28613, 1897; 2145, 1911; 1262, 1914; 124763, 127027, 127678, 128215, 131369, 131669, 158521, 184197, 184671, 195849, 209727. F. P. 432264, 452432, 464646, 472423, 495000, 521370, 530440, 611899. Aust. P. 7052. Jap. P. 34855.

air to the splitting off of chlorine with the development of acidity[1]. It boils at 129°—an ideal temperature.

"Solvent E 13," a commercial solvent is said to be a mixture of methyl and ethyl acetates. "Star Solvent" is ethyl acetate of about 87% ester.

Ethyl Acetate. As a direct solvent in cellulose ether compositions, ethyl acetate has been extensively used[2], as well as for dissolving cellulose acetate[3], the nitrocelluloses[4], and in the production of celluloid substitutes[5], films[6], especially photographic films[7], paint and varnish removers[8], motor fuels[9]. The processes of M. Smith[10], Imperial Chemical Industries[11], V. Scholz and B. Eibes[12], R. Martin[13],

1. H. Mork, U. S. P. 1039782; abst. C. A. 1912, **6**, 3517.
2. U. S. P. 1217027, 1217028, 1389084, 1418405, 1425173, 1429153, 1431906, 1432365, 1434465, 1437952, 1467091, 1467092, 1467093, 1467094, 1467095, 1467096, 1467097, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105, 1500366.
3. U. S. P. 1127871, 1132384, 1143979, 1175791, 1199798, 1201260, 1203756, 1217722, 1244107, 1244108, 1244347, 1244348, 1244349, 1245476, 1265216, 1303563, 1310841, 1319229, 1330543, 1343135, 1351652, 1353384, 1353385, 1354401, 1355976, 1355978, 1357447, 1365049, 1386576, 1393355, 1394890, 1406224, 1408095, 1410790, 1420028, 1421341, 1429153, 1434634, 1449157, 1488294, 1501206, 1508928.
4. U. S. P. 1127871, 1129770, 1135026, 1141224, 1173628, 1195040, 1208358, 1234921, 1266073, 1269339, 1301187, 1309581, 1320458, 1321611, 1321633, 1321634, 1329386, 1341710, 1350281, 1351672, 1354401, 1357876, 1360759, 1365049, 1370922, 1377761, 1393355, 1394890, 1397173, 1397493, 1398239, 1400196, 1408095, 1410790, 1411669, 1412770, 1416493, 1418405, 1421341, 1429153, 1431906, 1437170, 1439293, 1441332, 1449157, 1456782, 1464012, 1464242, 1474830, 1492123, 1493207, 1493208, 1496500, 1503453, 1508457, 1517892.
5. U. S. P. 1160063, 1195040, 1199798, 1217027, 1241738, 1245476, 1353384, 1353385, 1386576, 1420028, 1488294, 1501206, 1508928, 1512751.
6. U. S. P. 1217027, 1241738, 1351652, 1353384, 1353385, 1354401, 1400196, 1425173, 1429153, 1501206, 1508928.
7. U. S. P. 1203756, 1418405, 1431906, 1432365, 1434465, 1488294, 1500366, 1512751.
8. U. S. P. 1129770, 1143110, 1143111, 1147849, 1147852, 1167640, 1172773, 1173628, 1184164, 1499101.
9. U. S. P. 1412233, 1414759, 1420006, 1420007, 1421879, 1423048, 1423049, 1423050, 1423058.
10. E. P. 286006; abst. C. A. 1929, **23**, 277.
11. E. P. 298914; abst. C. A. 1929, **23**, 3113.
12. E. P. 281068; abst. C. A. 1928, **22**, 3499.
13. Chem. Met. Eng. 1928, **35**, 404; abst. C. A. 1928, **22**, 3306.

D. Carnegie[1], P. Glaser[2] and S. Shipley[3] are representative in the employment of nitrocellulose and cellulose acetate in conjunction with ethyl acetates. J. Walsh and A. Caprio[4] have recommended ethyl acetates 82.5, ethyl alcohol 8.5, water 9; M. Hitt[5] dissolves pyroxylin in a mixture of ethyl acetate, benzene and ethyl alcohol; the E. Flaherty[6] formula consists of a mixture of ethyl acetate, butyl alcohol and benzene; while W. Lindsay[7] has advocated ethyl acetate 60-70, methyl alcohol 40-30. The applications of anhydrous ethyl acetate have been set forth by H. Willkie[8].

Commercial ethyl acetate is a water-white liquid, not less than 85% ester, sp. gr. not less than 0.89 at 15.5°. Anhydrous ethyl acetate assays 99% ester, sp. gr. 0.905-0.907 at 15°/15°, boiling range 76-78°. Miscible with 10 volumes gasolene without turbidity. Ethyl acetate is one of the best nitrocellulose solvents, especially in combination with higher boiling direct solvents.

b-Chlorethyl Acetate has been recommended by I. Matthews[9] as a direct cellulose ether solvent, especially when admixed with benzene, toluene and xylene, a preferred formula being *b*-chlorethyl acetate 10, benzene 80, or 75 parts *b*-chlorethyl acetate to 25 parts benzene (both) by weight. For film manufacture, 1 part water-insoluble ethylcellulose is dissolved in 4-6 parts of the mixed solvent above mentioned. The Chemische Fabrik Kalk and H. Oehme[10] have found *b*-chlorethyl acetate to be a good solvent of nitrocellulose, cellulose acetate and various resins and oils, being unattacked by water or metals.

Ethyl Methylpropylacetate, Ethyl Propylmethylacetate,

1. E. P. 311739; abst. C. A. 1930, **24**, 981.
2. F. P. 617497.
3. U. S. P. 1744085.
4. E. P. 314087; abst. C. A. 1930, **24**, 1235. Can. P. 312793; abst. C. A. 1931, **25**, 4401.
5. U. S. P. 1321633.
6. U. S. P. 1321611; abst. J. S. C. I. 1920, **39**, 14-A.
7. U. S. P. 1143979; abst. C. A. 1915, **9**, 2311. See U. S. P. 1128468, 1133385, 1136248.
8. Chem. Met. Eng. 1921, **25**, 1186; abst. Ann. Rep. S. C. I. 1922, **7**, 137.
9. U. S. P. 1469816; abst. C. A. 1923, **17**, 3919.
10. D. R. P. 391667; abst. J. S. C. I. 1924, **43**, 527-B.

being the ethyl ester of methylpropylacetic acid, b. pt. 145-155°, has been described by O. Jordan[1] as a solvent dissolving both the cellulose ethers, resins, oils and essential oils. For instance, 5 parts benzene-soluble ethylcellulose are dissolved in toluene 70 and ethyl alcohol 5, this solution mixed with 5 parts colophony glycerol ester, linseed oil 5 and 10 parts ethyl methylpropylacetic acid to produce a lacquer.

Methyl, ethyl or propyl methylpropylacetates, methylpropylpropionates or methyl*iso*butyl acetates may likewise be used.

Propyl Acetate, Solval A, Solval B. The process of P. Seel[2] involves the use of propyl, butyl and amyl acetates as a cellulose ether solvent in conjunction with methyl alcohol, butyl acetate 25 to methyl alcohol 7 being an acceptable combination for this purpose. Both ethylcellulose and benzylcellulose are soluble in this binary solvent. The patented processes of W. Field[3] using propyl acetate 4, butyl acetate 4 and methyl alcohol 2; J. Stevens[4], W. Clough and C. Johns[5], S. Shipley and G. Given[6], F. Crane[7] and J. Clancy[8] are indicative of the preferred solvent combinations in the presence of propyl acetate. The W. Webb formula[9] is for a cellulose ether composition, preferably water-insoluble ethylcellulose or benzylcellulose, in which propyl acetate in conjunction with methyl or ethyl alcohols is prescribed. Propyl acetate containing ethyl and butyl acetates may be made by sulfation and esterification of petroleum gases[10]; by distilling a mixture of propyl alcohol, acetic acid and water[11]; or by obtaining complete "alcoholysis"[12].

1. D. R. P. 506677; abst. C. A. 1931, **25**, 784.
2. U. S. P. 1469825; abst. C. A. 1923, **17**, 3919.
3. U. S. P. 381354. E. P. 8253, 1887. U. S. P. 434330. E. P. 3345, 1891. U. S. P. 491880.
4. U. S. P. 552934, 552935.
5. U. S. P. 1485071.
6. U. S. P. 1618481. E. P. 250894. U. S. P. 1618484.
7. E. P. 12684, 1890.
8. U. S. P. 1439293. E. P. 190694. F. P. 553547.
9. U. S. P. 1434465.
10. C. Ellis, U. S. P. 1365049; abst. C. A. 1921, **15**, 865.
11. H. Buc, U. S. P. 1808155; abst. C. A. 1931, **25**, 4285. E. P. 300418.
12. J. Steffens, U. S. P. 1433308.

This latter is a general method of making higher esters from lower esters by boiling with sulfuric acid, the lower ester yielding alcohol and the acid radical uniting with the higher alcohol. Propyl, butyl, amyl, glyceryl, glycol acetate, propionate, butyrate, valerate, tartrate, oxalate may be thus prepared. The viscosity of propyl acetate solutions of nitrocellulose has been determined by F. Baker[1].

n-Propyl acetate is seldom used in the pure state, usually being unintentionally admixed with butyl and amyl acetates, i.e. commercial low boiling fusel oil is acetated without purification. Its properties therefore are either between ethyl and butyl acetates, or more closely approach pure butyl acetate. In addition to dissolving cellulose nitrate with avidity, it dissolves a wide range of cellulose ethers, especially in conjunction with the lower aliphatic alcohols and the aromatic hydrocarbons. It dissolves benzyl abietate, ester gum,, coumarone, mastic, elemi and sandarac, castor and other oils. Water dissolves 1.9% propyl acetate by weight at 20°. A mixture of *iso*propyl acetate 47.5% and *iso*propyl alcohol 52.5% has a constant b. pt. 80.1° and is a good solvent of nitrocellulose[2].

*iso*Propyl acetate has sp. gr. 0.93, b. pt. 92°, acidity 0.03%. Soluble 3.1% in water.

Chlorpropyl Acetate. M. Seaton[3] has described the applicability of this body as a cellulose ester solvent, a liquid boiling at 145°, insoluble in water and relatively stable. Chlorpropyl acetate 25, alcohol 20 and benzene 55 are recommended as a suitable solvent combination for nitro- or acetyl-cellulose.

Butyl Acetate, Tamasol, has been used as a cellulose ether solvent[4] and for dissolving cellulose acetate[5] and

1. J. C. S. 1913, **103**, 1662; abst. C. A. 1913, **7**, 4069; J. S. C. I. 1913, **32**, 991.
2. W. Clough and C. Johns, U. S. P. 1485071; abst. C. A. 1924, **18**, 1389.
3. U. S. P. 1397986; abst. J. S. C. I. 1922, **41**, 53-A.
4. U. S. P. 1217027, 1217028, 1434465, 1437952, 1469825, 1469826.
5. U. S. P. 1309980, 1365049, 1370879.

the nitrocelluloses[1]. The range of application is indicated in the processes of D. Bradner[2], J. Keating[3], G. Peters[4] who uses a mixture of butyl acetate 30, toluene 45.5, ester gum 7.5, tricresyl phosphate 5; V. Turkington[5] (butyl acetate 40, butyl alcohol 50), E. Flaherty[6] (butyl acetate, butyl alcohol and xylene), and[7] *n*-butyl acetate 40, benzene 60. The peculiar compound of G. Zeller[8] is obtained by distilling together butyl and amyl alcohol with formic and acetic acids in the presence of benzine and an oxidizing agent.

n-Butyl Acetate is probably the most widely used of cellulose nitrate solvents on account of the quantity of *n*-butyl alcohol produced by bacterial action on carbohydrates by specific micro-organisms. The commercial grade does not have its solvent activity impaired by dilution with other lower boiling aliphatic esters. It is non-toxic, has a less pronounced odor than amyl acetate and a better solvent for the general type of synthetic resins. Sp. gr. 0.87-0.89, b. pt. 110-130°. The pure ester boils at 124.5°. Soluble in water 1.2% at 10°, to 1.55% at 30°. Water dissolves 1% at 20°. It is produced by direct esterification of the alcohol with acetic acid. A binary mixture of *n*-butyl acetate 71.3% with water boils at 117.2°, with 27.4% *n*-butyl alcohol and butyl acetate, boils at 89.4°.

iso-Butyl Acetate, Tamasol J, is non-toxic, sp. gr. 0.868-0.875, b. pt. 116°, ester content 95-99%. With water it forms a binary constant boiling mixture of 83.4%, b. pt.

1. U. S. P. 1309981, 1320458, 1321611, 1323624, 1350274, 1350981, 1365049, 1370878, 1378804, 1439293. Tamasol IN, is said to be butyl acetate, b. pt. 109-130°, sp. gr. 0.865 at 20°. Tamasol II, is a mixture of solvents containing butyl acetate, b. pt. 124-160°, sp. gr. 0.844 at 20°. Tamasol III is said to be a similar mixture, boiling range 144-183°, sp. gr. 0.861. Dissolvan DN is claimed to be a solvent mixture containing butyl alcohol and butyl acetate. Formosol is ethyl formate and Solactol, ethyl lactate.
2. Can. P. 311489; abst. C. A. 1931, **25**, 3502.
3. Can. P. 320965; abst. C. A. 1932, **26**, 2834.
4. Can. P. 283058; abst. C. A. 1928, **22**, 4262. E. P. 293434; abst. J. S. C. I. 1929, **48**, 138-B.
5. Can. P. 317205.
6. U. S. P. 1323624.
7. E. Flaherty, U. S. P. 1356440; abst. C. A. 1921, **15**, 183.
8. U. S. P. 518388.

87.4°. Dissolves benzyl abietate, ester gum, coumarone, elemi, dammar, mastic and sandarac. Miscible with linseed, castor, tung and other oils. Dissolves some types of cellulose acetate in conjunction with alcohol or acetone. The cellulose ethers are soluble in all the isomeric butyl acetates.

sec-Butyl Acetate. Miscible with benzene without opalescence, and forms a constant b. pt. of 99° with 13.7% *sec*-butyl alcohol. Sp. gr. 0.86, b. pt. 111-114°, 3% dissolving in water. Dissolves benzyl abietate, ester gum and the softer resins. Miscible with the usual cellulose ester solvents including the paraffin and aromatic hydrocarbons.

Butyl Chloracetate. The I. G. Farbenindustrie[1] have described as efficient solvents for lacquer materials, methyl, ethyl, propyl and butyl chloracetates and methylglycol chloracetate.

Amyl Acetate, Banana Oil, is probably the best known of the nitrocellulose dissolving bodies and the doyen of acceptable high boiling solvents. The lacquer industry was initiated and for many years built around the use of this ester as a cellulose nitrate direct solvent. It has found considerable application for dissolving pyroxylin[2], cellulose acetate[3], celluloid[4], other cellulose esters[5] and

1. D. R. P. 515056; abst. C. A. 1931, **25**, 1692.
2. U. S. P. 269340, 340026, 352726, 384005, 417202, 422195, 428654, 434330, 445528, 463039, 471422, 491880, 502546, 507964, 543197, 552209, 552935, 561624, 578714, 587097, 587211, 597144, 610861, 622727, 690915, 694946, 797373, 841509, 861435, 888516, 893987, 894108, 909288, 961360, 982370, 1021569, 1089960, 1122554, 1133062, 1135026, 1142619, 1147850, 1148258, 1152625, 1158265, 1158961, 1160979, 1181758, 1190806, 1190807, 1195673, 1196144, 1197019, 1202490, 1208358, 1233333, 1242491, 1251862, 1253956, 1254791, 1262825, 1265648, 1266073, 1267445, 1290794, 1309981, 1320458, 1321611, 1321633, 1321634, 1322786, 1323624, 1329386, 1341207, 1341710, 1355976, 1356440, 1360759, 1360763, 1369467, 1370878, 1372021, 1375208, 1378804, 1381412, 1393355, 1397042, 1398239, 1400196, 1408095, 1410790, 1414115, 1419258, 1427754, 1427941, 1429295, 1436231, 1438395, 1439293, 1456782, 1480016, 1493207, 1493208, 1496457, 1503453, 1508457.
3. U. S. P. 1160979, 1165179, 1181758, 1199800, 1309980, 1388472, 1393355, 1408095.
4. U. S. P. 1128094, 1146336, 1146391, 1153574, 1167468, 1197019, 1205822, 1221457, 1235154, 1300550, 1342767, 1361783,

the cellulose ethers[1], and for the extraction of acetic acid[2]. The L. Riley process[3] employs cellulose acetate with amyl acetate and tetrachlorethane. The use of amyl acetate in lacquers is well established, this ester being water-white, neutral, miscible with benzene in any proportion, sp. gr. 0.876-0.89, b. pt. 139-141°, practically insoluble in water. Amyl acetate prepared from petroleum is known commercially as Pentacetate. Pentexcel is said to be amyl acetate of lower ester content.

Amyl Chloracetate, first brought to the attention of the industry by O. Amend[4] in 1887, is an excellent nitrocellulose solvent, but is prone to split off chlorine upon long exposure to the light. It is said to be a mixture of amyl chloracetate, amyl chloride and amyl acetate. T. Craddock and J. Thom[5] have also described the use of amyl chloracetate as a nitrocellulose dissolving body. Methylamyl acetate (methyl*iso*butylcarbinol acetate) with a smaller proportion of ethylene glycol is claimed to be especially advantageous for lacquer manufacture[6].

Glycol Acetates. As the glycols and homologues are dihydric, combination with monocarboxylic acid as acetic, gives rise to mono- and di-acetates, the di-acetates herein being expressed as "acetate."

Ethylene Glycol Monoacetate, Glycol Monoacetate, is the lowest member in this series, being an odorless, colorless liquid soluble in water and miscible with benzene, tolu-

1377677, 1382613, 1425510, 1472165, 1477880, 1477881, 1477882, 1477883.

5. U. S. P. 1342267, 1342268, 1375208, 1389084, 1390252, 1408095, 1437952.

1. U. S. P. 1217027, 1217028, 1389084, 1429179, 1437952, 1505043.

2. Soc. Anon. des Distilleries des Deux Sevres, E. P. 296974.

3. E. P. 15428, 1915; abst. J. S. C. I. 1916, **35**, 960. R. Calvert, U. S. P. 1702151, has described methylamyl acetate (4-methyl-2-pentanol acetate, methyl*iso*butyl carbinol acetate) b. pt. 146 at 748 mm., has been advocated as a desirable cellulose ester and synthetic resin solvent.

4. U. S. P. 371021 and Re-10879. U. S. P. 372100.

5. E. P. 194144. See D. R. P. 51554; abst. Ber. 1891, **24**, 133.

6. R. Calvert, U. S. P. 1702151; abst. C. A. 1929, **23**, 1517.

ene and xylene, b. pt. 181-182°. Chemically it is a combination of primary alcohol and ester, and as such should find wide application in the solvent field. In 1913, W. Plinatus called attention to the use of this ester as a solvent[1], and J. Davidson[2] has shown that ethylene monoacetate and glycol monoacetate are direct solvents for the cellulose ethers and linseed oil.

Ethyleneglycol Diacetate, Glycol Acetate, has been detailed by K. Meyer[3] as to its relative solvent capacity, and G. Young[4] has pointed out its applicability in cellulose acetate lacquers, its presence therein preventing "blushing" when working in a highly humid atmosphere. The cellulose ether composition of S. Carroll[5] involves the use of glycol acetate with methyl or ethyl alcohol and benzene. While glycol acetate alone is a non-solvent of water-insoluble ethylcellulose, in conjunction with active or direct solvents it imparts suppleness and pliability to cellulose ether films. Some methylcelluloses of the type of low water resistivity dissolve directly in glycol acetate, especially upon the application of moderate heat. E. I. du Pont de Nemours & Co.[6], the British Thomson-Houston Co.[7], I. G. Farbenindustrie[8], and M. Renker[9] all utilize glycol acetate in connection with cellulose ester combinations. W. Rodebush[10] has described methods of producing ethylene-, butylene- and amylene-glycol acetates, propionates and butyrates. Glycol acetate is a colorless liquid of odor resembling pure ethyl acetate, sp. gr. 1.12, b. pt. 187-190°. Dissolves mastic, rosin, sandarac, elemi, dammar, camphor, ester gum and coumarone. Known as "Solvent GC."

Ethyleneglycol Monoethylether Monoacetate, Cellosolve Acetate, is a colorless liquid of bland and not dis-

1. E. P. 16940, 1913; abst. C. A. 1915, **9**, 2589.
2. U. S. P. 1731333, 1791301. Can. P. 271382.
3. D. R. P. 332677; abst. J. S. C. I. 1921, **40**, 370-A.
4. U. S. P. 1522852; abst. C. A. 1925, **19**, 894.
5. U. S. P. 1735156; abst. C. A. 1930, **24**, 723.
6. E. P. 29963, 1912.
7. E. P. 283162; abst. J. S. C. I. 1928, **47**, 680-B.
8. E. P. 287124; abst. Chem. Zentr. 1928, I, 3144.
9. E. P. 297993.
10. U. S. P. 1430324.

agreeable odor, and is substantially insoluble in water. The J. Davidson lacquer thinner couples this ester with benzene and toluene[1], with which it is freely miscible. It dissolves nitrocellulose and some types of the cellulose ethers, especially those ethers as methyl- and ethyl-cellulose which do not have a high resistivity to water. Alcohol in small amounts is an aid to solution. Sp. gr. 0.975-0.981, b. pt. 153-154°, soluble 22% in water at 20°. The vapor pressure is 1.25 mm. at 20°. It is a poor solvent for cellulose acetate, but the addition thereto of small amounts of acetone increases materially the dissolving effect of this ester. Ethyleneglycol monomethylether is similar to the ethyl ester, but with a lower boiling range and higher evaporative capacity.

Ethylidene Diacetate, Ethylidene Acetate is isomeric with the corresponding ethylene acetate. It may be prepared by the action of acetylene and anhydrous acetic acid in the presence of mercury naphthalene sulfonate[2]. C. Claessen[3] uses this ester as a nitrocellulose direct solvent, and the Chemische Fabrik Griesheim-Elektron[4] dissolve cellulose acetate with ethylidene acetate in conjunction with vinyl acetate or benzoate, chlorethyl benzoate, ethylidene acetobenzoate and chlorethyl acetate. The manufacture of these esters has been described by F. Klatte[5], M. Bouvier and L. Hugoniot[6], and M. Marshall and G. Shaw[7]. The H. Matheson plastic composition[8] comprises cellulose acetate with ethylidene acetate and low boiling diluents. In nitrocellulose lacquers[9], the amyl acetate may advantagously be partially or wholly replaced by this ester. Ethyli-

1. U. S. P. 1731332; abst. C. A. 1930, **24**, 252. E. P. 289373.
2. M. Beudet and Soc. Chim. des Usines du Rhone, U. S. P. 1351990. D. R. P. 334554.
3. D. R. P. 174259, Addn. to D. R. P. 172966; abst. Chem. Zentr. 1906, II, 1631.
4. F. P. 461223. Belg. P. 259551. D. R. P. 271381, 313696, 338056, 341720.
5. U. S. P. 1084581. E. P. 14246, 1913.
6. U. S. P. 1680760. E. P. 252632.
7. U. S. P. 1450982; abst. J. S. C. I. 1923, **42**, 683-A.
8. U. S. P. 1488608; abst. J. S. C. I. 1924, **43**, 464-B.
9. Chem. Fabr. Griesheim Elektron, D. R. P. 281373; abst. C. A. 1915, **9**, 1850.

dene propionate and butyrate have as yet, insofar as aware, not been used commercially for cellulose ester solvent purposes. E. Sellig[1] manufactures benzyl acetate and ethylidene acetate in the same process. Amylene diacetate[2] has been described.

Glyceryl Acetates. Acetins. Mono-, Di-, Tri-acetin. In 1889, R. Schüpphaus[3] pointed out the value of three acetins as nitrocellulose direct solvents and softeners. The hygroscopicity of these three esters diminishes with increasing increment of glyceryl rest, i.e. triacetin is least deliquescent. W. Plinatus[4] has described the use of triacetin *per se* in the nitrocellulose lacquer industry, and the employment with dimethyl phthalate as a nitroacetylcellulose (cellulose acetonitrate) dissolvant[5]. Acetin, especially in admixture with acetochlorhydrin, benzicin, pulegone, thujone and condensation products of acetone with form-, acet- or benz-aldehyde forms ready solvent mixtures[6]. Methyl-, ethyl or benzyl-cellulose in the presence of triacetin, *p*-toluenesulfonamide, xylenealkylsulfonamides, ethyl phthalate, mannol, resorcin diacetate and nitrobenzene produce transparent, readily flowable solutions and celluloid substitutes, depending upon the increment of low boiling volatile solvent incorporated therein. The S. Carroll cellulose ether composition[7] is built up water-insoluble ethylcellulose 100, an acetin 10, with a common volatile solvent 300-500 parts. J. Kessler prefers a mixture of diacetin 40-30, triacetin 60-70[8], while methyl-, ethyl- and benzylcellulose in another method[9] is dissolved in a mixture of triacetin, benzene, toluene or gasolene, to which urea as a stabilizer may be added. Cellulose triacetate with triace-

1. D. R. P. 41507; abst. Friedlaender, 1877-1887, **1**, 577.
2. E. I. du Pont de Nemours Powder Co., Can. P. 153891.
3. U. S. P. 410208. 4. E. P. 25449, 1911.
5. Akt. Ges. fuer Anilin Fabrikation, E. P. 5633, 1914. F. P. 461058, 463622.
6. J. Goldsmith and British Xylonite Co., E. P. 13131, 1900.
7. U. S. P. 1658369; abst. C. A. 1928, **22**, 1237.
8. U. S. P. 1360759. Can. P. 214462.
9. American Cellulose and Chemical Mfg. Co., E. P. 249600. C. Dreyfus and G. Schneider, Can. P. 269482.

tin[1] as a coating for airplane fabrics is said to give the requisite tautness combined with adequate flexibility. Acetin is a solvent for almond oil[2], aniline black[3] and many dyestuffs[4].

Commercial diacetin is a mixture of isomeric esters with a preponderance of the di-ester. Sp. gr. 1.18, b. pt. 260°, miscible with water and hygroscopic. Not commercially obtainable in pure condition, and inferior to triacetin. The latter is a yellowish, odorless, non-inflammable liquid, fulfilling the function of a cheap softening agent exhibiting solvent capacity. Sp. gr. 1.16 at 15.6°, b. pt. 255-260°.

Triacetin possesses high colloiding capacity for nitro-, acetyl-, ethyl -and benzyl-cellulose—a rare property for one solvent to dissolve efficiently these three classes of cellulose compounds. Softness in film is proportional to the amount used. Being a rabid solvent of synthetic resins, benzyl abietate, colophony and blown castor, linseed and tung oils, it is indicated in the artificial leather industry, and unlike castor oil, does not come to the surface and "spew" under the heat of the embossing plate. Non-miscible with hydrocarbons. Triacetin dissolves 3.7% of water[5]. G. Noyer has reviewed the use of the acetins as camphor substitutes in acetylcellulose formulas[6].

Polyglyceryl Acetate. As useful plasticizers[7] there have been described glycerol derivatives etherified with one or more molecules of a monocarboxylic acid as *aa'*-diglyceryl tri(or tetra)-acetate and triglyceryl tri(or tetra) acetate. They are highly viscous, of high b. pt. and insoluble

1. Vickers, Ltd., J. McKechnie and A. Ryan, E. P. 142615; abst. C. A. 1920, **14**, 2863.
2. G. Esselen, U. S. P. 1378099.
3. J. Schiffmann, U. S. P. 1421728.
4. S. Tootal, U. S. P. 1367930. For other acetin-containing lacquers, see U. S. P. 1005454, 1015156. F. P. 432264. D. R. P. 210519. E. P. 165439.
5. For manufacture of acetin, see U. S. P. 1146854, 1378099, 1509864.
6. Caout. et Gutta. 1913, **10**, 6999; abst. Kunst. 1913, **3**, 353.
7. C. F. Boehringer & Soehne, E. P. 364807; abst. J. S. C. I. 1932, **51**, 519-B.

in water. Sp. gr. around 1.14-1.15. Glyceryl aceto-caproate, -caprylate, -caprate, -laurate, -myristate, -palmitate and -oleate form the basis of the softeners described by G. Schwartz[1], Nobel Industries, Ltd.[2], and I. G. Farbenindustrie[3].

Propionyl-diacetin (glyceryl diacetopropionate)[4], benzoated acetins as glyceryl monobenzoate (monobenzoin) and glyceryl dibenzoate (benzodiacetin), glyceryl mono-oleate (oleodiacetin), benzochlorhydrin, dinitroacetin, dinitromonoacetin, mononitrodiacetin have also been brought forward as desirable cellulose ester colloidants[5]. Acetin, mannol, triformin, epiformin and butyl and amyl tartrates and ricinoleates[6] have been recommended for this purpose.

Propionins, Glyceryl propionates, Glyceryl tripropionate, boil at 130-132°, sp. gr. 1.1 at 20°/18°, and may be prepared by slowly adding ethyl ketone to glycerol at 150° and fractionating *in vacuo*[7]. Tripropionin is a cellulose ether plasticizer in the presence of a solvent as acetone[8].

Butyrins, Glyceryl Butyrates, comprise mono-, di- and tri-butyrin. In a patent published in 1913[9] and one in 1926[10], W. Plinatus has gone into detail as to the applicability and limitations of this softener in connection with cellulose compounds. Glyceryl benzoate harmonizes with the butyrins and increases softness and pliability.

Pentaerythrol Acetates. Pentaerythritol Acetates, as pentaerythritol tetra-acetate, is a direct cellulose ether softener, 100 parts water-insoluble ethylcellulose being dissolved with 15 parts pentaerythritol tetra-acetate in 300-

1. U. S. P. 1558299; abst. J. S. C. I. 1926, **45**, 66-B.
2. E. P. 300157; abst. Silk J. 1929, **5**, #57, 74.
3. D. R. P. 548370; abst. C. A. 1932, **26**, 3516.
4. A. Davis, U. S. P. 1763955; abst. C. A. 1930, **24**, 3868.
5. R. Schuepphaus, U. S. P. 598648.
6. Nouvelle L'Oyonnithe, F. P. 465345.
7. R. Seuffert, Zts. Biol. 1913, **61**, 551; abst. C. A. 1913, **7**, 3761.
8. S. Carroll, U. S. P. 1826693.
9. W. Plinatus, E. P. 16940, 1913; abst. J. S. C. I. 1915, **34**, 793.
10. *Ibid.* E. P. 246272; abst. C. A. 1927, **21**, 496.

400 parts volatile solvent as methyl alcohol or methyl acetate[1].

The triglyceride of octadecadien-9.11-acid (1) as a benzylcellulose solvent and plasticizer forms the subject of the J. Scheiber disclosure, benzylcellulose 5 parts being dissolved by the aid of heat, in 50 parts glyceryl octadeca-9.11-oate[2]. Nitroformin and dinitroformin[3] form the basis of the non-freezing gelatinant of V. Vender, combined with the acetins.

Glycerylphenyl Acetates. Glycerylphenyl and glyceryl-cresyl acetates, abietates, benzoates and phthalates as suitable plasticizing bodies for cellulose compounds have been patented. Phenyl acetate as a suitable solvent for acetylcellulose has been pointed out by H. Dreyfus[4]. It dissolves cellulose acetate as does cresyl acetate, in conjunction with alcohol, heat aiding solution. Aniline acetate (amidophenyl acetate) has been patented as a cellulose ether dissolving and colloiding ester, the viscosity of the solution being regulated by the addition of methyl alcohol and methyl acetate thereto[5]. One part water-insoluble ethylcellulose will dissolve in 3-6 parts of this solvent. Aniline acetate also is a solvent for nitrocellulose and cellulose acetate.

Phenoxyethyl Acetate, a liquid substantially non-volatile at ordinary temperature[6] dissolves nitrocellulose, the preferred amount being 8 of nitrocellulose to 2 of solvent.

Resorcinol Diacetate. Of the three isomeric aromatic dihydroxy alcohols, hydroquinone, pyrocatechol and resorcinol, the latter esterified with acetic acid has been found an

1. H. Clarke, U. S. P. 1548933; abst. C. A. 1925, **19**, 3018.
2. J. Scheiber, D. R. P. 544697, Addn. to D. R. P. 522486.
3. V. Vender, U. S. P. 946294.
4. F. P. 432264.
5. E. Farrow, U. S. P. 1494469; abst. C. A. 1924, **18**, 2249.
6. J. Gardner, U. S. P. 1804503; abst. C. A. 1931, **25**, 3855.

Phenoxyethyl acetate is substantially non-volatile at ordinary temperatures and is a liquid. Naphthoxyethyl acetate is a solid and also a good pyroxylin solvent. The invention covers phenoxy- or naphthoxy-methyl (or propyl, butyl, amyl) acetate or methyl, ethyl, propyl, butyl and amyl cresoxyacetate, cresoxymethyl (or ethyl, propyl, butyl, amyl) acetate.

efficient emollient and colloidating agent for nitrocellulose, acetylcellulose and the cellulose ethers. The J. Donohue cellulose ether film composition involves combining resorcin acetate (resorcinol diacetate) or resorcin monoacetate, or the mono- or di-acetate of pyrocatechol (catechol) and hydroquinone (hydroxyquinol) or the trihydric aromatic alcohol pyrogallol with acetic acid. For example, 20 parts ethylcellulose may be dissolved with 2 of hydroquinone acetate and 140 parts of a mixture of methyl acetate and methyl alcohol. Pyrogallol triacetate acts similarly[1]. The Internationale Cellulose-ester Ges.[2] and L. Lederer[3], have been advocated for the same purpose. Knoll & Co.[4] prefer resorcinol monoacetate.

Benzyl Acetate. Plastolin I. As solvent for resins in metallic pigment ink manufacture, benzyl acetate with terpineol, terpinyl acetate, ethyl benzoate and dammar, oil resin has been recommended[5]. The cellulose ether solvent composition of W. Webb[6] is prepared by mixing benzyl acetate with methyl or ethyl alcohols. Homologues of benzyl acetate (the propionate or butyrate) are said to act equivalently. Benzyl acetate has been used in airplane dope[7], as a cellulose acetate solvent[8], varnish remover[9], and in polishes[10]. "Plastolin I" is stated to be benzyl acetate. This solvent has a powerful but agreeable odor reminiscent of jasmine flowers, sp. gr. 1.06-1.07, b. pt. 215-216°, non-toxic, the commercial grade containing small amounts of benzyl

1. J. Donohue, U. S. P. 1552803; abst. C. A. 1925, **19**, 3593. S. Carroll, U. S. P. 1552792, has disclosed a cellulose ether composition utilizing resorcinol diacetate in the presence of methyl or ethyl alcohols. Equal parts of resorcinol diacetate and methyl alcohol are mixed, 1 part water-insoluble ethylcellulose being soluble in 5-7 parts of this mixture.
2. D. R. P. 277529; abst. C. A. 1915, **9**, 862.
3. E. P. 8945, 1909; abst. J. S. C. I. 1909, **28**, 1271. F. P. 402083.
4. D. R. P. 298806; abst. Kunst. 1920, **10**, 22.
5. Alchemic Gold Co., E. P. 199923; abst. C. A. 1924, **18**, 336.
6. U. S. P. 1469863; abst. C. A. 1923, **17**, 3919.
7. H. Ross, U. S. P. 1440178.
8. U. S. P. 1199800, 1388472, 1394890.
9. U. S. P. 1167640, 1169783, 1185641, 1328080.
10. J. Inouye, U. S. P. 1415570.

alcohol, chlortoluene, dibenzyl ether and dibenzyl, nearly all of which exercise solvency on the cellulose ethers and esters. It exerts a temporary softening effect on films, is an excellent solvent for nitro-, acetyl-, ethyl- and benzyl-cellulose, dissolving benzyl abietate, coumarone, ester gum, sandarac, mastic, elemi and dammar.

Benzylidene diacetate (m. pt. 58°), *m*-chlorbenzylidene diacetate (m. pt. 65°) and *p*-chlorbenzylidene diacetate (m. pt. 82°)[1] have been patented as desirable camphor substitutes. Hexanol acetate[2] with ethyl *p*-toluenesulfonate, dichlorhydrin, triacetin or ethyl lactate has been advanced as useful nitro- and acetyl-cellulose solvent and gelatinant, and hexyl acetate as a direct cellulose ether solvent in conjunction with methyl or ethyl alcohols[3].

Naphthyl Acetate has been used as a softener and plastifier in the formulas of H. Dreyfus[4], and E. Zuehl[5], *a*- or *b*-naphthyl acetate being specified[6], or the corresponding benzoates. Esters of phenoxylacetic or naphthoxylacetic acids as the propyl, butyl, amyl, phenyl or naphthyl esters[7] are included in this category, one advantage being that they are inodorous. They are used in methyl or ethyl alcohol or acetate solution. Isobornyl acetate[8] has been detailed as a camphor substitute in plastic formation. As a solvent harmonious to both cellulose esters and rubber, tetrahydronaphthol acetate may be mentioned[9]. In an example

1. C. Claessen and the Badische Anilin & Soda Fabrik, D. R. P. 173020; abst. C. A. 1907, **1**, 672.
2. H. Wolff and R. Singer, E. P. 293732; abst. C. A. 1929, **23**, 1763.
3. J. Donohue, U. S. P. 1552801; abst. C. A. 1925, **19**, 3593.
4. F. P. 432264; abst. J. S. C. I. 1912, **31**, 24. Belg. P. 241251. E. P. 13100, 1910.
5. U. S. P. 729990; abst. J. S. C. I. 1903, **22**, 817. D. R. P. 162239.
6. Zuehl & Eisemann, D. R. P. 118052. Aust. P. 6545. E. Zuehl, U. S. P. 700885. E. P. 11751, 1900; 8072, 1901; 23445, 1902. F. P. 301703, 325585.
7. *Ibid.* D. R. P. 119636.
8. C. Claessen, D. R. P. 172941; abst. Chem. Zentr. 1906, II, 738.
9. E. Meyer and W. Claasen, D. R. P. 428058. R. Garke, E. Meyer and W. Claasen, E. P. 241858. F. P. 598715.

cited, 60 gms. benzylcellulose, 13 gms. phenol resin, 10 gms. india rubber are dissolved in 16 gms. tetrahydronaphthol acetate to which acetone may be added. Tetrahydronaphthol acetate (tetralol acetate) is a clear, viscous oil, b. pt. 150-152° at 11 mm., sp. gr. 1.096 at 15°. At normal temperature it is not volatile, is completely insoluble in, and not saponifiable with water. Readily soluble in the usual cellulose ether solvents.

Guaiacol Acetate, Eucolum, Eucol, has been patented as a useful adjunct in cellulose acetate compositions[1]. It is an antiseptic, b. pt. 123-124°[2]. For the manufacture of dimethylaminophenyl acetate, the process of H. Clarke may be used[3]. Bornyl acetate[4] has been advocated as a cellulose acetate solvent.

K. Stickdorn[5] has discussed the various new cellulose derivative plasticizers including the fatty acid esters of hexalin, and has recorded data on do-, tetra- and hexa-decyl acetate, dodecyl butyrate and oleate, octadecyl benzoate and oleate, and octyl-butyl and -phenyl ether.

Acetoacetic Esters. Acetoacetic acid (acetylacetic acid, acetone monocarboxylic acid, *b*-ketobutyric acid) forms a series of stable esters which are liquids, dissolve with difficulty in water, possess an ethereal odor, may be distilled without decomposition, and possess an *acid-like* character.

Methyl Acetoacetate. The process of A. Backhaus[6] for preparing plastic compositions employs methyl, ethyl, propyl, butyl, methylethyl and amyl acetoacetates, preferably in the presence of ethyl acetate, as solvents for methyl- and ethyl-cellulose. Cellulose acetate with methyl or ethyl ace-

1. H. Smith, U. S. P. 1858285.
2. R. Wegscheider and A. Klemenc, Monats. Chem. 1911, **31**, 709; abst. C. A. 1911, **5**, 1754.
3. U. S. P. 1434429.
4. W. Lindsay, U. S. P. 1199800, 1388472.
5. Farben Ztg. 1931, **37**, 341; abst. C. A. 1932, **26**, 1457; J. S. C. I. 1932, **51**, 196-B. See also "Solvent Balance," P. Symons, Brit. Plastics, 1932, **2**, 95, 101, 115, 118. S. Sheppard and S. Sweet, J. Phys. Chem. 1932, **36**, 819.
6. U. S. P. 1437952; abst. C. A. 1923, **17**, 879; J. S. C. I. 1923, **42**, 91-A; Kunst. 1925, **15**, 43; Chem. Zentr. 1923, II, 1123; Caout. et Gutta. 1923, **20**, 11931.

toacetates forms the lacquer basis of the L. Clement and C. Riviere patent[1]. Methyl acetoacetate boils at 170° corr., sp. gr. 1.038, and ethyl acetoacetate at 181°.

Methylene acetoacetate with monochlorhydrin constitutes an excellent cellulose acetate dissolvant[2].

Ethyl Acetoacetate (incorrectly Acetoacetic Ether). In 1893, C. Borgmeyer and L. Paget[3] pointed out the advantages of ethyl and amyl acetoacetates as direct solvents in the nitrocellulose industry, in which year J. Perl[4] published his bronzing composition of pyroxylin, ethyl acetoacetate, amyl acetate and dammar. The T. Tesse cellulose acetate airplane wing dope utilizes ethyl acetoacetate, eugenol, benzyl alcohol, triacetin, carvacrol, carvol, isoeugenol and methyl acetate[5], while H. Willkie[6] combined ethyl acetoacetate, ethyl phthalate, triacetin, ethyl succinate, methyl phthalate and toluene. H. Dreyfus accentuates the value of ethyl acetoacetate as a direct cellulose acetate dissolving body[7]. Plastic masses prepared from cellulose esters and the condensation product between ethyl acetoacetate and formaldehyde[8]; cellulose ester lacquers of ethyl acetoacetate and ethyl and amyl acetates[9]; airplane varnish containing ethyl acetoacetate with benzyl alcohol[10]; and the acetylcellulose lacquer of A. Martens[11] are indicative of the variety of fields of usefulness recommended for this solvent. The Chemische Fabrik von Heyden[12] lacquer is ace-

1. F. P. 479387; abst. C. A. 1916, **10**, 2308.
2. Farbenfabriken vorm. F. Bayer & Co., E. P. 228518; abst. C. A. 1925, **19**, 2878; J. S. C. I. 1925, **44**, 857-B; Chem. Zentr. 1925, I, 2732. D. R. P. 406426, Addn. to D. R. P. 383699; abst. J. S. C. I. 1925, **44**, 217-B; Chem. Zentr. 1925, I, 908.
3. U. S. P. 507964. E. P. 22137, 1893.
4. E. P. 3557, 1893. F. P. 228158, 233727; abst. J. S. C. I. 1896, **15**, 729. D. R. P. 68356; abst. Wag. Jahr. 1893, **39**, 1098.
5. T. Tesse, U. S. P. 1521055.
6. U. S. P. 1449156, 1449157.
7. F. P. 432264.
8. Farbenfabriken vorm. F. Bayer & Co., D. R. P. 379343.
9. L. Nottelle and R. Heraud, F. P. 445638.
10. T. Tesse, U. S. P. 1426521. E. P. 158521. F. P. 495000.
11. Mitt. kgl. Matieralprufungsamt, 1911, **29**, 57; abst. J. S. C. I. 1911, **30**, 414; C. A. 1911, **5**, 2943. See E. Worden, Tech. Cell. Esters, 1916, **8**, 2816.
12. D. R. P. 324786; abst. J. S. C. I. 1920, **39**, 779-A; Chem. Zentr. 1920, IV, 507. Aust. P. 79427; abst. Kunst. 1920, **10**, 150.

tylcellulose 10, acetone 75, ethyl acetoacetate 2, or nitrocellulose 10, amyl acetoacetate 4 with a sufficient amount of alcohol-ether to give the desired flowing qualities.

W. Lindsay[1] combines ethyl acetoacetate, diphenylamine, trichlorphenol, phenyl salicylate and benzoic ether and acetodichlorhydrin; T. Tesse[2] uses ethyl acetoacetate, benzyl alcohol and triacetin; while R. Carter[3] has described a method of manufacture. This ester has also been used as a camphor substitute, cellulose acetate solvent[4], cellulose ether solvent[5], and for dyestuff manufacture[6]. It is soluble in alcohol, ether, benzene and chloroform, slightly in water, sp. gr. 1.031 at 15°, b. pt. 94°. P. Seymour[7] has published a bibliography on the subject. *iso*Butyl acetoacetate has sp. gr. 0.979 at 0°[8], and the amyl ester, 0.954 at 10°[9]. The conditions of acceptance of ethyl acetoacetate by the French Ministre de la Guerre (F-2535, S. M.) is that it shall be colorless, neutral to litmus, have a density of 1.02-1.04 at 15°, and that nothing should distill below 150°, but 90% pass over at 175-185°. Ethyl acetoacetate has been prepared from ethyl acetate by the action thereon of sodium[10], sodium ethylate[11], sodamide[12], calcium[13] or

1. U. S. P. 1245476, 1319229, 1386576. See U. S. P. 1050065, 1199798.
2. U. S. P. 1590783. See U. S. P. 1521055.
3. U. S. P. 1472324; abst. C. A. 1924, **18**, 400; J. S. C. I. 1924, **43**, 77-B. U. S. P. Reissue-16591 to 1472324; abst. C. A. 1927, **21**, 1819; J. S. C. I. 1927, **46**, 380-B.
4. W. Lindsay, U. S. P. 1245476, 1319229, 1386576. T. Tesse, U. S. P. 1426521. A. Backhaus, U. S. P. 1437952. H. Willkie, U. S. P. 1449156, 1449157.
5. A. Backhaus, U. S. P. 1437952.
6. H. Geldermann, U. S. P. 1166346. C. Kincaid, U. S. P. 1216812. E. Reber, U. S. P. 1270325, 1338397, 1447485. A. Green and K. Saunders, U. S. P. 1483797.
7. Biblio. of Aceto-Acetic Ester, 1894 (Smithsonian Misc. Coll. V. 38, 1898). Biblio. of Acetacetic Ester and its Derivatives, 1840-1891 (Smithsonian Misc. Coll. #970, 1894, 136).
8. O. Emmerling and C. Oppenheim, Ber. 1876, **9**, 1097.
9. M. Conrad, Ann. 1877, **186**, 231.
10. J. Crafts, Compt. rend. 1863, **56**, 707; abst. Jahr. Chem. 1863, **16**, 323. A. Geuther, Anzeigen, 1863, 281; abst. Jahr. Chem. 1863, **16**, 323. Jen. Zts. Med. U. Nat. 1865, **2**, 387; abst. Jahr. Chem. 1865, **18**, 302. See Zts. Chem. 1866, **9**, 5. Ann. 1877, **186**, 214. J. prakt. Chem. 1902, (2), **65**, 528. Ber. 1905, **38**, 709. Am. Chem. J. 1908, **40**, 76. J. A. C. S. 1908, **30**, 1876. K. Roberts, J. S. C. I.

sodium ethoxide[1]. Methylethyl, diethyl and propyl aceto-acetates boil at 198, 218 and 208° respectively. *iso*-Butyl ester boils at 202-206°, sp. gr. 0.979. Recently large scale methods of production have been perfected whereby this solvent is obtainable in practically unlimited quantities.

Benzylidene acetoacetate and diacetoacetate[2] and the product of the action of HCl thereon, i.e. 3-methyl-5-phenyl-4.6-dicarboxyethyl-keto-R-hexane have been advocated as efficient camphor succedanea with the cellulose esters.

Propionic Esters. The propionic esters all have a distinctive but not disagreeable odor, and have basic similarity to the corresponding acetic esters except a higher boiling point, lower evaporative tendency and lower solubility in water. They are miscible with the usual cellulose ether and ester solvents without turbidity when in the substantially anhydrous condition.

Methyl Propionate. The cellulose ether composition of J. Donohue[3] comprises methyl, ethyl, propyl, butyl and amyl propionates in conjunction with methyl alcohol. If 5-7 parts water-insoluble ethylcellulose be dissolved in equal parts methyl propionate, ethyl propionate and ethyl alcohol, a clear transparent solution results which does not blush upon evaporation to dryness. The formula of R. Stinchfield[4] is ethylcellulose 10, tetrachlorethane 45, and 15 parts of methyl or ethyl acetate, propionate or butyrate. As a

1924, **43**, 295-T. U. S. P. 1425626; abst. C. A. 1922, **16**, 3314. U. S. P. 1472324; abst. C. A. 1924, **18**, 400.

11. A. Geuther, Zts. Chem. 1868, **11**, 652. See Ber. 1900, **33**, 3735; 1905, **38**, 709. Am. Chem. J. 1907, **37**, 299.

12. A. Titherley, J. Chem. Soc. 1902, **81**, 1527. M. Freund and E. Speyer, Ber. 1902, **35**, 2321.

13. F. Perkin and L. Pratt, J. Chem. Soc. 1909, **95**, 161.

1. K. Roberts, J. S. C. I. 1924, **43**, 295-T.

2. C. Claessen, F. P. 363090; abst. J. S. C. I. 1906, **25**, 865. D. R. P. 172966; abst. Jahr. Chem. 1905-1908, II, 992; Wag. Jahr. 1906, **52**, II, 526. D. R. P. 172967, Addn. to D. R. P. 172966; abst. Mon. Sci. 1908, (4), **68**, 45; Jahr. Chem. 1905-1908, II, 992. D. R. P. 174259, Addn. to D. R. P. 172966; abst. C. A. 1907, **1**, 1198; Jahr. Chem. 1905-1908, II, 992; Mon. Sci. 1911, (5), **74**, 63. Aust. P. 26335.

3. U. S. P. 1473217, 1473218, 1473219; abst. C. A. 1924, **18**, 469.

4. U. S. P. 1432365.

cellulose acetate dissolvant, P. Seel[1] advocates ethyl propionate, not used alone but in the presence of fusel oil. B. pt. 91°, sp. gr. 0.937 at 4°.

Ethyl Propionate. The R. Mitchell[2] solvent consists of ethyl propionate 20, toluene 50, ethyl alcohol 20 and ethyl acetate 10, especially applicable for dissolving pyroxylin intended for coating fabrics. As a cellulose ether and acetylcellulose solvent, ethyl *a*-brompropionate has been advanced[3], preferably in the presence of acetone[4]. Ethyl *b*-hydroxypropionate, b. pt. 187° and the corresponding methyl and propyl esters have been described as useful nitrocellulose plastifiants in conjunction with butyl propionate, ethyl alcohol and triphenyl phosphate[5]. Likewise, the Canadian Industries, Ltd.[6], have pointed out desirable characteristics of the methyl, ethyl and propyl *b*-hydroxypropionates. These ester-alcohols should find application as solvents and softeners in connection with cellulose ether fluid and solid solutions.

n-Butyl Propionate may be used as a succedaneum for amyl acetate and butyl acetate, being less soluble in water and evaporating more slowly. It is a solvent of cellulose nitrate and cellulose ethers, but dissolves acetylcellulose best in conjunction with a direct or active solvent. It is miscible with castor, linseed and other oils and hydrocarbons and insoluble in water. Sp. gr. 0.883, b. pt. 146°. The cellulose acetate composition of S. Carroll[7] contains 10-30% butyl propionate.

Amyl Propionate has been used to a limited state, principally in brushing lacquer formulae, where rate of evaporation is desired. It is a solvent for cellulose nitrate, dissolves ethyl- and benzyl-cellulose as a latent solvent, its

1. U. S. P. 1342603; abst. C. A. 1920, **14**, 2418.
2. U. S. P. 1397173, 1397493; abst. J. S. C. I. 1922, **41**, 10-A.
3. S. Carroll, U. S. P. 1826691.
4. For other cellulose ester and ether compositions employing ethyl propionate, see U. S. P. 622727, 1309980, 1309981, 1342603, 1369467, 1370878, 1370879, 1398239, 1432365, 1473217.
5. W. Jenkins and Imperial Chemical Industries, Ltd., E. P. 307528; abst. C. A. 1929, **23**, 5338.
6. Can. P. 299310.
7. U. S. P. 1841311.

latency being overcome by the presence of a small amount of ethyl alcohol or acetone. It is insoluble in water and non-toxic. Dissolves benzyl abietate, ester gum elemi, sandarac, dammar and the softer copals. *iso*-Amyl propionate boils at 160.2°, sp. gr. 0.888 at 4°. The allyl ester boils at 124-124.5° and the crotyl ester at 147-148°. Methyl, ethyl, *n*- and *iso*propyl *a*-ethoxypropionate and *a*-*n*-propoxypropionate (b. pt. 187-188°) have been brought forward as desirable nitrocellulose colloidants in pyroxylin enamel production[1]. Of the hexyl (*a*-dimethylbutyl) esters[2], methyl-*iso*butyl carbinol butyrate, valerate, palmitate, stearate, oxalate, citrate, tartrate, oleate, laurate and succinate have been described as desirable adjuncts in pyroxylin solutions.

A series of 67 esters of glycerol has been patented, most of them of a resinous or wax-like nature[3] and intended for incorporation with cellulose derivatives in the production of varnishes. They comprise glyceryl propionate and the glyceryl esters of chlorpropiono-, chlorbenzo-, chloraceto-, propiono-, stearo-, palmito-, oleo-, benzo-, lacto-, salicylo- and glycollo-succinate, -tartrate, -glutarate, -malate, -camphorate and -phthalate, glyceryl chlorpropionosuccinate being an example.

Levulinic Esters. *b-Acetylpropionic Esters.* Ethyl levulinate has been described as a cellulose ether solvent[4], being a colorless liquid, b. pt. 205.2° corr., sp. gr. 1.0325 at 0°. The methyl ester boils at 191-191.5° at 743 mm., and the propyl ester at 215-216°. Benzyl levulinate as a plasticizer for cellulose ethers has been described by the Deutsche Hydrierwerke[5], used either alone or with acetol, acetol acetate, laurate or ricinoleate, or acetoin ketobutylrate or acetoin benzoate. H. Dreyfus[6] has also described

1. W. Jenkins and Imperial Chemical Industries, Ltd., E. P. 305960; abst. J. S. C. I. 1929, **48**, 333-B.
2. R. Van Schaack, U. S. P. 1702180; abst. J. S. C. I. 1929, **48**, 935-B.
3. General Electric Co., E. P. 24254, 1912. See E. P. 12807, 1884; 9027, 1886.
4. L. Lilienfeld, U. S. P. 1217027, 1217028. F. P. 459972.
5. D. R. P. 547039, Addn. to D. R. P. 535168.
6. F. P. 432264; abst. C. A. 1913, **7**, 3414.

the use of ethyl levulinate (ethyl levulate) for dissolving acetylcellulose. Starch ethers are also soluble in ethyl levulinate[1].

Butyric Esters. The alkyl butyrates are used primarily in the nitrocellulose industry, less so in connection with fluid preparations of the cellulose ethers and cellulose acetates. They are stable compounds of a pronounced but not disagreeable odor, devoid of toxicity and obtainable in unlimited amounts. Their water solubility is less than the corresponding propionates and acetates, and the speed of evaporation correspondingly diminished.

Methyl Butyrate has been advocated as a desirable ethylcellulose solvent in the process of R. Stinchfield[2], and as a plasticizing component in celluloids by the British & Continental Camphor Co.[3]. R. Mitchell[4] combines methyl or ethyl butyrate with methyl, ethyl, propyl or butyl alcohols as a cellulose nitrate dissolvant. Methyl butyrate boils at 102° corr., sp. gr. 0.919 at 0°/4°.

Ethyl Butyrate. P. Seel[5] has described the value of ethyl butyrate as an ethylcellulose solvent in conjunction with ethyl alcohol and benzene, a preferred formula being ethylcellulose 100, benzene-ethyl alcohol 500, ethyl butyrate 50. Ethyl *n*-butyrate is preferred. The nitrocellulose composition of A. Sulzer is ethyl butyrate with an aliphatic alcohol as methyl or ethyl alcohol[6]. The processes of H. Clarke[7], A. Sulzer[8], Triplex Safety Glass Co.[9] and R. Eisen-

1. L. Lilienfeld, U. S. P. 1350820.
2. U. S. P. 1432365, which also covers the use of methyl, ethyl, *iso*-propyl, *n*-propyl acetate, propionate or butyrate in conjunction with alcohol and tetrachlorethane.
3. F. P. 428664; abst. Mon. Sci. 1913, **78**, 28.
4. U. S. P. 1398239; abst. C. A. 1922, **16**, 831.
5. U. S. P. 1405448; abst. C. A. 1922, **16**, 1316; J. S. C. I. 1922, **41**, 248-A; Chem. Zentr. 1922, II, 881; Kunst. 1924, **14**, 156; Caout. et Gutta. 1922, **19**, 11653. Cites U. S. P. 1188376.
6. U. S. P. 1429174; abst. C. A. 1922, **16**, 3757.
7. U. S. P. 1309980, 1309981, 1370878, 1370879.
8. U. S. P. 1398949; abst. C. A. 1922, **16**, 830.
9. E. P. 15386, 1913; abst. C. A. 1915, **9**, 137.

mann[1] all employ ethyl butyrate as a cellulose ester solvent. Ethyl butyrate boils at 120°, sp. gr. 1.3927 at 15.4°.

Ethyl Hydroxyisobutyrate, Ethyl oxybutyrate, Ethyl *a*-hydroxy*iso*butyrate, is a synthetic ester produced by the condensation of hydrocyanic acid with acetone, or from glycol, butyric acid and chlorine oxide at 100°. Sp. gr. 0.98-0.986 at 20°, b. pt. 142-145°, ester content above 96%. It dissolves nitrocellulose, cellulose acetate and the water-insoluble cellulose ethers, the latter especially in the presence of a small amount of ethyl alcohol. The American Cyanamid Co.[2] and G. Buchanan[3] have described cellulose ester compositions containing this solvent.

Propyl Butyrate. The cellulose ether composition of J. Donohue[4] involves the use of propyl, butyl or amyl butyrate in coalition with methyl or ethyl alcohols, producing flexible and transparent films. *n*-Propyl butyrate boils at 142.7° at 760 mm., sp. gr. 0.8789 at 15°, while the *iso*propyl ester boils at 128°, sp. gr. 0.8652 at 13°.

Butyl Butyrate. D. Legg and C. Bogin[5] produce this ester by passing *n*-butyl alcohol at 280-300° over cupric oxide, butaldehyde being simultaneously formed. The patented formulas of J. Stevens[6] and Cellon, Ltd., Tyrer & Co., and T. Tucker[7] employ butyl butyrate as a cellulose ester solvent. Commercial *n*-butyl butyrate consists usually of a preponderance of *n*-butyl butyrate with relatively smaller amounts of the *iso*butyl ester. Sp. gr. 0.870, b. pt.

1. D. R. P. 192666; abst. Chem. Zentr. 1908, I, 180. For manufacture of ethyl butyrate see U. S. P. 1400852, 1421605, 1425624, 1425625, 1426457, 1459971.
2. E. P. 312469; abst. J. S. C. I. 1929, **48**, 691-B.
3. Can. P. 285149; abst. C. A. 1929, **23**, 980; Plastics, 1929, **5**, 693.
4. U. S. P. 1552804; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Ann. Rept. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, I, 796; Caout. et Gutta. 1926, **23**, 13316. Cites U. S. P. 1188376.
5. U. S. P. 1580143; abst. J. S. C. I. 1926, **45**, 608-B. Cf. U. S. P. 1401117; abst. J. S. C. I. 1922, **41**, 89-A. E. P. 166249; abst. J. S. C. I. 1921, **40**, 614-A.
6. U. S. P. 627727. U. S. P. 269340 discloses ethyl butyrate as a pyroxylin solvent.
7. E. P. 123628; abst. J. S. C. I. 1919, **38**, 269-A; Chim. et Ind. 1920, **4**, 793.

160-165°. It dissolves in water 0.38% at 10°, 0.42% at 16°, 0.5% at 25° and 0.57% at 33°. The odor is reminiscent of fall pippin apples. Non-toxic. "Butol" is butyl butyrate. Amyl butyrate has been used as a cellulose acetate plasticizer[1] and solvent[2], motor fuel[3] and in the production of cellulose ester plastics.

S. Carroll[4] has described as a desirable cellulose ether solvent, trimethyleneglycol dibutyrate in the presence of acetone, this plasticizer boiling at 125-130° at 8 mm. Benzyl butyrate has also been advocated as a useful cellulose ester plasticizer. In the production of plastic masses as substitutes for celluloid[5], glucose dibutyrate, distearate, ditartrate, diacetate and tetratartrate; acetochlorhydrose, tri-, tetra- and octa-acetyldiglucose, penta-acetyllevulose, tetra-acetyllactose, lactose tartrate and saccharose mono-, tetra-, hepta- and octo-acetate have been claimed as of value, but they nearly all have a well defined hygroscopicity.

Glyceryl butyrate, glyceryl *iso*butyrate and glyceryl phthalate[6] have been recommended as flexilizing bodies, particularly useful for softening hard, brittle, resinous products.

Valerianic and Higher Esters. The valerianates have been used but to a limited extent in solvents for the two reasons of comparatively high cost and pronounced odor. Amyl valerianate (amyl valerate) has been proposed by W. Field[7] and J. Stevens[8] for dissolving nitrocellulose, alone or in combination with ethyl sebacate or lower boiling sol-

1. W. Lindsay, U. S. P. 1388472; abst. C. A. 1921, **15**, 3950; J. S. C. I. 1921, **40**, 732-A. Cites U. S. P. 1050065, 1067785, 1199800.
2. *Ibid.* U. S. P. 1199800; abst. C. A. 1916, **10**, 3159; J. S. C. I. 1916, **35**, 1215.
3. M. Whitaker, U. S. P. 1421879.
4. U. S. P. 1836701; abst. Chem. Zentr. 1932, I, 1464.
5. Rheinische Gummi u. Celluloidfabrik, D. R. P. 140263; abst. Chem. Ztg. 1903, **27**, 333; Jahr. Chem. 1903, **56**, 1019; Wag. Jahr. 1903, II, 569. See also U. S. P. 366231.
6. British Thomson-Houston Co., E. P. 24255, 1912.
7. U. S. P. 478955. A. Trivelli (U. S. P. 1205822; abst. C. A. 1917, **11**, 124) has described a varnish for cinematograph films of nitro- or acetyl-cellulose and drying oils, the formula for the solvent portion being ethyl alcohol 50-60, methyl valerianate 45-35, drying oil 5.
8. U. S. P. 269340.

vents. Methyl, ethyl, propyl and butyl valerianates are direct solvents of the nitrocellulose, poor solvents of cellulose acetate, but dissolve the cellulose ethers readily, especially in the presence of a small amount of methyl or ethyl alcohol. Menthyl *iso*valerate (Validol), menthyl ethoxyacetate (Coryfin) and menthyl salicylate (Salimenthol) are solvents of low dissolving capacity. Menthyl borate (Estoral) with alcohol has both solvent and fire-retarding action.

The glycol esters of fatty acids of rape oil—glycol erucate, linoleate and linolenate—have been described as useful additions to cellulose ester lacquers to increase pliability[1]. R. Manning[2] has described ethyl gallate, m. pt. 141°, and ethyl tannate, m. pt. 157°. They are soluble in ether, alcohol and water. Methyl, ethyl, propyl, butyl and amyl palmitate, stearate, oleate, ricinoleate and linoleate have been advocated to replace camphor in cellulose plastics[3], and A. Luttringer[4] has described their apparent advantages, especially those of ethyl ricinoleate and linoleate.

Ethyl oleate forms the softener basis of the cellulose ester stencil sheet of E. Novotny[5], methyl, propyl and butyl oleates being considered as equivalents. Butyl oleate is occasionally employed to impart water-resisting qualities to cellulose ester films and plastics, usually in conjunction with benzyl alcohol or butyl phthalate. It is an excellent cellulose ether emollient and softener in connection with the lower aliphatic alcohols. E. Preiswerk[6] has described a method for *iso*butyl oleate manufacture.

1. A. Hildesheimer, D. R. P. 338475; abst. Chem. Tech. Uebers, 1923, **47**, 55; Chim. et Ind. 1922, **8**, 647; Chem. Zentr. 1921, IV, 471.
2. J. A. C. S. 1910, **32**, 1312; abst. J. S. C. I. 1910, **29**, 1261; J. C. S. 1910, **98**, i, 851.
3. Soc. anon. nouvelle "L'Oyonnithe," F. P. 387179; abst. C. A. 1909, **3**, 1819; J. S. C. I. 1908, **27**, 828; Mon. Sci. 1909, (4), **70**, 14.
4. Bull. soc. ind. Rouen, 1920, **48**, 81; abst. C. A. 1920, **14**, 3790.
5. U. S. P. 1776368; abst. C. A. 1930, **24**, 5446; J. S. C. I. 1931, **50**, 583-B; Plastics, 1931, **7**, #1, 57.
6. U. S. P. 1318461; abst. C. A. 1920, **14**, 94; Chim. et Ind. 1921, **5**, 561.

J. Kessler[1] has described cellulose combinations with a series of 72 solvents and softeners, being the methyl, ethyl, butyl, glyceryl, phenyl and naphthyl formyl-(or -acetyl, -propionyl, -benzoyl)-oxystearate, or oxyoleate or ricinoleate. Their solvent usefulness is considerably augmented by the presence of relatively small amounts of low boiling active solvents. Glyceryl ricinoleate[2] and the sulforicinoleates of manganese, zinc, aluminum, lead, magnesium and copper[3] or the corresponding ricinates[4] have been put forward as useful adjuncts to the cellulose esters in high body lacquers, varnishes and enamels.

Ethyl sebacate (commercially, sebacylic ether) is a mixture of methyl, monoethyl and diethyl sebacates, all of which boil above 250°. Where waterproof materials containing cellulose esters lack in desired softness and pliability, even after the maximum addition of castor oil, alkyl sebacates may be added to the extent of 50% on the weight of the cellulose ester or ether without tackiness appearing. Cost consideration is the only thing that precludes extensive use of the sebacic esters[5]. The J. Goldsmith plastic nitrocellulose mass employs methyl or ethyl sebacate[6], while H. Bruson uses glyceryl sebacate[7]. Ethyl sebacate has also

1. U. S. P. 1357876; abst. C. A. 1921, **15**, 437. Can. P. 214461. He has also included (U. S. P. 1739315) diethyleneglycol (*bb'*-dihydroxyethyl ether), triethyleneglycol, ethylglycol, butylglycol, propylglycol and ethylenepropylenediglycol caprates, caproates, laurates, palmitates, stearates, oleates, linoleates, ricinoleates, as nitrocellulose plasticizing agents.

2. J. Scheiber, E. P. 316538; abst. C. A. 1930, **24**, 2315; Brit. Plastics, 1930, **2**, #17, 101. See F. P. 669423; abst. C. A. 1930, **24**, 1753. E. P. 306452.

3. E. Peyrusson, F. P. 374395; abst. J. S. C. I. 1907, **26**, 776; 1908, **27**, 765; Revue de Chim. Ind. 1907, **18**, 219.

4. *Ibid.* F. P. Addn. 8760 to F. P. 374395.

5. Gummi Ztg. Suppl. 1907, July 19, 91.

6. J. Goldsmith and British Xylonite Co., Ltd., D. R. P. 139738; abst. Chem. Zentr. 1903, I, 749; Mon. Sci. 1904, **60**, 92. E. P. 15914, 1894; abst. J. S. C. I. 1895, **14**, 814. The patent also covers the application of methyl and ethyl adipate, pimelate, suberate and azaelate for dissolving and plastifying cellulose esters.

7. U. S. P. 1761813, 1761814; abst. C. A. 1930, **24**, 3662. See U. S. P. 1188376, 1199800, 1217027, 1217028, 1350820, 1388472. His process also includes the utilization as plastifiers of glyceryl adipate, pimelate, suberate as well as azaelate. In a more recently issued

been used in agglutinating mixtures and insulating materials[1].

For producing silky and glossy effects on threads, L. Lilienfeld[2] employs acetylcellulose with ethyl palmitate or acetylpalmitate, while B. Brown and C. Bogin[3] advocate butyl stearate. The stearate of diethylene glycol monomethyl ether (*b*-hydroxy-*b'*-ethoxydiethyl stearate)[4], benzyl stearate[5] and pentaerythrite 9.10-dihydroxystearate[6] are other esters which have been advanced for their solvent and plastifying effect.

Butyl stearate is a stable, water-insoluble cellulose ester solvent and thermoplasticizer, being used in amounts seldom exceeding 10% of the weight of the cellulose ester, and preferably used in conjunction with amyl tartrate or phthalate. Sp. gr. 0.855-0.859 at 20°, m. pt. 19°, b. pt. 360-365° for the commercial product. Ester content substantially 100%. Insoluble in water. Amyl stearate is of little value used alone, but in admixture with lower boiling active solvents imparts a desirable softness and silky feel to cellulose ester films and plastic bodies, to which it gives a high water-

patent (U. S. P. 1835203) he has described as plasticizers for cellulose derivatives ethyleneglycol, trimethyleneglycol, diethyleneglycol, glyceryl, mannitol and pentaerythrite mono-, di-, tri-, tetra- and hexahydroxystearic acid and dihydroxybehenic acid, mannitol 9-10-dihydroxystearate and glyceryl dihydroxybehenate being especially useful.

1. L. Lilienfeld, Can. P. 150646. Belg. P. 255253. Norw. P. 24818. Span. P. 55263. Hung. P. 59446. Ital. P. 133188.

2. U. S. P. 904269; abst. C. A. 1909, **3**, 721; J. S. C. I. 1908, **27**, 1202; Mon. Sci. 1909, **71**, 142. U. S. P. 1217027, 1217028, 1188376. E. P. 4597, 1906; abst. C. A. 1907, **1**, 927; J. S. C. I. 1907, **26**, 146; J. Soc. Dyers Col. 1906, **22**, 179; 1907, **23**, 179. E. P. 6387, 1913; 3370, 1914. E. P. 149320, 163016, 163017, 163018, 171661. D. R. P. 357707, 380651. F. P. 459972, 468162. D. R. P. 357707, 380651. Aust. P. 55527, 56250, 61055, 65288, 78217. Dan. P. 28835, 30677. Belg. P. 254591. Hung. P. 51653. Ital. P. 132825. Norw. P. 27507. Span. P. 55104. Swed. P. 38905. Swiss P. 66512. See U. S. P. 834739. D. R. P. 175664.

3. U. S. P. 1641529; abst. C. A. 1927, **21**, 3473; J. S. C. I. 1927, **46**, 822-B; Plastics, 1927, **3**, 674.

4. J. Kessler and O. Helfrich, U. S. P. 1739315; abst. J. S. C. I. 1930, **49**, 939-B.

5. H. Shonle and P. Row, U. S. P. 1553271; abst. C. A. 1925, **19**, 3491; J. S. C. I. 1925, **44**, 943-B.

6. H. Bruson, U. S. P. 1835203; abst. Chem. Zentr. 1932, I, 1179.

repellent effect. *n*-Butyl stearate, m. pt. 18°, renders nitrocellulose films soft and flexible[1].

The celluloid composition of J. Aylsworth involves the use of one or more of the following 36 high-boiling solvents and flexilizers: the methyl, ethyl, propyl and amyl fluor- (or chlor-, brom-) stearate, palmitate or myristate[2].

Ethyl palmitate[3], calcium ricinoleate[4], and glycol oleate and ricinoleate[5] have been proposed as colloiding and softening bodies. R. Van Schaack has described butyl esters of higher fatty acids, liquids or soft waxes, and soluble in alcohol, acetone, ether and ethyl acetate. Butyl pelargonate, caprate, laurate, myristate, palmitate, stearate and arachidate are specified. *n*-Butyl stearate, for example, is a colorless liquid at temperatures above 18°, below which it freezes to a white, opaque wax. It is practically odorless, insoluble in water, and unaffected by long exposure to air.

Glycollic, Acetoglycollic, Thioglycollic Esters. Methyl, ethyl, *n*-propyl, *n*-butyl and *iso*butyl glycollates and thioglycollates have been described as desirable cellulose ester solvents, especially in conjunction with triphenyl phosphate, butyl propionate and low boiling solvents[6], and have been patented in Germany[7] for use with nitrocellulose and resins in lacquers and varnishes. Ethyl glycollate (ethyl hydroxyacetate) also dissolves resins, colophony, shellac and copal. Ethyl acetylglycollate[8] is a direct solvent of cellulose

1. R. Van Schaack, U. S. P. 1613366; abst. C. A. 1927, **21**, 593; J. S. C. I. 1927, **46**, 237-B.
2. U. S. P. 962877; abst. J. S. C. I. 1910, **29**, 940; Mon. Sci. 1911, **75**, 11.
3. E. I. du Pont de Nemours & Co., E. P. 356256; abst. Chem. Zentr. 1931, II, 3296.
4. C. Schroeder, L. Levi and A. Lasche, U. S. P. 951582; abst. C. A. 1910, **4**, 1515.
5. S. Horii, E. P. 310181; abst. C. A. 1930, **24**, 699.
6. J. Payman, H. Swann, W. Jenkins and Imperial Chem. Ind., Ltd., E. P. 311664. Imperial Chem. Ind., Ltd., F. P. 662721. Can. P. 300990. Australia P. 16635, 1928.
7. Byk-Guldenwerke Chem. Fabr., D. R. P. 381413. For mfr. ethyl glycollate see U. S. P. 1160595.
8. H. Smith, U. S. P. 1858287. G. Austerweil, Aust. P. 78982; abst. Kunst. 1920, **10**, 214.

acetate and the cellulose ethers, being a water-white liquid of weak ester-like odor, boiling at 187°, sp. gr. 1.092 at 15°. Kalle & Co.[1] have described as cellulose ester dissolvants diamyl and cyclohexanol glycollates and thioglycollates. The glycollic esters are very similar to the lactic esters to which they are closely related.

The ethyl ether of ethyl glycollate, which may be made by the action of sodium ethylate on ethyl monochloracetate, dissolves the cellulose nitrates readily.

Phenoxylacetic and Naphthoxylacetic Esters. Phenoxylacetic acid (Phenylethylglycollic acid), naphthoxylacetic acid and their anhydrides and amyl and naphthyl esters have been claimed as efficient nitrocellulose plastifiers[2]. Methyl and ethyl phenoxylacetates melt at 245° and 251° respectively, and the phenyl ester at 58°[3]. *b*-Dinaphthoxylacetic acid melts at 134°, and the tolyl ester at 91-92°. *a*-Phenoxylpropionic acid melts at 115°, the ethyl ester being an oil. *b*-Phenoxylbutyric acid melts at 99° and its ethyl ester likewise is an oil. But little authentic information appears available concerning these plastifiers.

Lactic Esters. Hydroxypropionic Esters[4]. C. Piestrak[5] has described the usefulness of methyl, ethyl, propyl, butyl and amyl lactates and oxalates as a basis for the production of cellulose ether and ester lacquers, and T. Takahashi[6] the usefulness of methyl lactate in the lacquer industry. However, methyl lactate is readily hydrolyzed, and hence the keeping qualities of a lacquer containing large proportions of this ester soon develop acidity.

Ethyl Lactate. A powerful nitrocellulose solvent, at

1. D. R. P. 434640; abst. J. S. C. I. 1927, **46**, 580-B.
2. Zühl & Eisenmann, D. R. P. 119636; abst. Mon. Sci. 1901, (4), **57**, 216.
3. Farbenfabriken vorm. F. Bayer & Co., D. R. P. 85490.
4. For general data on ethyl lactate as a solvent for cellulose compounds, see H. Gardner, U. S. Paint and Varnish Mfrs. Assoc. Circ. #225, Jan. 1925. A. Wolff, Farb. u. Lack. 1926, T-**31**, #22, 276; Anon., Oil, Paint and Drug Reporter, 1925, **107**, 32-A.
5. F. P. 535466; abst. Chem. Zentr. 1922, IV, 274; Chim. et Ind. 1922, **8**, 1080; Caout. et Gutta. 1922, **19**, 11495.
6. Bull. College of Agric. Tokyo, 1907, **7**, 565; abst. Chem. Zentr. 1907, II, 1660; Kunst. 1916, **6**, 227.

the same time dissolving the cellulose ethers and acetylcellulose. In chemical constitution it is both an alcohol and an ester, and will stand an abnormal dilution with hydrocarbon non-solvents without the cellulose derivative precipitating or opalescing. The odor is not disagreeable, and the speed of evaporation slow. It is defective in the two respects that the commercial ester varies considerably in composition and hence in solvent avidity, and its rate of evaporation when used alone is rather slow for commercial work. For this reason, films and sheets made using ethyl lactate have a tendency to remain soft for a considerable period beyond what may be regarded as normal. As compared with butyl and amyl acetates the solvent power is inferior, but it will permit of dilution with petroleum hydrocarbons from two to three times as great. The viscosity of solutions is also higher. Sp. gr. 1.03-1.04; b. pt. 90% between 140-152°. Estinol, Eusolvan, Solactol and Actylol are claimed as commercial names for ethyl lactate.

Chemische Werke vorm. H. Byk[1], G. Bonwitt[2], K. Brown and C. Bogin[3], C. Clouth[4], R. Calvert[5], J. Donohue[6], H. Dreyfus[7], H. Feldmann[8], Celluloid Corp.[9], British Celanese, Ltd.[10], H. Hopkins and J. Segur[11], and W. Moss[12]

1. E. P. 25182, 1913. F. P. 464617. Swiss P. 66510, 67708.
2. D. R. P. 331285; abst. Chem. Zentr. 1921, II, 574. See also E. P. 138078. F. P. 519536.
3. U. S. P. 1591652. Can. P. 260927.
4. D. R. P. 319723; abst. Chem. Zentr. 1920, IV, 19.
5. U. S. P. 1848105; abst. Chem. Zentr. 1932, I, 3354.
6. U. S. P. 1552796; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Ann. Rept. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, I, 541; Caout. et Gutta. 1926, **23**, 13316. Refers to U. S. P. 1188376.
7. U. S. P. 1363763; abst. C. A. 1921, **15**, 752; J. S. C. I. 1921, **40**, 114-A; Paper, 1921, **27**, #26, 27; Mon. Sci. 1922, (5), **12**, 5. F. P. 432264.
8. E. P. 148117; abst. J. S. C. I. 1922, **41**, 22-A.
9. E. P. 308657; abst. C. A. 1930, **24**, 499; J. S. C. I. 1930, **49**, 943-B; Brit. Plastics, 1930, **2**, #18, 278; Kunst. 1931, **21**, 16; Chem. Zentr. 1929, II, 814. E. P. 308658; abst. C. A. 1930, **24**, 499; J. S. C. I. 1930, **49**, 1146-B; Chem. Zentr. 1929, II, 814.
10. E. P. 315279; abst. C. A. 1930, **24**, 1740; J. S. C. I. 1931, **50**, 108-B. E. P. 345521; abst. J. S. C. I. 1931, **50**, 597-B; Brit. Plastics, 1931, **3**, #28, 63.
11. U. S. P. 1855744.
12. U. S. P. 1844365. For manufacture of ethyl lactate see U. S. P. 1160595, 1421604.

have all described cellulose ether and ester compositions utilizing ethyl lactate, to which reference is made as to details. A. Davis[1] prepares stencil sheets of cellulose acetate with ethyl lactate, benzylbutyl tartrate, diamyl phthalate, acetylbutyl tartrate, hexachlornaphthalene, acetylamyl tartrate and benzoylamyl salicylate.

According to F. Eisemann[2] an ideal incandescent mantle lacquer results when nitro- or acetyl-cellulose is compounded with ethyl lactate, oxalate, salicylate, stearate, palmitate, phthalate, butyrate, tartrate or the corresponding methyl esters, including propyl oxalate, butyrate and salicylate. C. Bogin[3] combines nitrocellulose with resins by the mutually harmonious ethyl, propyl, or butyl lactate, butyl propionate or phthalate, diacetone alcohol or hexahydrophenol. A. Eichengruen[4] combines acetylcellulose, ethyl lacetate and acetylmethylacetanilid, and M. Thau[5] ethyl lactate with butyl acetate. The enamel and varnish of D. Burke[6] and of J. Keats[7] employ ethyl lactate with cellulose esters.

The R. Grüter lacquer is composed of cellulose esters, ethyl lactate, amyl acetate and benzene, toluene or xylene[8], that of P. Schidrowitz and D. Burke[9] of ethyl lactate and benzoate as the solvent portion, while the Bakelite Corporation[10] combine ethyl lactate with ethyleneglycol mono-

1. U. S. P. 1639080; abst. Pulp & Paper Mag. 1929, 323; Plastics, 1927, **3**, 540.
2. D. R. P. 192666; abst. Chem. Zentr. 1908, I, 180. See also D. R. P. 195312.
3. U. S. P. 1651578; abst. Chem. Zentr. 1928, I, 1237.
4. U. S. P. 1185074; abst. C. A. 1916, **10**, 2044; J. S. C. I. 1916, **35**, 734; Chem. Ztg. 1916, **40**, 794; Kunst. 1916, **6**, 315. F. P. 418744; abst. J. S. C. I. 1911, **30**, 79; Mon. Sci. 1913, **79**, 551. E. P. 18189, 1910; abst. C. A. 1911, **5**, 3340; J. S. C. I. 1911, **30**, 79; Mon. Sci. 1913, **78**, 551; Kunst. 1911, **1**, 92.
5. U. S. P. 1793726; abst. J. S. C. I. 1931, **50**, 936-B; Brit. Plastics, 1932, **3**, #32, 102. Cites Swiss P. 66509. Griesheim Elektron, Chemical Review, 1906, 56.
6. U. S. P. 1814823; abst. C. A. 1931, **25**, 5304.
7. U. S. P. 1816330; abst. C. A. 1931, **25**, 5584.
8. U. S. P. 1195673; abst. C. A. 1916, **10**, 2646; J. S. C. I. 1916, **35**, 1026; Ind. Eng. Chim. 1925, **17**, 1120. F. P. 464617; abst. J. S. C. I. 1914, **33**, 557.
9. E. P. 304334; abst. C. A. 1929, **23**, 4835.
10. F. P. 695588; abst. C. A. 1931, **25**, 2866.

methyl ether. Processes of Societe des Brevets J. Paisseau[1], Imperial Chemical Industries[2], C. Cunningham[3], and Staniolfabr. Burgdorf A. G.[4] are along similar lines. In laminated glass manufacture[5], a combination of ethyl and butyl lactates are specified with cellulose acetate, while the Deutsche Hydrierwerke A. G.[6] produce emollients and gelatinants with cellulose ethers and ether-esters by means of ethyl lactate in the presence of butyl acetate, cyclohexanone, cyclohexyl acetate and 2.2(methylpentamethylene)-4-oxymethyldihydrodioxol.

G. Padgham[7] has detailed as ethylcellulose dissolving and gelatinizing bodies, ethyl, butyl and amyl lactate and phthalate; butyl formate, propionate, stearate and oxalate; amyl propionate and stearate; benzyl alcohol and acetate, diacetone alcohol and resorcinol diacetate. W. Jenkins[8] has described methods of preparing nitrocellulose compositions utilizing methyl, ethyl, propyl, butyl and amyl lactates whose boiling points fall within the range of 110-190°.

Butyl Lactate. C. Burke and R. Kramer[9] have patented as nitrocellulose colloidants *n*-butyl lactate and *n*-butyl nitrolactate, and have given methods for their preparation. The lacquer composition of C. Gabriel and C. Bogin[10] combines butyl lactate 10, ethyl acetate 30, benzene 25, toluene 20 and xylene 15. Butyl lactate is a colorless liquid, sp. gr. 0.987-1.012, boiling at 185-195°. The com-

1. E. P. 293391; abst. C. A. 1929, **23**, 1750; J. S. C. I. 1929, **48**, 849-B.
2. F. P. 687597; abst. C. A. 1931, **25**, 786. Can. P. 298454.
3. U. S. P. 1562544; abst. Plastics, 1926, **2**, 62. Can. P. 265988.
4. E. P. 338340; abst. C. A. 1931, **25**, 2311; J. S. C. I. 1931, **50**, 127-B.
5. Newtex Safety Glass Co., Ltd., and W. Dougan, E. P. 355604; abst. J. S. C. I. 1931, **50**, 972-B.
6. F. P. 714837; abst. Chem. Zentr. 1932, I, 2101.
7. E. P. 347597; abst. C. A. 1932, **26**, 1810. See E. P. 2256, 1856; 3150, 1874; 3647, 1877; 2266, 1883; 12013, 1887; 19772, 1909; 6387, 1913; 105137.
8. Can. P. 310119. For purifying ethyl lactate see E. Schwenk and F. Hartwich, D. R. P. 548371; abst. C. A. 1932, **26**, 3515.
9. U. S. P. 1598474; abst. C. A. 1926, **20**, 3460; J. S. C. I. 1926, **45**, 995-B.
10. U. S. P. 1673111; abst. Chem. Zentr. 1928, II, 2292.

mercial ester varies widely in physical constants due primarily to the presence of condensation products as lactide. While it is a direct but not powerful solvent of the cellulose esters when used alone, its relatively high boiling point causes slow drying, although it imparts high brilliancy to cellulose ether films. It is miscible with linseed and castor oils and hydrocarbons, and is substantially insoluble in water.

Amyl Lactate is used primarily as a softener in conjunction with nitrocellulose, cellulose acetate or the cellulose ethers. Sp. gr. 0.957-0.960°, b. pt. 210°, acidity, not over 0.03%. The technical ester is apt to contain lactides. It is a weak solvent of acetone-soluble cellulose acetate, especially in conjunction with a small amount of acetone and upon the application of heat. R. Van Schaack[1] has disclosed the applicability of benzyl lactate, tartrate, citrate, chlorbenzyl lactate and tolyl ricinoleate in nitrocellulose and cellulose acetate compositions.

The methyl, ethyl, propyl and *iso*propyl esters of lactic acid ester, such as may be made by treating *a*-chlor- or *a*-brom-propionic acid esters with the corresponding sodium alcoholate, have been brought forward as desirable nitrocellulose dissolvants[2]. Ethoxyethyl lactate, b. pt. 155°, has been mentioned as a cellulose ether solvent.

Nitrolactic Esters. As nitrocellulose colloiding agents[3], *n*-butyl, amyl, hexyl and cyclohexyl nitrolactates have been patented, being bodies insoluble in water, but dissolving readily in ether, acetone and other common organic solvents, and are non-hygroscopic.

As a desirable solvent for cellulose ethers and cellu-

1. U. S. P. 1612669; abst. C. A. 1927, **21**, 649; J. S. C. I. 1927, **46**, 228-B.

2. W. Jenkins and Imperial Chemical Industries, Ltd., E. P. 305960; abst. C. A. 1929, **23**, 5051.

3. C. Burke and R. Kramer, U. S. P. 1598474. They are obtained by the action of a mixture of nitric and sulfuric acids upon the corresponding lactate. D. Burke, U. S. P. 1814823, has developed a paint for application to rubber surfaces containing nitrated cotton dissolved in a mixture of ethyl lactate and ethyl benzoate.

ose acetate[1], *b*-ethoxyethyl lactate has been set forth by H. Smith, this liquid distilling over at 100-102° at 16 mm. It is used in 20-30% on the weight of the cellulose derivative.

Oxalic Esters. The oxalic esters are relatively inexpensive to produce, but the lower esters are not stable in the presence of moisture, liberating oxalic acid and ethyl oxalic acid (ethyl hydrogen oxalate) for which reasons, the technical esters vary considerably in uniformity and composition.

F. Eisemann[2] has described a dipping lacquer containing ethyl benzoate, stearate, palmitate or oxalate; ethyl oxalate, lactate, salicylate, stearate or palmitate; propyl oxalate, butyrate; amyl oxalate, lactate or tartrate or phenyl salicylate. C. Shrager and R. Lance[3] combine resinates of zinc, magnesium, aluminum, tungsten with ethyl oxalate, formate or butyrate, and R. Scheuble[4] uses as cellulose ester solvents, methyl, ethyl or propyl oxalate. The penetrative ink of C. Cunningham[5] for application to lacquered surfaces comprises ethyl oxalate, lactate and phthalate, and the fibrous thermoplastic sheet of Bakelite Corporation consists of a phenol-aldehyde type of reactive resin with ethyl or butyl oxalate, tartrate or phthalate[6]. Glyptal type of soluble resins dissolves in ethyl oxalate or glycol diacetate[7].

Ethyl oxalate is a solvent for cellulose ethers, acetylcellulose and the cellulose nitrates and is a partial solvent of shellac. It is a water-white liquid, sp. gr. 1.07. Its nitrocellulose solutions will stand twice as much dilution with hydrocarbons as a similar butyl acetate solution. Its odor is mild and it has a low vapor pressure, and does not produce as glossy a surface with cellulose compounds as

1. U. S. P. 1884318.
2. D. R. P. 192666. See D. R. P. 195312.
3. F. P. 470726. E. P. 8283, 1913. Both methyl and ethyl oxalates have been known for some time (E. P. 15914, 1894) as cellulose nitrate solvents.
4. Aust. P. 42260. See J. Steffens, U. S. P. 1421604, 1433308.
5. U. S. P. 1562544.
6. E. P. 356260; abst. J. S. C. I. 1931, **50**, 1045-B.
7. Bakelite Corp., F. P. 638121; abst. Plastics, 1929, **5**, 336.

does ethyl lactate[1]. It boils at 186°. The methyl esters melt at 54° and boil at 163°. *iso*-Propyl oxalate boils at 111° at 13 mm.[2], and *n*-propyl oxalate at 214°.

Butyl oxalate plasticizes cellulose ethers and esters, and is a solvent for mastic, coumarone, benzyl abietate, is miscible with castor, linseed and other oils, but not with water. The ester content is usually above 97%. The *n*-butyl ester boils at 243° and the *iso*butyl ester at 224°. The sp. gr. is substantially the same as water. Amyl oxalate boils at 265° for the *iso*amyl oxalate, sp. gr. 0.968 at 11°. It has a moderate solvent action for nitrocellulose and the cellulose ethers, less so for cellulose acetate. Its solvency is similar to that of butyl oxalate. Ethyl oxalate has been used as a solvent in paint removers[3].

Oxamic Esters. Oxamic acid is amido-oxalic acid. E. Zühl[4] has described the use of methyl, ethyl, propyl and amyl oxamate (amido-oxalate) for the partial or total replacement of camphor in the preparation of thermoplastic cellulose ester compounds.

Malonic Esters. A series of malonic esters compatible with cellulose derivatives has recently been disclosed, being plastifiers of cellulose ethers, cellulose acetate, propionate, butyrate, acetostearate, acetomalate, nitrate or nitroacetate. Methyl, ethyl[5], ethyldiethyl, ethyl-*n*-butyl, ethyl*iso*-butyl, ethyl-*sec*-butyl and ethyldi-*n*-butyl malonates have been described. They are preferably incorporated with acetone, methyl alcohol or other low boiling solvent. Dimethyl malonate boils at 181.5°, monoethyl malonate at 147° at 21 mm., and diethyl malonate at 198°. Ethyl-

1. E. Clayton and C. Clark, Text. Mfr. 1931, **57**, 454. *n*-Dibutyl oxalate, a colorless liquid, b. pt. 243° at normal atmospheric pressure and 113° at 10 mm., practically insoluble in water, and diamyl oxalate, both in conjunction with acetone or methyl alcohol, both constitute valuable cellulose ester solvents (H. Clarke, U. S. P. 1309981).
2. R. Anschütz and F. Schönfeld, Ber. 1886, **19**, 1442.
3. U. S. P. 1516064.
4. F. P. 309963; abst. J. S. C. I. 1902, **21**, 65; Mon. Sci. 1902, **58**, 171.
5. H. Smith, U. S. P. 1880507.

propyl malonate boils at 211°, the dipropyl ester at 228°, and di-*act*-amyl malonate has sp. gr. 0.9657 at 20°/4°.

Monobromomalonic acid, dibromomalonic acid or their alkyl esters as ethyl bromomalonate or ethyl dibromomalonate have been recently described as cellulose ester plastifiants, and methods for the preparation published[1]. They are best utilized in the presence of acetone, methyl alcohol or ethyl acetate, and combine solvency and thermoplasticity with reduction in inflammability.

Succinic and Malic Esters. Ethyl succinate (diethyl succinate) with methyl alcohol forms an excellent solvent for water-insoluble ethyl cellulose[2], and although methyl, ethyl, propyl, butyl and amyl succinates alone are but partial solvents for the cellulose ethers, in conjunction with methyl and ethyl alcohols their solvency is considerably augmented. Monochlornaphthalene or camphor may be added to the solutions as plasticizing agents. H. Willkie[3] gives as type formula for a cellulose ester solvent, ethyl succinate 3.75, ethyl acetate 11.25, benzene 25, to which ethyl acetoacetate, triacetin, or dimethyl phthalate may be added. The non-oxidizable bronzing liquid of J. Perl[4] comprises nitrocellulose with methyl succinate.

Dibenzyl succinate is claimed as a useful plasticizer for cellulose ethers and esters on account of its ready compatibility and solvency in acetone and other liquids which readily dissolve the cellulose ethers and esters[5]. With cellulose acetate, it may be used up to 30-50% by weight. Diphenyl succinate melts at 118° and boils at 330° without decomposition.

Ethyl malate (diethyl malate, ethyl hydroxysuccinate) is an excellent solvent for nitrocellulose and will dissolve

1. H. Smith, U. S. P. 1880508.
2. J. Donohue, U. S. P. 1473219. See U. S. P. 1473217, 1473218.
3. U. S. P. 1449156, 1449157. For manufacture of ethyl, propyl, butyl, glycol and glyceryl succinate, malate or maleate, see J. Steffens, U. S. P. 1421604, 1421605.
4. D. R. P. 68356. For manufacture of benzyl succinate, see L. Carlson and M. Bye, U. S. P. 1439605, 1439377. Benzycin is sodium benzyl succinate. Benzicin is glyceryl benzoate.
5. H. Smith, U. S. P. 1880506.

shellac and many other resins. The b. pt. 248-252° is too high for ordinary high boilers in lacquers, hence it should be attenuated with lower boiling solvents[1].

Malic esters of polyhydric alcohols of a resinous or gummy consistency such as glyceryl malate, glycol malate and sorbitol malate[2] have been described for incorporation into lacquers and varnishes.

Maleic and Fumaric Esters. The esters of fumaric acid (trans-form) and maleic acid (cis-form) are direct solvents of the cellulose ethers, and have been described in this connection by O. Drossbach and O. Jordan[3]. They also dissolve the cellulose nitrates and acetates. Dimethyl, diethyl, dipropyl, diamyl, dihexyl, dicyclohexyl, and ethyleneglycol monomethyl maleate and fumarate form plastifiers in the absence of volatile solvents. For example, ethylcellulose is kneaded alone or with alcohol and about 75% of its weight of dimethyl maleate at an elevated temperature, whereby a transparent homogeneous mass results.

Tartaric Esters. The lower tartaric esters have the defect from a cellulose ether viewpoint of being water-soluble, although many of the tartrates dissolve water-soluble methyl- and ethyl-cellulose. F. Redlich[4] has described a cellulose acetate lacquer made by dissolving 10 parts acetylcellulose in 12 parts diethyl tartrate, acetone or alcohol being added as thinner if desired. L. Lilienfeld[5] has patented a combination of cellulose ethers, resins and diethyl tartrate.

Dibutyl Tartrate dissolves both ethyl -and benzyl-cellulose and resins, being employed in amounts up to 100% of the cellulose ether. Its boiling range is 295-310°, sp. gr. 1.06-1.09. Dissolves 4% in water at 25° and 3% at 180°. Water dissolves 1% at 25°. It is miscible with oils and hydrocarbons. The J. Grolea and J. Weyler process for

1. D. Keyes, Ind. Eng. Chem. 1925, **17**, 1120.
2. General Electric Co., E. P. 24060, 1912.
3. U. S. P. 1677753. D. R. P. 512321; abst. Chim. et Ind. 1931, **25**, 1218.
4. D. R. P. 304224; abst. J. S. C. I. 1920, **39**, 264-A.
5. F. P. 459972; abst. J. S. C. I. 1913, **32**, 1153.

lacquers uses as a dissolvant for acetylcellulose[1], butyl, *iso*-butyl and *iso*amyl tartrates and citrates. All of these esters boil above 300°, their vapor tension at average pressure being extremely small. They are neutral. The manufacture of dibutyl, monoacetylbutyl and monobenzoylbutyl tartrates has been patented by A. Davis[2]. Methyl-, ethyl- and benzyl-cellulose are brought into solution by virtue of dibutyl tartrate[3] either alone or with adjuvant solvents as diphenylol propane, triacetin, diethyl phthalate and monomethylxylene sulfonamide. The nitrocellulose varnish of K. Takemura[4] utilizes dibutyl tartrate. Monobenzyl, dibenzyl and butylbenzyl tartrates have been advocated for the production of cellulose ester lacquers and films[5], butyl tartrates being useful in a transfer ink for marking leather[6]. As a direct ethylcellulose solvent[7] butyl tartrate has been used either alone or in conjunction with acetone or ethyl alcohol. The manufacture of butyl tartrate has been patented by F. Arentz[8]. *n*-Butyl mesotartrate is claimed as an efficient plasticizer for nitrocellulose lacquers[9], m. pt. 48-50°, boiling at 205° at 20 mm. The cellulose ether composition of C. Fawkes[10] utilizes butyl tartrate in combination with furyl alcohol.

Diamyl Tartrate. An exceptionally efficient plasticizer for cellulose acetate, cellulose ethers and glyceryl phthalate resin. Sp. gr. 1.05-1.06; b. pt. 398-400°. Miscible with linseed and castor oils and hydrocarbons. Insoluble in water. J. Steffens[11] has patented a method for amyl tartrate manufacture. Di*iso*propyl tartrate 275°, and the di-*n*-propyl ester at 303°.

1. E. P. 123712; abst. J. S. C. I. 1919, **38**, 714-A. F. P. 489037.
2. U. S. P. 1834686; abst. C. A. 1932, **26**, 994.
3. G. Seymour, U. S. P. 1828449.
4. U. S. P. 1791879. K. Takemura and K. Oiwa, E. P. 266214.
5. Celluloid Corp., E. P. 358428. See E. P. 308657.
6. W. Lawrence and F. Barker, U. S. P. 1545836.
7. S. Carroll, U. S. P. 1467103; abst. C. A. 1923, **29**, 679.
8. E. P. 246526; abst. C. A. 1927, **21**, 415. Can. P. 278985.
9. C. Bogin, U. S. P. 1659906, 1659907; abst. J. S. C. I. 1928, **47**, 376-B.
10. U. S. P. 1732124; abst. C. A. 1930, **24**, 252.
11. J. Steffens, U. S. P. 1433308.

Citric Esters. These esters as solvents for cellulose compounds, were first described by A. Nobel in 1899, and include methyl, ethyl, propyl, butyl, amyl citrate, oxalate, lactate, tartrate, succinate, benzoate, hippurate, toluate, mesitylenate, salicylate and phthalate as dissolvants for the cellulose nitrates[1]. As solvents for the acetated cellulose, *n*- and *iso*-butyl and amyl tartrates and citrates[2] have been brought forward, and L. Lilienfeld[3] has detailed the solvency for cellulose ethers and cellulose esters of ethyl citrate, phthalate, sebacate, succinate, tartrate, benzoate and levulinate. In 1896, J. Stevens[4] described in some detail the methyl, ethyl, propyl and butyl citrates, trichlorethyl citrate, and acetyltriethylcitric ether, primarily as nitrocellulose solvents. Trimethyl citrate melts at 78.5°, while triethyl, tripropyl and tri*iso*butyl citrates are liquids.

H. Young[5] has given formulae for pyroxylin lacquers containing methyl, ethyl, propyl, butyl, butyryl, *b*-acetoxyethylbutyl, amyl, benzyl and tolyl phthalate, citrate, succinate, tartrate, phenylmalonate, trimesate and succinylsuccinate, and R. Van Schaack[6] methyl*iso*butylmethyl propionate, oxalate, citrate, valerate, palmitate, stearate, oleate, tartrate, laurate and succinate, all boiling above 130°, and direct cellulose nitrate solvents. C. Gabriel[7] adds to this list methyl, ethyl, propyl, butyl and amyl citrate, malate, maleate, mucate, tartrate, phthalate, oxalate and phosphate as "adhesivators," substantially synonymous with plastifiers, and dissolving both acetylcellulose and shellac. The starch ethers are soluble in ethyl citrate[8].

Benzyl citrate, lactate or tartrate, chlorbenzyl lactate or tolyl ricinoleate are also direct cellulose acetate sol-

1. E. P. 4479, 1889; 15914, 1894. See E. P. 20234, 1894; 14231, 1901.
2. J. Grolea and J. Weyler, E. P. 123712; abst. J. S. C. I. 1919, **38**, 714-A.
3. F. P. 459972. U. S. P. 1188376, 1217027, 1217028.
4. U. S. P. 568105.
5. U. S. P. 1786404; abst. C. A. 1931, **25**, 610.
6. U. S. P. 1702180; abst. C. A. 1929, **23**, 1505.
7. U. S. P. 1813735.
8. L. Lilienfeld, U. S. P. 1350820.

vents[1]. Ethyl citrate has been used as a component in a paint remover[2], as an agglutinant[3], and as a general cellulose ether solvent[4].

Adipic Esters. As cellulose ether solvents methyl and ethyl adipate and *b*-methyladipate have received patent protection[5]. Methyl adipate melts at 8°. Ethyl adipate, pimelate, suberate and sebacate, either alone or with acetylmethyl aniline, acetylbenzoyl aniline; and methyl, ethyl, propyl, butyl or amyl acetyl- (or benzoyl-) lactate, tartrate or glycerate form a series of compounds, the details of which as nitrocellulose solvents were first disclosed in 1901[6]. Glycol and glyceryl adipate, pimelate, suberate, azaleate and sebacate comprise ten solvents advocated for combination with cellulose esters in conjunction with colophony and other resins as lacquers and varnishes[7]. G. Genin[8] has discussed the use of methyl, ethyl, propyl and butyl adipate and *b*-methyladipate in the artificial leather industry as cellulose ester solvents.

Oxidation products of hydrogenated crude phenols, comprising *a*-, and *b*-methyladipic and glutaric acids[9], in the form of their methyl, ethyl, methylcyclohexanol and methylhexyl esters are recommended as efficient camphor substitutes in the manufacture of celluloids.

Acrylic and Crotonic Esters. Methyl, ethyl, propyl, butyl and allyl acrylate, b. pt. 80°, 98-101°, 120-123°, 141-146° and 119-124° respectively; and methyl, ethyl, propyl

1. R. Van Schaack, U. S. P. 1612669.
2. C. Ellis, U. S. P. 985405; abst. C. A. 1911, **5**, 1527.
3. Can. P. 150646. Belg. P. 255253. Norw. P. 24818. Ital. P. 133188. Span. P. 55263. Hung. P. 59446.
4. E. P. 6387, 1913; 3370, 1914; 149320, 163016, 163017, 163018, 171661. D. R. P. 357707. Dan. P. 28835. Aust. P. 55527, 56250, 65288, 78217. Belg. P. 254591. Dan. P. 30677. Hung. P. 51653. Ital. P. 132825. Norw. P. 27507. Can. P. 55104. Swed. P. 38905. Swiss P. 66512.
5. Farbenfabr. vorm. F. Bayer & Co., D. R. P. 317412.
6. J. Goldsmith and British Xylonite Co., E. P. 22662, 1901.
7. H. Bruson, U. S. P. 1783165, 1783166; abst. C. A. 1931, **25**, 424.
8. Halle aux cuirs, 1929, 305; abst. C. A. 1930, **24**, 1233.
9. W. Claasen, E. P. 250910; abst. C. A. 1927, **21**, 1355.

and butyl *a*-crotonate, b. pt. 118-121°, 142-143°, 157-163° and 177-182° respectively, in conjunction with methyl oleate or ethyl or butyl cinnamates, form the nitrocellulose or acetylcellulose spraying lacquer of I. G. Farbenindustrie[1]. Ethyl or *iso*propyl acrylate and ethyl crotonate with alcohol and benzene comprise the lacquer of Chemische Fabrik vorm. Weiler-ter-Meer[2]. Cellulose ether artificial filaments have been described[3], obtained by dissolving ethylcellulose in ethyl acrylate, vinyl acetate or *m*-styrol (phenylethylene, vinylbenzene). Roehm & Haas[4] prepare ethyl acrylate by passing ethylhydracrylic acid at 200° over silica gel impregnated with concentrated sulfuric acid, and methyl acrylate from methylmethoxypropionic ester.

Glyceric Esters. Glyceric acid (*ab*-dihydroxypropionic acid) forms a non-crystallizable syrup, soluble in water, alcohol and acetone. The methyl ester (methyl *d*-glycerate boils at 119-120°, sp. gr. 1.2798 at 20°/20°. Ethyl ester boils at 230-240°, sp. gr. 1.193 at 6°; propyl ester, sp. gr. 1.14448; *iso*propyl ester, sp. gr. 1.1308; butyl ester, sp. gr. 1.1084, (all at) 15°/15°.

The ethyl ester has been commented on as to its possible solvent applicability in the cellulose ether and ester art[5]. It may be made by heating glyceric acid with 3-4 vols. absolute alcohol at 170-190°[6], or by heating an absolute alcoholic solution of *d*-glyceric acid at 180-190°[7].

Abietic Esters. A class of quick drying lacquers has been granted patent protection to L. Bent[8], comprising the ethyl, propyl, butyl, amyl, phenyl, benzyl and glycol abietates, fluids or semi-solids, in conjunction with nitrocellulose or nitrostarch. Methyl or ethyl abietate form the

1. E. P. 321258. A. Huegel and I. G. Farbenind., D. R. P. 483002, 511477; abst. C. A. 1932, **26**, 1078, 1810.
2. D. R. P. 367294; abst. J. S. C. I. 1923, **42**, 446-A.
3. Roehm & Haas, A. G., and R. Herzog, E. P. 311784. F. P. 681156. See E. P. 308284.
4. F. P. 707154; abst. C. A. 1932, **26**, 479.
5. D. Keyes, Ind. Eng. Chem. 1925, **17**, 1120.
6. L. Henry, Ber. 1871, **4**, 706.
7. P. Frankland and J. McGregory, J. C. S. 1893, **63**, 511.
8. U. S. P. 1839529; abst. C. A. 1932, **26**, 1460.

basis of the A. Johnston varnish, on account of their slow colloiding action on nitrocellulose[1]. A linoleum or floor covering has been patented[2] in which cellulose nitrate 28 is dissolved in a mixture of ethyl abietate 31, tricresyl phosphate 7, wood powder 34. Both methyl and ethyl abietates are viscous, amber colored liquids, soluble in the usual cellulose ether solvents, and solvents for elemi, dammar, sandarac and mastic. Ethyl abietate has sp. gr. 1.03, and may be prepared by heating abietic acid and ethyl alcohol in the presence of a suitable condensing agent[3].

Propylene glycol abietate, ethylene glycol abietate and trimethylene glycol abietate have been described by G. Norman[4], and glycol and glyceryl monoabietates and diabietates by H. Wolff and H. Zellner[5]. The latter compounds have been put forward as excellent cellulose ester colloidants. Glyceryl abietate is a brown, semi-resinous colloidant, soluble in alcohol, ethyl acetate, ether and other solvents, imparting both body and flexibility. It comes into commerce as "Plastabrac AA," being glyceryl diaceto-abietate. Tetrahydronaphthol abietate[6] has been proposed for use in lacquers. Its boiling range is 300-320° at 2-5 mm.

Carbamic Esters. Urethanes. The carbamates (amidocarbonates) or urethanes as a class, have been used to a limited extent in the pyroxylin plastic industry as solvents and gelatinants which possess antacid properties as well. In 1896 J. Stevens[7] disclosed methods of using methyl, ethyl, propyl, butyl and amyl carbamates, benzyl carbamate, ethylidene urethane, acetyl-*p*-oxyphenyl urethane (neurodin) and acetyl-*p*-ethoxyphenyl urethane (thermodin). All are crystalline substances soluble in alcohol, and are intended for incorporation with the cellulose derivative dis-

1. U. S. P. 1682280; abst. C. A. 1928, **22**, 3892.
2. Hercules Powder Co. and J. Rile, E. P. 308524. F. P. 656204. Can. P. 287513.
3. I. Gubelmann and C. Henke, U. S. P. 1829481.
4. U. S. P. 1839161.
5. D. R. P. 502263; abst. C. A. 1930, **24**, 4944.
6. I. Gubelmann and C. Henke, U. S. P. 1829480.
7. U. S. P. 568106.

solved in a volatile solvent as methyl alcohol or acetone.

Methyl or ethyl ethylcarbamate as a solvent for cellulose acetate when used in amount equal to the cellulose ester, either as such or with the addition of ethyl lactate or amyl acetate forms the preferred plasticizing medium of H. Smith[1].

Phenyl urethane (formed by the action of ethyl chlorformate upon aniline), methylphenyl urethane, naphthyl urethane and phenanthryl urethane have been described by F. Nathan, W. Rintoul and F. Baker[2] as suitable gelatinants and antacids for nitrocellulose compositions. They have included as desirable products in this group[3] phenyl, *o*-tolyl, ethylphenyl, ethyl-*o*-tolyl and diphenyl urethane; ethylphenyl urea, methylphenyl urea, methyldiphenyl urea and phenyl ethylphenylcarbamate, to which may be added formanilid, ethylacetanilid, acet-*o*-anisidid, aceto-*o*-phenetidid, phenylacetanilid, phenylacet-*a*-(or *b*-)naphthalid, ethylacet-*b*-naphthalid, form-*o*-(or -*p*-)toluidid, methyl, ethyl and phenyl formanilid; and phenyl diethylcarbamate. All of these bodies are solids and freely soluble in acetone, methyl and ethyl alcohols.

Benzyl-*o*-tolyl urethane, b. pt. 195° at 11 mm., and benzylphenyl urethane, b. pt. 185-190° at 10 mm., also gelatinize nitrocellulose[4], used either alone or in conjunction with ethyl-*b*-naphthyl ether. Benzyl-*p*-tolyl urethane acts similarly.

The carbanilates (phenylamidocarbonates) have also dissolving powers on the cellulose esters, especially nitrocellulose. Methyl, ethyl, propyl, butyl, amyl[5], *iso*butyl

1. U. S. P. 1836687; abst. C. A. 1932, **26**, 1120.
2. U. S. P. 1090644. E. P. 12743, 1912. Swiss P. 65138. W. Rintoul and T. Nolan, U. S. P. 1348741, E. P. 131389, plasticize nitrocellulose with diphenyl-, phenylbenzyl-, benzyl-tolyl-urethane in the presence of a small amount of ethyl-*b*-naphthyl ether, while W. Rintoul and D. Cross, U. S. P. 1303115, 1310489, employ urethanes and esters of carbamic acid for the same purpose, usually in conjunction with nitrobenzene, dinitrobenzene and methyl or ethyl nitrates.
3. U. S. P. 1090641. F. P. 459451. E. P. 4941, 1913. Swiss P. 65139, 65925.
4. W. Rintoul and T. Nolan, U. S. P. 1348741.
5. J. Stevens and F. Axtell, U. S. P. 568104, 568105.

and *iso*amyl carbanilates have been patented for this purpose. Ethyl carbanilate is identical with phenyl urethane, ethyl phenylcarbamate and ethyl amidophenylcarbonate.

Carbanilic Esters. Phenylurethanes. Phenylcarbaminic esters. J. Stevens and F. Axtell[1] in 1896 disclosed a series of pyroxylin plasticizers and camphor substitutes, being organic carbanilates formed by the action of chloroformic esters of the fatty alcohols on aniline. They included methyl, ethyl, propyl, butyl and amyl carbanilates, ethyl carbanilate being identical with phenylurethane or ethylphenyl carbamate. The methyl ester melts at 47°, the ethyl ester at 52°, the *n*-propyl ester at 55.2°, the *iso*-butyl ester at 82.2° and the *iso*-amyl ester at 52°.

Benzoic and Salicylic Esters. These esters are volatile, stable and have a wide range of dissolving power for cellulose derivatives. In 1896, J. Stevens[2] called attention to the value of methyl, ethyl, propyl, butyl and amyl benzoates as solvents for the nitrocelluloses.

Methyl Benzoate (Oil of Niobe) is a pleasant smelling liquid, b. pt. 199°, sp. gr. 1.1026 at 0°, and miscible with alcohol, ether, chloroform and ethyl and butyl acetates. It is a solvent of the cellulose ethers and esters, of coumarone, ester gum and rubber. Practically insoluble in water, the solubility diminishing with increase in molecular weight of introduced alkyl. It has been patented as a nitrocellulose solvent by W. Lindsay[3] and by R. Eisenmann[4], the latter in conjunction with ethyl oxalate, lactate, salicylate, stearate, palmitate, phthalate, butyrate, tartrate, methyl stearate or palmitate, or amyl lactate, tartrate or oxalate; as a cellulose acetate solvent by W. Lindsay in combination with amyl butyrate or salicylate; benzyl alcohol, ether, acetate or benzoate: bornyl acetate and a large list of other solvents[5]. Knoll & Co.[6] specify methyl or ethyl benzoates with

1. U. S. P. 568104.
2. U. S. P. 559824.
3. U. S. P. 1199800; abst. C. A. 1916, **10**, 3159.
4. D. R. P. 192666; abst. Wag. Jahr. 1908, **54**, I, 96.
5. U. S. P. 1388472; abst. C. A. 1921, **15**, 3950.
6. D. R. P. 276013; abst. C. A. 1915, **9**, 386.

b-naphthyl benzoate, benzyl alcohol and anisol, and A. Nobel[1] methyl, ethyl, propyl and amyl benzoates with chlor (or brom) -benzene, -toluene, -xylene, -cumene and -cymene. S. Carroll[2] has described the advantages as a cellulose ether solvent combination of methyl benzoate in conjunction with methyl or ethyl alcohols, considerable of the benzoic ester remaining in films made therefrom due to its low volatility. The water-insoluble ethylcellulose is readily dissolvable by methyl benzoate. He has also described as a cellulose ether solvent of low inflammability[3] methyl *m*-brombenzoate and *p*-brombenzaldehyde, preferably in the presence of acetone, monochlornaphthalene being a useful addition thereto to modify the speed of evaporation.

Ethyl Benzoate gives films of high gloss and imparts desirable brushing qualities to solutions of cellulose derivatives. It is a colorless liquid, boils at 211.2° corr., sp. gr. 1.0502 at 16°, and the commercial product usually has an ester content above 98%. It is a direct solvent of the cellulose nitrates, acetates and cellulose ethers, and dissolves sandarac, shellac, mastic, ester gum, benzyl abietate and some of the harder copals with heat. Miscible with the usual cellulose ether solvents, but not with water. W. Webb[4] has described the advantages of ethyl benzoate as a cellulose ether solvent, in combination with methyl or ethyl alcohol to the extent of 50%.

Butyl Benzoate. *n*-Propyl benzoate boiling at 229.5° corr., and *iso*-propyl benzoate, b. pt. 218°, have apparently not been used as cellulose ether solvents to any extent. *n*-Butyl benzoate is a colorless liquid, b. pt. 247.3°, sp. gr. 1.00 at 20°, and has been described, along with *iso*-butyl and amyl benzoates by H. Clarke[5] as a solvent for the cellulose ethers. As an acceptable formula is given 100 parts

1. E. P. 15914, 1894; abst. J. S. C. I. 1895, **14**, 814.
2. U. S. P. 1469813; abst. C. A. 1923, **17**, 3919.
3. U. S. P. 1826688.
4. U. S. P. 1469862; abst. C. A. 1923, **17**, 3919. J. Stevens, U. S. P. 622727, uses ethyl benzoate with nitrocellulose for artificial leather production.
5. U. S. P. 1405490; abst. C. A. 1922, **16**, 1316.

ethylcellulose, 500 parts alcohol-benzene and 50 parts *n*-butyl benzoate. T. Aldrich[1] has described tribrom- *ter*-butyl benzoate.

Amyl Benzoate is not employed as a cellulose ether plastifier to any great extent. It is a colorless liquid of agreeable odor, the *iso*amyl ester boiling at 260.7°, sp. gr. 1.0039 at 0°. While amyl benzoate is not a powerful solvent alone for cellulose nitrate, cellulose acetate and the cellulose ethers, its solvent efficiency is considerably augmented by the addition thereto of lower boiling solvents as acetone. It is possible to simulate whiteness in a film by the addition of large proportions of amyl benzoate in the absence of other plasticizers. It has been used in photographic film production[2].

Phenyl Benzoate has been advocated as a colloiding agent for nitrocellulose[3], and as a cellulose ether solvent. E. Farrow gives as an acceptable combination[4] ethylcellulose, phenyl benzoate and methyl alcohol and acetate, the presence of phenyl benzoate causing a marked diminution in viscosity in the mixture. Glycol benzoate[5] and glyceryl benzoate[6] have been detailed as desirable solvents in connection with cellulose compounds.

Benzyl Benzoate, Ergol, is a very stable ester, m. pt. 20°, b. pt. 323°, sp. gr. 1.114°. It occurs in Peru Balsam associated with benzyl cinnamate and cinnamyl benzoate, cinnamate (styracin) and phenylpropyl cinnamate. Balsam of Peru, tolu and storax are auxiliary nitrocellulose solvents, probably by virtue of the above esters which they contain. Isobornyl benzoate gelatinizes both ethyl- and ben-

1. U. S. P. 1397913; abst. C. A. 1922, **16**, 719.
2. W. Lindsay, U. S. P. 1199800; abst. C. A. 1916, **10**, 3159. U. S. P. 1388472; abst. C. A. 1921, **15**, 3950.
3. H. Matheson, U. S. P. 1161063; abst. J. S. C. I. 1916, **35**, 40.
4. U. S. P. 1494476; abst. C. A. 1924, **18**, 2249.
5. L. Taub and H. Hahl, U. S. P. 1014859; abst. C. A. 1912, **6**, 670.
6. H. Dreyfus, F. P. 461544; abst. J. S. C. I. 1914, **33**, 196. Compagnie Gen. de Phon. Cinemato. et Appareils de Precision, Swiss P. 61929; abst. C. A. 1914, **8**, 2124. H. Danzer, U. S. P. 1089910; abst. C. A. 1914, **8**, 1551.

zyl-cellulose, best with the application of heat and in the presence of a relatively small amount of ethyl alcohol. Benzyl benzoate, especially in conjunction with ethyl or butyl phthalates makes an excellent but slow-drying cellulose ether gelatinant and flexilizer. Benzyl benzoate for nitrocellulose[1], in the proportion of 3 of ester to 2 of cellulose nitrate[2], especially when using damp pyroxylin[3], forms masses of high flexibility.

The Seldon Co. have described a large class of plasticizing agents[4] comprising the methyl, ethyl, propyl, butyl, amyl, cyclohexyl, tetrahydrofurfuryl and benzyl benzoylbenzoate, toluylbenzoate, naphthoylbenzoate, acetnaphthoxybenzoate, fluorenecarbonylbenzoate, toluylacrylate, maleate and tetrahydronaphthylbenzoate. Of these 72 plastifiants, methyl benzoylbenzoate is a crystalline solid, the butyl and amyl esters being liquids. Butyl naphthoylbenzoate is a very viscous, yellow liquid and methyl tetrahydronaphthylbenzoate melts at 75°. The chlorine substitution products of the above, as methyl chlorbenzoylbenzoate, are said to be highly stable and equally good solvents and plastifiants.

Methyl benzoate and salicylate are solvents of pyroxylin[5].

Benzyl benzoate has also been used rather extensively in the cellulose acetate industry, not so much on account of its solvent power which is low, but on account of the desirable flexibility imparted. The processes of W. Lindsay[6] and H. Gault[7] who combine benzyl benzoate with methylethyl ether, acetone oil, benzyl alcohol, benzyl acetate, furfural, eugenol, cresol and urea for the covering of airplane wings, are illustrative.

1. W. Lindsay, U. S. P. 1233374; abst. C. A. 1917, **11**, 2612.
2. *Ibid.* U. S. P. 961360; abst. C. A. 1910, **4**, 2581. E. P. 13692, 1910. F. P. 416843. D. R. P. 251372.
3. *Ibid.* U. S. P. 1292819; abst. C. A. 1919, **13**, 1017.
4. F. P. 703018; abst. C. A. 1931, **25**, 4423; Chem. Zentr. 1931, II, 3051.
5. J. Stevens, U. S. P. 269340.
6. U. S. P. 1027619, 1199800, 1388472. E. P. 13692, 1910. F. P. 416843. D. R. P. 251372.
7. U. S. P. 1394890; abst. C. A. 1922, **16**, 502.

b-Naphthyl Benzoate or naphthyl acetate in conjunction with methyl alcohol[1] has been recommended by Zuehl & Eisemann as a desirable nitrocellulose plastifier. It may be produced by the method of C. Bleiberger[2]. Of the monoarylglycol ethers, ethylene glycol monocresyl ether benzoate[3] has been patented for increasing the plasticity and softness of cellulose ester and cellulose ether masses.

Glyceryl Benzoate. Tribenzoin. This solid plasticizer, comparatively new in the art, although described as a desirable solvent in the cellulose industry in 1898[4], 1900[5] and 1913[6], is white, odorless crystals, soluble in the usual solvents in the anhydrous condition, m. pt. 71°, sp. gr. 1.25°. In contradistinction to glycerol, it is non-hygroscopic. H. Dreyfus[7] has discussed the desirability of glyceryl benzoate as a cellulose acetate plastifier; A. Pouteaux[8] has pointed out the advantages in the acetylcellulose art of glycol, glyceryl and benzyl benzoates; and J. Hirsh and A. Robson[9] advantages of glyceryl benzoate as a polishing material for cellulose acetate surfaces. F. Hahn[10] has dilated on the advantages as a cellulose ether and ester solvent of glyceryl benzoylbenzoate. The coating composition of Imperial Chemical Industries[11] combines cellulose acetate with monoethylin benzoyl benzoate, glycerol trilactate, or

1. D. R. P. 118052; abst. Chem. Zentr. 1901, I, 551. Roland Fireproof Celluloid Corp., Belg. P. 357463, prepare a celluloid substitute from acetylcellulose, tetrachlorethylene, benzyl benzoate, triacetin and dichlorhydrin.
2. U. S. P. 1254970; abst. C. A. 1918, **12**, 703. See J. Stevens, U. S. P. 572134, 572135.
3. A. Steindorff and G. Balle, D. R. P. 372546, Addn. to D. R. P. 366115; abst. Kunst. 1923, **13**, 70.
4. R. Schuepphaus, U. S. P. 598648. He also patented the use of glyceryl monobenzoate, benzochlorhydrin, dichloracetin, benzomonoacetin, benzodiacetin, oleoacetin, oleodiacetin, dinitroacetin and mononitrodiacetin as a softener and solvent for nitrocellulose.
5. J. Goldsmith and British Xylonite Co., E. P. 13131, 1900. F. P. 307242. D. R. P. 125315.
6. W. Plinatus, E. P. 16940, 1913. F. P. 476991.
7. F. P. 461544; abst. C. A. 1914, **8**, 3859.
8. F. P. 541643; abst. Chem. Zentr. 1923, II, 642.
9. U. S. P. 1621780.
10. Can. P. 312568.
11. E. P. 316321, 316322, 316323. In E. P. 316322 are included monomethyl-, monoethyl-, monopropyl- and monobutyl-glyceryl ethers.

glyceryl benzoylbenzoate, glyceryl pyruvate, glyceryl salicylate or glyceryl tartrate.

Benzyl *p*- and *m*-aminobenzoates have been prepared by H. Shonle and P. Row[1]. Ethyl amidobenzoate is Anaesthesin.

Methyl Salicylate. Wintergreen Oil. Methyl Hydroxybenzoate. A colorless, highly refractive, agreeable smelling liquid, sp. gr. 1.18-1.185, b. pt. 219-224° for the commercial ester. Freely soluble in alcohol and glacial acetic acid; soluble in about 7 volumes 70% alcohol at 25°. Slightly soluble in water. As a solvent for cellulose compounds, methyl salicylate has been known since 1882, in which year J. Stevens[2] described its advantages with pyroxylin, either alone or in conjunction with methyl nitrate, butyric, valeric or benzoic ethers; amyl formate, acetate, butyrate and valerianate; ethyl oxalate or sebacate; of oils of cherry, laurel, heavy cinnamon, melissa (balm), birch tar and pennyroyal. In 1892 he patented methyl salicylate in the form of naturally occurring wintergreen oil[3], and three years later described plastic pyroxylin bodies containing methyl salicylate, naphthalene and oil of cassia[4]. W. Lindsay[5] pointed out its applicability in acetylcellulose solutions, especially in combination with ethyl sebacate, and the use of methyl and amyl salicylates in conjunction with triphenyl phosphate for cellulose acetate plastics[6]. S. Carroll[7] dissolves the cellulose ethers in methyl salicylate to which an equal amount of methyl alcohol is added, and L. Malone and S. Carroll[8] prepare a transparent, flowable acetylcellulose film using methyl salicylate, acetone and castor oil. For plastic manufacture[9] and direct solvents for cellulose acetate[10], methyl salicylate has been used to a

1. The Lilly Sci. Bull. June 1, 1921, (2), #1, 14.
2. U. S. P. 269340.
3. U. S. P. 478543.
4. U. S. P. 543197.
5. U. S. P. 1199800.
6. U. S. P. 1388472.
7. U. S. P. 1450715.
8. U. S. P. 1575778.
9. A. Healy, U. S. P. 1194176. E. P. 10320, 1910. D. R. P. 192666. L. Paget, E. P. 7277, 1893.
10. U. S. P. 1368954, 1421974.

limited extent. The French used large amounts during th war for airplane wing dopes, both nitro- and acetylcellulos

Methyl Acetylsalicylate. Methyl Acetosalicylate. J Kessler[1] has described a series of cellulose ether and este plastifying and high-boiling solvent bodies, includin methyl, ethyl, butyl, amyl, phenyl, *a*- and *b*-naphthyl formyl (or acetyl, propionyl and benzoyl) salicylate, and has give physical constants for many of these 28 esters. Methy acetylsalicylate is a solid, m. pt. 49-50°, ethyl acetylsalicyl ate boiling at 272°. L. Thorp[2] prepares methyl acetyl salicylate (methyl aspirin) by mixing methyl salicylat and acetic anhydride in the presence of an alkali meta acetate.

Ethyl Salicylate is superior in every respect in solvenc to the methyl ester and has the same characteristic odo B. pt. 233° at 733 mm., sp. gr. 11843 at 20.5°. An excellen solvent for water-insoluble ethylcellulose and benzylcellu lose in conjunction with a small amount of alcohol. Th J. Stockhausen nitrocellulose composition[3] employs eth salicylate as a camphor substitute—for which purpose i would be a failure on account of its low thermoplasticit

Butyl and Amyl Salicylate. Butyl, *iso*butyl and am salicylates have been set forth by H. Clarke as desirabl nitrocellulose compositions intended for film and va nishes[4], and also these three esters as direct cellulose ethe dissolvants in conjunction with ethyl alcohol and benzene The range of combination is about 30 parts *n*-butyl salic late to 100 parts ethylcellulose. W. Lindsay[6] pointed ou the applicability of amyl salicylate as a solvent for acetone soluble cellulose acetate, either alone or admixed with benzy salicylate, alcohol, acetate or ether; bornyl acetate, carvene ethyl sebacate, phenyl ether, safrol, terpineol, anisol, benzy formate or butyrate, or oils of camphor, cedar leaves, ceda

1. U. S. P. 1408095; abst. Mon. Sci. 1923, (5), **13**, 15.
2. U. S. P. 1255950.
3. D. R. P. 281262. F. P. 428468. Aust. P. 8192.
4. U. S. P. 1444333; abst. C. A. 1923, **17**, 1329.
5. U. S. P. 1395905; abst. C. A. 1922, **16**, 646.
6. U. S. P. 1199800; abst. C. A. 1916, **10**, 3159.

wood, cinnamon, eucalyptol, sassafras, citronella, clove, fennel, hedeoma (pennyroyal), juniper, mace, peppermint, pineneedles, rosemary, rue, sage, spruce and thyme. To this category was added, phenyl ether, carvol, cinnamic alcohol, eugenol, geranyl formate and acetate, isoeugenol, isosafrol, methyl anthranilate, methylene acetate, methyl nitrobenzoate, methyl and ethyl oleate, methyl phenylacetate, phenylethyl alcohol and terpinyl acetate. Plastolin II is said to be amyl salicylate.

Glycol Salicylate (spirosal) is an excellent solvent for hydrated cellulose acetate, and dissolves ethyl- and benzylcellulose by the application of heat, facilitated by a small amount of ethyl alcohol. Glycol benzoate, toluate, anthranilate, cinnamate, mandelate, naphthoate, gallate, malonate, malate, succinate, aspartate and tartrate, all have a moderate solvent action on the cellulose ethers, which is materially augmented by the presence of alcohol and acetone, and is aided by the application of heat. Farbenfabriken vorm. F. Bayer & Co. have described glycol monosalicylate[1].

Phenyl Salicylate was first described as a nitrocellulose plastifier by J. Stevens[2], employed with alcohol, or in conjunction with naphthalol (betol), naphthyl benzoate (benzonaphthol), salacetol (salicylacetol) and benzoic anhydride. Phenyl salicylate (salol), a white, crystalline powder, is readily soluble in alcohol, acetone and ethyl acetate, and is odorless. Phenyl salicylate and cellulose acetate combined with a solvent harmonious to both have been advocated by W. Lindsay[3] as an efficient non-inflammable celluloid. H. Mork and G. Esselen still further diminish the inflammability of cellulose esters[4] by combining phenyl salicylate and triphenyl phosphate[5]. Antipyrin salicylate (salipyrin) and tolypyrin salicylate[6], dissolved in alcohol

1. D. R. P. 404999; abst. J. S. C. I. 1925, **44**, 425. For mfr. glycol benzoate, see L. Taub and H. Hahl, U. S. P. 1014859.
2. U. S. P. 572134.
3. U. S. P. 1319229; abst. C. A. 1920, **14**, 223.
4. U. S. P. 1193178; abst. C. A. 1916, **10**, 2404.
5. See U. S. P. 1199800, 1388472, 1436304.
6. J. Stevens, U. S. P. 566349.

as camphor substitutes, have been brought forward, alone or in conjunction with dimethylphenylpyrazolon (antipyrin), or methylphenyldimethylpyrazolon (tolypyrin, tolyl). Antipyrin melts at 110-113°, tolypyrin at 136-137°, salipyrin at 92° and tolysal at 101-102°. Menthyl salicylate and menthyl acetylsalicylate[1] dissolve ethylcellulose in the presence of alcohol.

Diglyceryl tetracetate and diacetyldiglyceryl diacetylsalicylate[2] have been recommended as efficient methylcellulose solvents and plastifiers, 100 parts methylcellulose being combined with 240 parts each methyl alcohol, benzene, toluene and ethyl alcohol, to which 50 parts of one of the above plastifiers is added. E. Hill[3] prepares a stencil sheet with cellulose acetate dissolved with phenyl salicylate, dibutyl tartrate, diamyl phthalate, diacetin, triacetin, acetanilid and *o*-nitrotoluene.

Benzyl Salicylate dissolves cellulose nitrate and is a solvent of water-insoluble ethylcellulose in the presence of methyl alcohol or methyl acetate. W. Lindsay[4] has described the application of benzyl salicylate as a cellulose acetate colloidant.

Naphthenic Esters. Hexahydrobenzoic Esters. These are high boiling, viscous liquids or semi-solids, combining a dissolving action with a softening quality to the cellulose ester or ether with which they are incorporated. W. Plinatus[5] has described the applicability of methyl and ethyl naphthenates (hexahydrobenzoates) in conjunction with other esters and mono-, di- and tri-butyrin as desirable cellulose ester gelatinants, and G. Ruth and E. Asser[6] the utilization of metallic naphthenates as those of aluminum, chromium, iron, cobalt or magnesium, or glyceryl, glycol

1. Kantor Chemischer Preparate Ernst Alexander, D. R. P. 244787; abst. J. S. C. I. 1912, **31**, 511.
2. C. F. Boehringer & Soehne, F. P. 718919; abst. C. A. 1932, **26**, 3377.
3. U. S. P. 1608743.
4. U. S. P. 1199800, 1388472.
5. F. P. 581177. Swiss P. 95376.
6. D. R. P. 327376; abst. Chim. et Ind. 1922, **7**, 544; J. S. C. I. 1921, **40**, 188-A. D. R. P. 332866; abst. J. S. C. I. 1921, **40**, 400-A; Kunst. 1920, **10**, 47.

or mannitol naphthenates in combination with either nitro- or acetylcellulose. Naphthenic acid glycerides in the presence of the unsaturated hydrocarbon oil called squalene[1], together with low boiling liquids such as acetone, ethyl alcohol or acetate, form a solvent combination for starch acetate, starch palmitate, mannan acetate or cellulose nitrate or acetate. A series of esters applicable for varnishes has been patented[2], comprising pentaerythritol, sorbitol, mannitol and dulcitol naphthenates, linoleates, ricinoleates, oleates, stearates, montanates and resinates, the above 28 esters being included in a group of trihydroxy alcohols coupled with difficultly volatile monobasic, aliphatic carboxylic acids of cyclic or open chain structure. The naphthenic esters, especially phenyl, tolyl, xylyl and benzyl naphthenates are more ductile and flexible as the increment of combined naphthenic acid increases[3]. Propyl, butyl, amyl and methylamyl naphthenates have as yet been imperfectly investigated.

Anisic Esters. Methyl anisate (methyl *p*-methoxybenzoate) as a cellulose ether solvent has been recommended in conjunction with acetone[4], and in the presence of camphor, castor oil, triphenyl phosphate and monochlornaphthalene. It is a solid at ordinary atmospheric temperature, and boils at 269-270°[5]. The ethyl ester boils at 255°[6], the phenyl ester melts at 75°[7], and the guaiacol ester, m. pt. 97°[8].

Mandelic Esters. Ethyl mandelate (phenylhydroxyacetate, amygdalinate, phenylglycollate, benzoylglycollate) has been described as a nitrocellulose solvent[9] in the proportion

1. S. Horii, U. S. P. 1792095; abst. J. S. C. I. 1931, **50**, 968-B.
2. I. G. Farbenindustrie, E. P. 351945; abst. C. A. 1932, **26**, 3391; Chem. Zentr. 1931, II, 3050. F. P. 660510; abst. C. A. 1930, **24**, 252.
3. G. Ruth and E. Asser, D. R. P. 334983; abst. Kunst. 1921, **11**, 87.
4. S. Carroll, U. S. P. 1826692.
5. W. Perkin, J. C. S. 1889, **55**, 551.
6. A. Ladenburg and A. Fitz, Ann. 1867, **141**, 252.
7. M. v. Nencki and F. v. Heyden, D. R. P. 46756.
8. *Ibid.* D. R. P. 57941.
9. H. Matheson, U. S. P. 1815655. Can. P. 291762. E. P. 270650.

of 4 parts, to nitrocellulose 10 and alcohol 6. Methyl *p*-mandelate melts at 52° and the ethyl ester at 34°.

Phthalic Esters. This being a dibasic acid, mono- and di-esters result. Herein as elsewhere, the di-esters do not have the prefix "di," i.e. dibutyl phthalate is given as butyl phthalate, whereas the acid ester is called "mono." The phthalic esters are a wide and important class of direct and latent softeners and solvents, some of the members dissolving a wide range of cellulose ethers in addition to the organic (acetic) and inorganic (nitric) esters of cellulose.

Methyl Phthalate, methyl, ethyl and propyl phthalates were described in 1900 as successful solvents of both acetate and cellulose nitrate[1], alone or in admixture with the acetins (glyceryl acetates), benzicins (glyceryl benzoates), phthalic anhydride, methyl, ethyl or propyl succinates, pulegone, thujone or pennyroyal oil. As a colophony or other resin solvent, methyl or ethyl phthalate has been known since 1909[2]. E. Clayton and C. Clark[3] have described the physical properties and applicability as cellulose ether and ester solvents of methyl, ethyl, butyl, *iso*butyl and cyclohexanol phthalates. The commercial products Palatinol M (methyl phthalate), Palatinol A (ethyl phthalate), Palatinol C (butyl phthalate) and Palatinol JC (*iso*butyl phthalate) are said to have physical constants as follows:

	Palatinol M	A	C	JC
Boiling Range	280–283°	298–300°	310–320°	305–315°
Sp. gr. at 15°	1.195	1.127	1.054	1.049
Flash Point	132°	140°	160°	161°
Molecular Weight	194	222	278	278
Ester Number	577	504	403	403

1. J. Goldsmith and British Xylonite Co., E. P. 13131, 1900; abst. J. S. C. I. 1900, **19**, 807; 1901, **20**, 741; Chem. Ztg. 1901, **25**, 1065; Mon. Sci. 1902, (4), **58**, 163. F. P. 307242; abst. Mon. Sci. 1902, (4), **58**, 157. D. R. P. 125315; abst. Chem. Zentr. 1901, II, 1192; Mon. Sci. 1902, (4), **58**, 78; Jahr. Chem. 1901, 900; Wag. Jahr. 1901, II, 609.

2. A. Hesse, E. P. 12633, 1910; abst. J. S. C. I. 1911, **30**, 815; Chem. Ztg. Rep. 1911, **35**, 450; C. A. 1911, **5**, 3125. D. R. P. 227667; abst. C. A. 1911, **5**, 2155; J. S. C. I. 1910, **29**, 1398; Zts. ang. Chem. 1910, **23**, 2348; Chem. Zentr. 1910, II, 1579; Jahr. Chem. 1910, II,

They are esters of *o*-phthalic acid. Fermine is said to be methyl phthalate, and is a colorless, odorless liquid.

Ethyl Phthalate[1]. As a cellulose ether solvent, British Celanese, Ltd.[2], employ ethyl phthalate with ethyl lactate, acetone, alcohol and benzene as a direct dissolvant for methyl-, ethyl- or benzyl-cellulose, preferably as a top coat over a nitrocellulose lacquer. W. Moss[3] utilizes ethyl phthalate as an adjunct to triphenyl phosphate, tricresyl phosphate, monomethyltoluenesulfonamide, triacetin, diphenylol propane and thiocarbanilid, and a volatile solvent as ethyl lactate, benzyl alcohol, diacetone alcohol or ethylene dichloride together with methyl- or benzyl-cellulose. The H. Clarke cellulose ether composition comprises ethyl phthalate and a common solvent, being especially applicable to water-insoluble ethylcellulose[4].

In the nitrocellulose industry, ethyl phthalate has been used conjointly with butyl phthalate and ethyl tartrate also as an acceptable solvent for ethylcellulose and benzylcellulose[5]; with bromcresyl phosphate or methyltoluenesulfonamide[6]; in association with ethylbutyl, butyl or amyl phthalate, benzyl benzoate and amyl cinnamate[7]; ethyl and amyl phthalate with mono-, di- or tri-acetin, di-or tri-nitrotolu-

867; Chem. Tech. 1910, **34**, 596; Chem. Zts. 1911, **10**, No. 2167; Kunst. 1911, **1**, 90. F. P. 416806; abst. J. S. C. I. 1910, **29**, 1398. U. S. P. 1003741; abst. C. A. 1911, **5**, 3922; J. S. C. I. 1911, **30**, 1223; Mon. Sci. 1912, **77**, 165; Kunst. 1912, **2**, 77.

3. Text. Mfr. 1931, **57**, #684, 455.

1. R. Herzog, A. Hildesheimer and F. Medicus, Zts. ang. Chem. 1921, **34**, 57; abst. Caout. et Gutta. 1922, 11379; C. A. 1921, **15**, 2003. Chem. Met. Eng. 1925, **32**, 570.

2. E. P. 298608; abst. Chem. Zentr. 1930, I, 2973.

3. E. P. 307292. See Alox Chemical Corp., E. P. 303560. Can. P. 283892.

4. U. S. P. 1405491; abst. C. A. 1922, **16**, 1316; J. S. C. I. 1922, **41**, 248-A. See R. Wietzel, U. S. P. 1732392; abst. C. A. 1930, **24**, 131.

5. British Celanese, Ltd., E. P. 316984; abst. C. A. 1930, **24**, 1996. See E. P. 299065, 299066, 299067, 307290, 307291.

6. British Celanese, Ltd., E. P. 317457; abst. C. A. 1930, **24**, 2291.

7. G. Schwartz, U. S. P. 1710078. In the production of artificial leather from cellulose ethers or esters (the Compagnie Francaise d'Exploitation des Procede Plinatus, E. P. 301759, 317824) ethyl phthalate with dibutyrin and methyl and ethyl glycol constitutes the solvent portion.

ene, methyl or ethyl *b*-naphthyl ethers, phenyl benzyl ether and phenanthrene[1]; and ethyl, butyl or amyl phthalates with a softener as castor oil[2], in the manufacture of linings for use between rubberized fabric. The C. Ellis nitrocellulose and synthetic resin coating employs the mutual solvent ethyl phthalate[3], while the floor covering of C. Taylor embodies ethyl or butyl phthalate with butyl or amyl acetates[4]. The three processes for preparing floor coverings of J. Baldwin[5] are based on the use of a plasticizer (butyl or amyl phthalate or butyl tartrate), a solvent (ethyl alcohol, benzene, toluene or naphtha), a resin (cumar, acaroid, copal, shellac, ester gum) and a modifier (montan wax, rubber, tung oil, spinacene or squalene).

In the cellulose acetate art, ethyl phthalate solutions are used as a dressing composition on textiles to produce a silky luster after the goffering process[6]. The I. G. Farbenindustries[7] combine copals with acetylcellulose by virtue of the mutually harmonious solvent ethyl, propyl, butyl or amyl phthalates, while A. Zimmerli of Acetol Products, Inc.,[8] produces films adapted to pass ultraviolet rays in the region most biologically efficient by means of cellulose acetate made into a lacquer by virtue of ethyl phthalate.

1. F. Nathan, W. Rintoul and F. Baker, E. P. 4940, 1913. See E. P. 4179, 1875; 10376, 1889; 14231, 1901; 12472, 12743, 12744, 12745, 12746, 1912. The Soc. des Usines Chimique Rhone-Poulenc, E. P. 351390, produce moldable materials by stirring a cellulose ester vigorously with a water suspension of ethyl phthalate or camphor. See F. P. 707593.

2. L. Sebrell, U. S. P. 1749743. E. P. 288244. Can. P. 291007. L. Sebrell, U. S. P. 1763618, prepares a liner for interposition between layers of rubberized fabric by a cement of nitrocellulose and ethyl phthalate.

3. U. S. P. 1529056. Cf. E. Zühl, F. P. 310942.

4. U. S. P. 1562386. E. P. 243614; abst. Caout. et Gutta. 1926, **23**, 13314; Chem. Zentr. 1926, I, 2987.

5. U. S. P. 1856369; abst. C. A. 1932, **26**, 3686. See also U. S. P. 1856370, 1856371.

6. L. Lilienfeld, E. P. 592, 1907. Aust. P. 47238, Addn. to Aust. P. 47237.

7. E. P. 294911; abst. C. A. 1929, **23**, 2050. For information concerning dibornyl tetrachlorphthalate, see A. Haller, U. S. P. 1415340, 1429342.

8. U. S. P. 1842640; abst. C. A. 1932, **26**, 1781.

The H. Willkie solvent composition[1] combines ethyl phthalate, ethyl acetate, benzene and alcohol, the ethyl acetate being preferably anhydrous[2]. The G. Leonard stencil sheet for typewriting or stylographic work[3] involves the application of ethyl phthalate as a shellac solvent as a coating for Yoshino paper, while R. Kienle and L. Adams[4] admix ethyl or butyl phthalates with glyceryl diacetate (diacetin), ethyl lactate, benzyl acetate or glycol monoethyl ether.

Commercial ethyl phthalate contains substantially 100% ester, and in films tends to introduce toughness coupled with considerable pliability. It is non-hygroscopic and non-toxic, available in quantity[5]. Soluble in water less than 1%.

Butyl Phthalate. In conjunction with the cellulose ether art, the Imperial Chemical Industries, Ltd., and B. Foster[6] have submitted formulas for combining cellulose ethers with butyl phthalate, and for the fabrication of plastic floor coverings utilizing this solvent with camphor oils or *p*-toluenesulfonamide[7]. The I. G. Farbenindutrie[8] employ either butyl or *iso*amyl phthalate, a specific example being to knead 10 parts ethylcellulose with 10-12 parts *iso*-amyl phthalate (b. pt. 185-190° at 8 mm.) and one of the usual low boiling solvents until a clear, syrupy paste is obtained, which may then be thinned to the consistency

1. U. S. P. 1449156, 1449157; abst. J. S. C. I. 1923, **42**, 494-B.
2. H. Willkie, U. S. P. 1449157; abst. C. A. 1923, **17**, 1896; J. S. C. I. 1923, **42**, 494-A.
3. U. S. P. 1576663. For application of dichlorhydrin phosphates as camphor substitutes, see Zühl & Eisemann, D. R. P. 128120, 173796.
4. E. P. 284348; abst. C. A. 1928, **22**, 4845. Compagnie Francaise pour L'Exploitation des Procedes Thomson-Houston, F. P. 655281; abst. C. A. 1929, **23**, 4089.
5. A. Claflin, Chem. Markets, 1928, **23**, 471, 579; abst. C. A. 1929, **23**, 1187.
6. E. P. 331837; abst. J. S. C. I. 1930, **49**, 872-B; Br. Plastics, 1930, **2**, #17, 100. Compare E. P. 293435. F. P. 687597; abst. C. A. 1931, **25**, 786.
7. Imperial Chem. Industries, Ltd., and B. Foster, E. P. 348156; abst. C. A. 1932, **26**, 2072; J. S. C. I. 1931, **50**, 728-B; Brit. Plastics, 1931, **3**, #30, 269. See E. P. 331837.
8. E. P. 245469; abst. C. A. 1927, **21**, 333. E. P. 253328, Addn. to E. P. 245467; abst. C. A. 1927, **21**, 1548; Chem. Zentr. 1927, I, 667.

desired. The leather adhesive formula of W. Stelkens[1] is a cellulose ester softened with a mixture of butyl phthalate and cresyl phosphate, which also makes an excellent solvent for rosin, ester gum, coumarone resin or polymerized linseed oil[2].

In the pyroxylin art *n*-butyl phthalate in the hands of E. Reid[3], butyl phthalate with butyl acetate, toluene and ethyl alcohol[4]; or butyl phthalate with a non-solvent softener as ethyl palmitate[5], are examples of combinations with nitrocellulose which have been recommended for special purposes. The pyroxylin varnish of the I. G. Farbenindustrie[6] is butyl phthalate 10, castor oil 30, and 500 parts ketones boiling between 120-170°, with 300 of toluene and 100 of light petroleum. Butyl phthalate and ethyl carbonate produce a liquid dissolving both nitrated cellulose and blown drying oils[7], while G. Frey & Co.[8] claim to raise

1. E. P. 314867; abst. J. S. C. I. 1930, **49**, 1081-B. The I. G. Farbenind., F. P. 685163; abst. C. A. 1930, **24**, 6040, prepare varnishes by emulsifying dibutyl phthalate in water containing methylcellulose and mixing this emulsion with nitrocellulose, ocher and water. They coat porous materials (F. P. 688315; abst. C. A. 1931, **25**, 834) by emulsifying a nitrocellulose lacquer in a solution of methyl-, ethyl- or benzyl-cellulose in water, and add dibutyl phthalate.

2. J. Baldwin, U. S. P. 1793667; abst. Plastic 1931, **7**, #6, 353. Dibutyl phthalate, m. pt. 295°; diethyl phthalate, m. pt. 296°; diamyl phthalate, m. pt. 340°, and butyl stearate form the solvent portion of the nitrocellulose lacquer of S. D. Warren Co. and W. Driersen, E. P. 344471, and nitrocellulose with butyl phthalate, the coating composition for fibrous materials, as published by F. Morton, U. S. P. 1842978. The cellulose derivative lacquer undercoat of C. Gabriel, U. S. P. 1813735, comprises 2-4 lb. shellac and 2-10 ounces dibutyl phthalate per gallon of volatile solvent.

3. U. S. P. 1554032; abst. J. S. C. I. 1925, **44**, 971-B. See also W. Baer, Chem. Tech. Rundschau, 1929, **44**, 51; abst. C. A. 1929, **23**, 3586. W. Munzinger, Melliand's Textilber. 1930, **11**, 117; abst. C. A. 1930, **24**, 6005.

4. G. Roelandts, F. P. 37088, Addn. to F. P. 652410; abst. C. A. 1931, **25**, 1048.

5. G. Schwartz, U. S. P. 1710078; abst. C. A. 1929, **23**, 2822; Brit. Plastics, 1929, **1**, #5, 191.

6. E. P. 330735; abst. J. S. C. I. 1930, **49**, 828-B. Belg. P. 330723, 330725. Ital. P. 254252, 254253, Addns. to Ital. P. 244959.

7. H. Hopkins and A. Tanberg, Can. P. 314398; abst. C. A. 1931, **25**, 5304.

8. Swiss P. 134370; abst. C. A. 1930, **24**, 1754. According to C. Staud (U. S. P. 1884337) claims highly acetylated cellulose acetate (41-42% acetyl) dissolves readily in a mixture of diethyl phthalate and *o*-cresyl-*p*-toluenesulfonate. See U. S. P. 1560542.

the amount of resin which may be incorporated with nitrocellulose by means of butyl phthalate and a resinate of magnesium, zinc, calcium or manganese. As a colloiding agent for wet pyroxylin[1], and for waterproofing Cellophane and other forms of regenerated cellulose[2], butyl phthalate has been advocated. In the preparation of a non-caking Titanox lacquer[3], the pigment is mixed with a gasolene solution of rubber, and this is then admixed with nitrocellulose dissolved by a mixture of butyl acetate, butyl phthalate and a small amount of dammar resin. Polymers of vinyl chlorides also dissolve in butyl phthalate[4], especially in the presence of toluene and solvent naphtha. One method for utilizing butyl phthalate is to admix 10 parts with 30 parts nitrocellulose[5], knead until a homogeneously appearing mass results, which is then thinned with a readily volatile solvent as acetone until a 10-15% nitrocellulose solution results, the latter being of low viscosity. Or[6], nitrocellulose of over 12.4% N may be first colloided by denatured ethyl alcohol, seasoned for 2-4 weeks at about 60° and until a standard testing solution shows a viscosity of less than 200 sec., after which it is dissolved in butyl phthalate and a volatile solvent.

The pyroxylin composition of R. Van Schaack[7] comprises butyl phthalate, methyl*iso*butyl carbinol and methylamyl acetate, and the celluloid formula of J. Walsh[8] camphor and butyl phthalate with alcohol. He prepares a

1. R. Hucks, E. P. 298914; abst. J. S. C. I. 1930, **49**, 678-B. Can. P. 305160; abst. C. A. 1931, **25**, 834.
2. Du Pont Cellophane Co., Inc., F. P. 647330; abst. C. A. 1929, **23**, 2542.
3. Canadian Industries, Ltd., Can. P. 307398.
4. E. I. du Pont de Nemours & Co., F. P. 717886; abst. C. A. 1932, **26**, 2879.
5. I. G. Farbenindustrie, Akt.-Ges., E. P. 245469, 247611; abst. Chem. Zentr. 1926, I, 2988; C. A. 1927, **21**, 333. See D. R. P. 127816. E. P. 245469 describes di-*n*-butyl phthalate, and E. P. 247611 that of di*iso*butyl phthalate.
6. H. Bradshaw, E. Nollau and R. Woodbridge, U. S. P. 1703415; abst. C. A. 1929, **23**, 2034; Chem. Zentr. 1929, II, 1104.
7. U. S. P. 1702181; abst. C. A. 1929, **23**, 1504.
8. U. S. P. 1772529.

wood fil[1] of pyroxylin 100, butyl phthalate 15-25, resin 60-65, castor oil 20-25, wood flour 175-200 parts, and 400-640 parts volatile solvent. The "glyptal" resins may be plasticized with 20% of either butyl phthalate, oleic acid, furfuraldehyde, or glycol diacetate[2].

Mono-butyl phthalate, a white crystalline solid melting at 73-74°, is claimed as an especially efficient gelatinant for both nitro- and acetyl-cellulose, especially in the presence of a low-boiling solvent[3]. Inasmuch as the raw materials (butyl alcohol and phthalic acid) are available in the United States in large quantities, butyl phthalate is used in considerable amounts in the industries employing cellulose derivatives. It is very stable, is miscible with castor, linseed, tung and other oils, but does not readily wet pigments[4].

E. Reid[5] has called attention to the advantages of employing mixed ester phthalates as methylbutyl, ethylbutyl, and propylbutyl *o*-phthalates, and N. Boehmer[6] to the advantages of *sec*-butyl, butylhexyl, butylamyl, butylbenzyl, butylethoxyethyl, butylglycol and butylglyceryl phthalates, glutarates, pimelates, citrates, terephthalates, methylphthalates, phenylsuccinates, malates, tartrates, trimesates or maleates, being a series of 77 individual solvents and colloidizing bodies.

Monomethylin and monoethylin phthalates or butyl phthalate[7], mono- or di-alkyl (or aryl) -pentaerythrite (or

1. J. Walsh, Can. P. 321641.
2. Brit. Thomson-Houston Co., Ltd., H. Warren and A. Ward, E. P. 303915, 303936; abst. J. S. C. I. 1929, **48**, 255-B.
3. E. Reid, U. S. P. 1554033; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 955-B; Rayon, 1925, **1**, #10, 23. See Can. P. 271948; abst. C. A. 1927, **21**, 3742. H. Wolff and B. Rosen, Farben-Ztg. 1929, **34**, 2564; abst. C. A. 1929, **23**, 4835. W. Harrison, Am. Paint & Varnish Mfrs. Assoc. Circ. 1929, **356**, 900. Am. Paint J. 1929, **13**, #52D, 30. Paint, Oil & Chem. Rev. 1929, **88**, #17, 120; abst. C. A. 1930, **24**, 514.
4. E. Clayton and C. Clark, Textile Mfr. 1931, **57**, #684, 455.
5. U. S. P. 1554033. 6. U. S. P. 1848155.
7. W. Lawson, E. P. 316325; abst. C. A. 1930, **24**, 1754; Chem. Zentr. 1929, II, 3189. See U. S. P. 1774500 and E. P. 316323.

-mannitol or -sorbitol) phthalates in synthetic monoethylin phthalate, dimonoethylin phthalate, monobenzylin phthalate and butylmonobenzylin phthalate[1]. *b*-Hydroxyethoxy-*n*-propylbutyl phthalate is included, and the phthalic acid may be replaced by oxalic or succinic acid in all of the above. The series of 18 solvents dissolves ethylcellulose and other cellulose ethers, the recommended proportions being, ethylcellulose 8, plasticizer 3, and benzene and xylene, each 40. They constitute a class of compounds concerning which but little is as yet definitely known.

Metal Alkyl Phthalates. Recently a class of bodies of satisfactory solvent capacity and high stability has been brought to the attention of workers in this field, being combinations of a mono- or poly-valent metallic salt of an alkyl half ester of phthalic acid. Included in this category are the double lead, cadmium, iron, manganese, nickel and cobalt butyl or amyl phthalates in conjunction with butyl phthalate, ethyl, propyl or butyl lactates or tetrachlorethane[2]; zinc butyl phthalate[3] with tricresyl phosphate; copper, lead or aluminum methyl (or butyl or benzyl) phthalate[4], preferably in conjunction with tricresyl phosphate; and ethyl, butyl and amyl phthalates ground together with 5% of zinc butyl, zinc methyl, copper butyl, copper benzyl, iron butyl, aluminum butyl or zinc butyl phthalates. They combine pigmentation with solvency, and result, especially with nitrocellulose, in the production of lacquers, paints and enamels in which the color is of great fastness to light and to the elements[5].

In this classification, there has also been advocated and made the basis of patent issuance the tin, lead, mercury, nickel, iron, zinc, manganese, copper, cobalt, (and even)

1. W. Lawson, E. P. 316324; abst. C. A. 1930, **24**, 1650; J. S. C. I. 1931, **50**, 476-B; Chem. Zentr. 1930, I, 295; Brit. Plastics, 1931, **3**, #28, 179. See U. S. P. 1774500.
2. B. Brown and C. Bogin, U. S. P. 1591652. D. R. P. 141925. Can. P. 260927, 260928.
3. Commercial Solvents Corp., Can. P. 295541, 295542.
4. C. Simms, W. Bannister and L. Swallen, U. S. P. 1864152.
5. *Ibid.* U. S. P. 1864151; abst. C. A. 1932, **26**, 4486.

silver, gold and platinum methyl, ethyl, propyl, butyl and amyl phthalates, a series of 60 metal-alkyl phthalic esters, all said to be soluble in acetone, turpentine or oil[1]. Iron, copper or zinc methyl, ethyl, cyclohexyl, benzyl and phenyl phthalates[2] involve 15 additional heavy metal half-esters of phthalic acid. Ferrous or ferric butyl phthalates are brownish red compounds, the corresponding zinc salt is colorless, and exists initially in the form of viscous oils. The ferric salts are somewhat unstable in the presence of water, and the zinc salts unstable above 100°. The colors of the iron salts are remarkably fast in nitrocellulose films to both visible and ultraviolet light[3].

Amyl Phthalate has been employed as a cellulose nitrate stabilizer and as a glyceryl nitrate (nitroglycerin) solvent[4]. Sp. gr. 1.0281 at 25°/4°, b. pt. 225° corr. Mixes in all proportions with aliphatic hydrocarbons without turbidity. Methyl amyl phthalate (b. pt. 170°, 4 mm.), terephthalate, benzoate, salicylate and phenylacetate[5] have been claimed as pyroxylin solvents.

Glycol Phthalates. Methylglycol phthalate (Softener P. M., Methyl Cellosolve Phthalate) is a colorless liquid, sp. gr. 1.17, b. pt. 230° and is a good softener for the cellulose ethers in the presence of a small amount of ethyl alcohol or alcohol-benzene. It also dissolves—more readily with heat—the cellulose nitrates and acetates. Butylglycol phthalate boils at about 365° with incipient decomposition, and may be used up to 30% as an acetylcellulose plasticizer. Soluble in the usual organic solvents, but not dissolvable by water. Ethylglycol phthalate, the phthalic acid ester of ethylene glycol monoethyl ether, both softens and gelatinizes nitrocellulose, cellulose acetate and the cellulose

1. C. Henning and C. Burke, U. S. P. 1742508; abst. J. S. C. I. 1930, **49**, 957-B; Brit. Plastics, 1930, **2**, #18, 120.
2. *Ibid.* U. S. P. 1742507, 1742509; abst. C. A. 1930, **24**, 1236; J. S. C. I. 1930, **49**, 957-B; Brit. Plastics, 1930, **2**, #18, 120.
3. E. I. du Pont de Nemours & Co., Farbe und Lack, 1930, 585; abst. Nitrocellulose, 1931, **2**, #1, 17.
4. F. Nathan, W. Rintoul and F. Baker, U. S. P. 1338691.
5. H. Young, U. S. P. 1702188; abst. C. A. 1929, **23**, 1505; J. S. C. I. 1929, **48**, 729-B.

ethers, the latter best in the presence of a relatively small amount of a lower aliphatic alcohol. It is a colorless crystalline solid melting at 34° and boiling at 345°. Sp. gr. 1.12. Commercially known as "Cellosolve Phthalate" and "Softener P. A." Butylglycol phthalate is both a nitro- and acetyl-cellulose solvent, used in conjunction with cyclohexanone, methylglycol acetate and methyl acetate[1]. Monomethylin phthalate or oxalate combined with ethyl phthalate or butyl phthalate comprises the coating composition of Imperial Chemical Industries, Ltd.[2].

Cyclohexyl Phthalate. E. Reid[3] has described the application to cellulose esters of cyclohexyl*iso*propyl, cyclohexyl-*n*-butyl, cyclohexylamyl, cyclohexylphenyl, cyclohexylbenzyl, cyclohexylxylyl and dicyclohexyl phthalates, the cyclohexylbutyl ester being particularly desirable[4].

Glyceryl Phthalate. As plasticizing masses for pyroxylin or cellulose acetate[5], W. Mooser-Schiess has described combinations of dry yeast, with glyceryl phthalate, naphthalate or camphorate. A coating composition has been patented[6] in which a cellulose ester is incorporated with a mixed ester of glycerol with phthalic acid and acids obtained by the hydrolysis of drying oil, glyceryl phthalate-linoleate being an example. Novelty in the W. Lawson coating composition resides in the use of *m*-styrenebutyl phthalate, butyl phthalate, dixylylethane, glyceryldibenzyl ether and butyl stearate[7].

Phenyl Phthalate. The cellulose ester composition of H. Clarke[8] involves the phenolic esters of phthalic acid, a suitable combination being cellulose acetate 100, acetone

1. G. Steimmig, U. S. P. 1864099. F. Biehler and Farbwerke vorm. Meister, Lucius & Brüning (D. R. P. 369447, Addn. to D. R. P. 366115) have described thiodiglycol phthalates as useful for increasing the plasticity and softness of cellulose ester masses.
2. Imperial Chemical Industries, Ltd., E. P. 316323; abst. C. A. 1930, **24**, 1754; Chem. Zentr. 1929, II, 3190. See E. P. 302961.
3. U. S. P. 1778567.
4. E. Reid, U. S. P. 1643393.
5. U. S. P. 1317721; abst. C. A. 1919, **13**, 3289.
6. H. Hopkins and F. McDermott, Can. P. 311488; abst. C. A. 1931, **25**, 3502. See Can. P. 310124.
7. W. Lawson, Can. P. 312341.
8. U. S. P. 1398939; abst. Chem. Ztg. 1922, **46**, 46.

400-600, phenyl *o*-phthalate 10. In another formula[1] 1 part phenyl or cresyl phthalate is combined with 2 parts nitrocellulose and a sufficient amount of methyl alcohol to produce a celluloid upon malaxation. According to R. Kramer[2] carboxylic acid esters of aryloxyethanol, xylenoxyphenoxyethanols and similar bodies constitute excellent cellulose acetate softeners. He has described *b*-phenoxyethyl, methylphenoxyethyl, *b*-methylnaphthoxyethyl, *b*-methylxylenoxyethyl phthalates and *b*-methylphenoxyethyl laurate, usable in abount 10% based on the weight of the ester. Benzyl phthalate[3], and benzylbutyl phthalate with acetyllaurin[4] are also cellulose ester plasticizers which recently have been described. Propylbenzyl phthalate, cyclohexylbenzyl phthalate, and *iso*amylcyclohexyl phthalate[5] are high boilers, and examples of plasticizers of phthalic esters having one carboxyl group esterified with the radical of an aromatic or hydroaromatic alcohol and the other with the radical of an aliphatic or aromatic alcohol.

Methyl or butyl 1.4-methylene-1.2.3.4-tetrahydrophthalate has been patented as a cellulose ether solvent, 10 parts ethylcellulose and 2 parts artificial resin obtained by condensing cyclohexanone or methylcyclohexanone being dissolved in a mixture of toluene 80, benzene and alcohol each 5, and 4 parts of the above butyl ester[6].

A series of simple and mixed esters has been de-

1. Farbwerke, vorm. Meister, Lucius & Brüning, D. R. P. 127816; abst. Wag. Jahr. 1902, II, 594; Bied. Tech. Chem. Jahr. 1901-2, **24**, 601; Chem. Zentr. 1902, I, 288; Chem. Ztg. 1902, **26**, 189; Zts. ang. Chem. 1902, **15**, 114; Jahr. Chem. 1902, **55**, 1056; Mon. Sci. 1902, **58**, 78. See D. R. P. 122272.

2. U. S. P. 1676612; abst. Plastics, 1928, **4**, #12, 688; J. S. C. I. 1928, **47**, 810-B. U. S. P. 1874310. E. P. 314571; abst. C. A. 1930, **24**, 1528; J. S. C. I. 1929, **48**, 728-B.

3. R. Van Schaack, U. S. P. 1734657; abst. C. A. 1930, **24**, 515; J. S. C. I. 1930, **49**, 26-B; Brit. Plastics, 1930, **1**, #10, 449.

4. M. Hitt, U. S. P. 1710453; abst. C. A. 1929, **23**, 2841; J. S. C. I. 1929, **48**, 786-B.

5. E. Schwabe and I. G. Farbenindustrie, D. R. P. 531642. E. P. 302961.

6. I. G. Farbenindustrie, D. R. P. 543825; abst. Chem. Zentr. 1932, I, 2245.

scribed[1] as suitable for solvents and impregnating liquids, embracing glyceryl phthalate, glyceryl phthalyl-oleate, -benzoate, -palmitate and -salicylate, and glycol and mannitol camphorates, citrates and cinnamates.

Dibenzyl Phthalate, Benzyl Phthalate, has been described by A. Zimmerli[2]. It boils at 260-285° at 10 mm., and melts at 42-44°. The camphor substitute of E. Zühl[3] comprises ethyl phthalate or *o*-phthalonate. Phthalonic acid (*o*-carbophenylglyoxylic acid), b. pt. 138-140°, neutral methyl phthalonate, b. pt. 66-68°. Glyceryl phthalate has been advocated as a satisfactory primer coat over which to place a nitrocellulose lacquer in coating metal surfaces as automobile bodies[4].

A series of plasticizing agents which do not volatilize readily, are soluble in the usual solvents for cellulose ethers and esters, and are said by virtue of their low volatility to render the cellulose derivatives permanently elastic, are phthalic acid esters of benzylmethylglycol, benzylpropyl, benzyl*iso*amyl, benzylglycolmonomethyl, benzylglycolmonoethyl, benzyltolyl, benzylcyclohexyl and *iso*amylcyclohexyl[5].

Cinnamic Esters. *b-Phenylacrylic Esters.* Methyl and ethyl cinnamate have been patented as cellulose ester solvents dissolved in alcohol, to which ethyl sebacate may be added[6]. The methyl ester melts at 33° and boils at 263°; the ethyl ester boils at 271°; the phenyl ester melts at 72° and boils at 206°, 15 mm. The benzyl ester melts at 30°. Ethyl cinnamate has been used with cellulose acetate as an airplane wing dope[7]. W. Lee[8] reports that ethyl cinnamate has a slight action on cellulose acetate in the cold,

1. E. Dawson and General Electric Co., E. P. 22544, 1913. See E. P. 12807, 1884; 9985, 1913.
2. U. S. P. 1708404; abst. C. A. 1929, **23**, 2449.
3. E. P. 4326, 1901. F. P. 308372. Methyl or ethyl phthalaminate or phthanilate may also be used.
4. H. Hopkins, U. S. P. 1771538; abst. C. A. 1930, **24**, 4647.
5. I. G. Farbenind., E. P. 302961; abst. J. S. C. I. 1929, **48**, 180-B.
6. W. Lindsay, U. S. P. 1199800, 1388472.
7. Soc. Nauton Freres & de Marsac and T. Tesse, E. P. 126989; abst. C. A. 1919, **13**, 2460. F. P. 492698. See E. P. 124763.
8. J. S. C. I. 1930, **49**, 226-T.

but our experience is that when dissolved in alcohol and heat, or heat and pressure applied, it is an excellent gelatinizing agent. F. Medicus[1] has described the use of cinnamic esters as solvents for cellulose esters, finding amyl cinnamate especially suitable.

Glycol monocinnamate[2] is a colorless oil, b. pt. 190-195° at 11 mm. pressure[3]. Glyceryl monocinnamate is a yellowish oil, soluble in alcohol, ether and chloroform and a direct cellulose acetate dissolvant[4]. (See p. 483, n. 6; 579, n. 6; 890, n. 1). Styracin (styryl cinnamate, cinnamyl cinnamate), m. pt. 14°, is a direct cellulose acetate solvent dissolved in alcohol, and also dissolves ethylcellulose.

In the preparation of pyroxylin plastic masses[5], K. Ott and K. Schaffganz utilize alkyl esters of *o*-cyanocinnamic acid, preferably amyl *o*-cyanocinnamate.

Oxanilic and Oxynaphthylaminic Esters. In 1901 appeared a disclosure[6] as to the use of methyl, ethyl, *iso*butyl, amyl, phenyl, benzyl and naphthyl oxanilates and oxynaphthylaminates as nitrocellulose colloidants in the proportion of 25-30% on the cellulose ester used. Methyl oxanilate melts at 114°, the ethyl ester at 66°[7], the propyl ester at 92°, *iso*butyl ester at 85°, *iso*amyl ester at 50°. Little authentic information is extant on the value of this class of plastifiants. They are colorless, stable and of low volatility, with practically no odor.

Polymethylene Derivatives. The polymethylene hydrocarbons cyclopropane (trimethylene), cyclobutane (tetramethylene), cyclopentane (pentamethylene) and cyclohexane (hexamethylene, hexahydrobenzene) form a series, which with their alcohols, ketones and esters comprise a

1. D. R. P. 351228; abst. Chem. Zentr. 1922, I, 1144.
2. P. Schickler and H. Hahl, U. S. P. 1000040. For glyceryl cinnamate, see D. R. P. 235357. Boils at 190-195° at 11 mm.
3. F. Bayer & Co., D. R. P. 235357.
4. J. Callsen, U. S. P. 999955.
5. D. R. P. 412884; abst. J. S. C. I. 1925, **44**, 707-B.
6. Zühl & Eisemann, D. R. P. 128119; abst. Chem. Zentr. 1902, I, 387.
7. R. Anschütz, Ann. 1889, **254**, 10.

series of more than ordinary usefulness as cellulose ether solvents and colloiding bodies.

Cyclobutane, Tetramethylenecyclobutane, is a colorless liquid, b. pt. 39-42°, which in conjunction with methyl alcohol or methyl acetate forms a low-boiling ethyl- or benzylcellulose direct solvent, as likewise does cyclopentane, b. pt. 49°, sp. gr. 0.7635 at 4°.

Cyclohexane, b. pt. 81°, sp. gr. 0.7934 at 4°, is a hydrocarbon somewhat similar to benzene, having a less pungent odor and a lower toxicity. It forms the following constant boiling point mixtures: with 55% benzene, b. pt. 77.8°; 10% *n*-butyl alcohol, 79.8°; 14% *iso*butyl alcohol, 78.1°; 30% ethyl alcohol, b. pt. 64.9°; 37% methyl alcohol 54.2°; 20% *n*-propyl alcohol, 74.3°; 33% *iso*propyl alcohol 68.6°.

The O. Schmidt glass substitute[1] comprises a wire fabric coated with synthetic resin dissolved in cyclohexane or in association with butadiene, and the motor fuel of T. Midgley[2] is said to consist of cyclohexane 4, benzene 1, with a freezing point of —40° F. Cyclohexane is an excellent synthetic resin solvent[3], and finds use in the production of molded articles[4]. W. Moss[5] has described bis-(hydroxyphenyl)naphthene(bis(hydroxyphenyl)cyclohexane) as a desirable plasticizer for cellulose derivatives, and the British Celanese, Ltd.[6] use of synthetic resins of diphenylolcycloparaffins (diphenylolpropane, diphenylolcyclohexane) especially applicable for admixture with cellulose acetate, and for the fabrication of reinforced glass[7]. 3-Methyl-5-phenyl-4.6-dicarboxethyl-d_2-keto-R-hexene has been described by C. Claessen[8].

1. D. R. P. 536119; abst. C. A. 1932, **26**, 1087.
2. U. S. P. 1491998; abst. Chem. Met. Eng. 1924, **30**, 876.
3. E. P. 203310. F. P. 537207, 568840. D. R. P. 348297.
4. C. Ellis, U. S. P. 1514509.
5. Can. P. 323146; abst. C. A. 1932, **26**, 4172.
6. E. P. 344413; abst. J. S. C. I. 1931, **50**, 598-B; Chem. Zentr. 1931, I, 3620.
7. British Celanese, Ltd., E. P. 342429; abst. J. S. C. I. 1931, **50**, 405-B; Brit. Plastics, 1931, **3**, #25, 37.
8. D. R. P. 172967; abst. Chem. Zentr. 1906, II, 736.

Chlorcyclohexane in the presence of acetone dissolves nitro-, acetyl-, ethyl- and benzyl-cellulose[1], being a colorless liquid plasticizer suitable for both films and solid cellulose bodies. Chlorinated naphthalene and chlorinated anthracene[2], together with mono- and tetra-chlornaphthalene[3] have been recommended as nitrocellulose solvents.

Cyclic Alcohols. Of interest in the cellulose ether and ester art are cyclohexanol and methylcyclohexanol, both distinctly toxic oily liquids with a camphoraceous or fusel-like odor.

Cyclohexanol, Hexahydrophenol, Hexalin, Adronol, has sp. gr. 0.935-0.945, b. pt. 160°, and comprises a mixture of two geometric isomers. This secondary alcohol dissolves both cellulose ethers and esters, better in conjunction with relatively smaller amounts of methyl alcohol or acetate or acetone. Its presence in lacquers increases the tolerance of the lacquer for non-solvent petroleum hydrocarbons, i.e. the lacquer may be attenuated to a greater degree with a non-solvent before incipient gelatinization occurs. The corresponding acetate boils but 10° higher than the alcohol.

The cellulose ether composition first described by S. Carroll[4] consists of cyclohexanol mixed with certain alkyl compounds as methyl or ethyl alcohols or acetates. For instance, a mixture of equal volumes of cyclohexanol and ethyl acetate will dissolve about 20% of its weight of water-insoluble ethylcellulose to form a thick, viscous, flowable solution suitable for film manufacture in the usual way. F. Raschig[5] substitutes cyclohexanol and cyclohexanone for camphor in celluloids; G. Bonwitt[6] combines as a solvent cyclohexanol with ethyl lactate, furfural; while P. Friesenhahn employs cyclohexanols and cyclohexanones directly as cellulose ester solvents[7]. The Badische Anilin & Soda

1. S. Carroll, U. S. P. 1826689. 2. C. Paul, U. S. P. 1342602.
3. S. Carroll, U. S. P. 1580189.
4. *Ibid.* U. S. P. 1467097; abst. J. S. C. I. 1923, **42**, 1065-A; Chem. Met. Eng. 1923, **29**, 679.
5. U. S. P. 900204. D. R. P. 174914.
6. D. R. P. 331285. See E. P. 138078. F. P. 519536.
7. D. R. P. 332909, 334761.

Fabrik[1] hydrogenate ketone oils containing alcohols mixed with cyclohexanol and cyclohexanol acetate as a solvent combination, especially usable in the preparation of pyroxylin lacquers[2]. Cyclohexanol admixed with cyclohexanol phenoxyacetate and cyclohexanol 2.4.6-trichlorphenoxyacetate[3] constitutes another advocated solvent combination.

The W. Lazier solvent mixture[4] comprises cyclohexanol, cyclohexanone and acetone; while W. Moss[5] dissolves acetylcellulose with methylene chloride and cyclohexanol or methylcyclohexanol, to which ethylene glycol, methylglycol, ethylglycol or diacetone alcohol may be added. A cellulose ether plasticizing mixture has been recommended[6] consisting of the compound obtained by the condensation of carbonyl compounds with cyclohexanol and glycerol, and consisting principally of 2.2-pentamethylene-4-oxymethyldihydrodioxol, a so-called dihydrodioxol. One advantage alleged to accrue from the use of this solvent is that it likewise is an excellent solvent for rubber. The C. Bogin nitrocellulose lacquer formula contains cyclohexanol as a component[7].

A solvent for cellulose formate, acetate, butyrate, oxalate, phthalate or salicylate[8] is claimed to result from the addition of ethyl, propyl, butyl or amyl alcohols to cyclohexanol. If borneol phthalate, salicylate or oxalate be added, then alcohol should be employed in addition. The coating composition of G. King and R. Threefall[9] comprises alkyl silicic esters (methyl, ethyl or propyl silicates) in a

1. D. R. P. 406924.
2. Badische Anilin & Soda Fabrik, E. P. 3869, 1912. F. P. 440733. D. R. P. 251351. Aust. P. 66526. Swiss P. 59164. Also E. P. 21368, 1912. F. P. 459006. D. R. P. 272391, 284672. Aust. P. 64393. Swiss P. 64710.
3. Meister, Lucius & Brüning, D. R. P. 374322; abst. J. S. C. I. 1923, **42**, 1126-A; Chem. Zentr. 1923, IV, 218; Kunst. 1923, **13**, 69.
4. U. S. P. 1829869; abst. C. A. 1932, **26**, 788.
5. U. S. P. 1844365. Can. P. 306829.
6. Deutsche Hydrierwerke A.-G., F. P. 714837; abst. Chem. Zentr. 1932, I, 2101.
7. U. S. P. 1651578; abst. J. S. C. I. 1928, **47**, 164-B.
8. J. Schindelmeiser, E. P. 283619; abst. J. S. C. I. 1928, **47**, 237-B; Chem. Zentr. 1928, I, 2028.
9. E. P. 290717; abst. C. A. 1929, **23**, 3062.

solvent as alcohol, to which is added cyclohexanol, and turpentine or bromnaphthalin added to retard the setting. P. Breteau and H. Leroux[1] employ cyclohexanone with hexahydrobenzyl ketone, tetrahydrobenzyl ketone and/or hydronaphthyl ketone in celluloid manipulation. The S. Carroll lacquer[2] adds 10-30 parts cyclohexanol to 100 parts acetylcellulose, being then thinned with low boiling solvents to the fluidity required.

In the manufacture of substantially solid bodies showing thermoplasticity, G. Balle and K. Sponsel[3] take that type of methylcellulose which is soluble in water above 16° as well as in a mixture of alcohol-chloroform or alcohol-benzol, and add thereto cyclohexanol, glycol, glycerol, benzyl alcohol or borneol, producing a homogeneous mass by malaxation aided by heat. Thus, 100 parts methylcellulose, 80 parts of camphor or camphor substitute, 150 alcohol and 70 benzene are treated in a kneading or mixing machine until an indistinguishable mass is obtained. Or, 60 parts waste cellulose are swollen with 150-200 parts alcohol, and after the addition of 20 parts benzyl alcohol, the mass is kneaded with 100 parts methylcellulose until perfect homogeneity results.

Cyclohexanol has also been used in the preparation of shoe creams and polishes[4], in artificial resin manufacture[5], and for producing plastic masses[6]. Cyclohexanol and methylcyclohexanol have been used in emulsion forms as "spinning solutions" with olive oil. A too high concentration exerts a solvent action on acetate and cellulose ether silk, thereby affecting its handle and luster.

1. F. P. 409557; abst. Revue des Produits Chimiques, **24**, #12, 367; Mon. Sci. 1910, **73**, 454.
2. U. S. P. 1841312.
3. D. R. P. 512912; abst. C. A. 1931, **25**, 1350; Chim. et Ind. 1931, **25**, 1218. See Imperial Chemical Industries, Ltd., F. P. 683290; abst. C. A. 1930, **24**, 4648. Chem. Age, 1931, **24**, 580. P. Schuster, Drug and Chemical Markets, 1925, **16**, #8, 566.
4. P. Friesenhahn, D. R. P. 331050; abst. J. S. C. I. 1921, **40**, 311-A.
5. E. P. 21367, 1912. D. R. P. 349905, 351688, 358400, 402996.
6. E. P. 193524. F. P. 533575, 533579. Can. P. 232641, 232642. Swiss P. 103432.

Methylcyclohexanol, Methylhexahydrophenol, Sextol, Methylhexalin, Methyladronol, Heptalin, exists as six isomers, usually together with small amounts of cyclohexanol in the commercial product. B. pt. 165-175°, sp. gr. 0.925-0.93. Soluble 3% in water. Its solvent action is similar to but less powerful than cyclohexanol.

Cyclic Ketones. Methylcyclohexanone in composition is quite similar to camphor, and methylcyclohexanol is analogous in constitution to Borneo camphor.

Cyclobutanone is a colorless liquid, b. pt. 99°, sp. gr. 0.93. Cyclobutanone and dimethyl- and diethyl-cyclobutanone have been described by H. Dreyfus as desirable dissolvants for acetylcellulose[1]. For preparing a varnish 1 part cellulose acetate may be dissolved in 10 parts cyclobutanone, or 50 parts cyclobutanone with 100 parts methyl acetate, acetone or alcohol, together with 12-15 parts triphenyl phosphate. The details of cellulose acetate artificial film manufacture using cyclobutanone have been published[2].

Cyclopentanone, Adipin-ketone, Keto-pentamethylene, is the ketone of adipic acid, as is cyclohexanone (pimelic ketone) the ketone of *n*-pimelic acid, and cycloheptanone (suberone) the ketone of suberic acid. It is a peppermint-like smelling liquid, b. pt. 130°. Dissolves many types of ethyl- and benzyl-cellulose, especially when assisted by a small amount of ethyl alcohol or ethyl acetate. The O. Schmidt, T. Eichler and O. Allemann nitrocellulose lacquer is said to owe its intrinsic merit to the presence of cyclopentanone and methylcyclohexanone[3]. T. Tyrer combines cyclopentanone and cyclohexanone[4], or cyclopentanone

1. H. Dreyfus, U. S. P. 1440006; abst. C. A. 1923, **17**, 1141; J. S. C. I. 1923, **42**, 600-A; Chem. Ztg. 1923, **47**, #37, 269. E. P. 184671; abst. J. S. C. I. 1922, **41**, 693-A; Phot. Abst. 1922, **2**, 137. Ital. P. 233801.

2. *Ibid.* U. S. P. 1566384; abst. C. A. 1926, **20**, 511; J. S. C. I. 1926, **45**, 122-B. E. P. 182166. Can. P. 281189.

3. U. S. P. 1166790. E. P. 21368, 23544, 1912. D. R. P. 263404, 272391. F. P. 459006. Aust. P. 64393. Swiss P. 64710. See D. R. P. 287933 and Addn. D. R. P. 289498.

4. U. S. P. 1339728. E. P. 130402. F. P. 510535.

admixed with cyclohexanone[1]. R. Phillips and H. Thurlow[2] combine cyclopentanone and cyclohexanone with cyclopentanone formate or acetate.

Cyclohexanone, Ketohexamethylene, Sextone, Anon, Hexanone, colorless oil, sp. gr. 0.93-0.96, b. pt. 155-160°, cyclohexanol being the chief impurity in the commercial product which assays about 80% ketone. It is an excellent solvent for the cellulose ethers and for nitrocellulose, producing solutions of about the same viscosity as ethyl lactate. It also dissolves kauri, dammar, elemi, sandarac, shellac, boiled oils, bitumen and waxes. It forms the following constant boiling point mixture: with 44% camphene, b. pt. 151°; 45% acetylenetetrachloride, b. pt. 159°; 61% trichlorhydrin, 160°. Of interest in the formulation of colored lacquers is the property of cyclohexanone and methylcyclohexanone of dissolving many basic dyes as fuchsine, diamond green, methyl violet, victoria blue, and auramine, in the usual concentration proportions.

The cellulose ether composition of S. Carroll[3] comprises cyclohexanone with methyl, ethyl, propyl or butyl alcohols, a preferred composition being water-insoluble ethylcellulose 5 parts with a mixed solvent of cyclohexanone and methyl acetate in equal proportions. The Badische

1. O. Schmidt, G. Lutz and T. Eichler, assignors to Badische Anilin- and Sodafabrik, U. S. P. 1045895; abst. C. A. 1913, **7**, 712; J. S. C. I. 1913, **32**, 19; Mon. Sci. 1913, **78**, 110. E. P. 3869, 1912; abst. C. A. 1913, **7**, 2683; J. S. C. I. 1912, **31**, 1176; Kunst. 1913, **3**, 94. E. P. 7292, 1912; abst. J. S. C. I. 1912, **31**, 1176. F. P. 440733, 1912; abst. J. S. C. I. 1912, **31**, 828; Kunst. 1912, **2**, 414; 1913, **3**, 17; Mon. Sci. 1914, **81**, 14. D. R. P. Anm. B-66376, 1912 (Addn. to D. R. P. 251351); abst. Kunst. 1912, **2**, 399. D. R. P. 251351; abst. J. S. C. I. 1912, **31**, 1191; Chem. Zentr. 1912, II, 1246; Chem. Ztg. Rep. 1912, **36**, 584; Wag. Jahr. 1912, **58**, II, 604; Bayer. Indust. u. Gewerbebl. 1913, **45**, 358. D. R. P. 255692 (Addn. to D. R. P. 251351); abst. C. A. 1913, **7**, 1815; Chem. Ztg. Rep. 1913, **37**, 68; Kunst. 1914, **4**, 37; Wag. Jahr. 1913, **59**, II, 585; Zts. ang. Chem. 1913, **26**, II, 80. Aust. P. 66526, 1914; abst. Chem. Ztg. 1914, **38**, 1042.

2. E. P. 254041.

3. U. S. P. 1467101; abst. J. S. C. I. 1923, **42**, 1065-A; Chem. Met. Eng. 1923, **29**, 679.

Anilin & Soda Fabrik[1] employ cyclohexanone, cyclopentanone, ligroin and benzene; H. Dreyfus admixes cyclohexanone, methylcyclohexanone with methyl or ethyl alcohols[2], or methyl- or dimethyl-cyclohexanone with diphenyl carbinol, aceto-, *o*- or *p*-methylaceto-, benzo-, methoxy-, or ethoxy-phenone[3]. Cyclonaphthone has also been specified[4]. As a direct cellulose acetate solvent[5] or pyroxylin dissolvant[6], either alone or combined with alcohol[7], acetone[8] admits of the preparation of clear lacquers with a variety of types of cellulose esters. B. Szelinski[9] associates cyclohexanone with carvone, pulegone, benzyldihydrocarvone with acetone, chloroform and alcohol. Cyclohexanone with ethyl acetate is a rapid solvent for cellulose acetate[10], as is cyclohexanone and benzene[11]. Cyclohexanone with cyclohexanol acetate[12], or with diacetone alcohol[13], or combined with lower aliphatic alcohols and acetates[14] are indicative of the trend of solvent manipulation for the attainment of special effects in cellulose ester solutions.

Artificial masses have been detailed by the I. G. Far-

1. U. S. P. 1166790. E. P. 21368, 23544, 1912; 14042, 1914. F. P. 459006. D. R. P. 263404, 284672. Swiss P. 64710. Aust. P. 64393.
2. H. Dreyfus, U. S. P. 1395401.
3. *Ibid.* E. P. 128215. F. P. 432264.
4. *Ibid.* U. S. P. 1395401.
5. Cellon, Ltd., T. Tyrer & Co., P. Chambers and G. Feasey, E. P. 130402. U. S. P. 1339728.
6. I. G. Farbenindustrie, A.-G., E. P. 263175.
7. Badische Anilin & Soda Fabrik, E. P. 145511.
8. Cellon, Ltd., T. Tyrer & Co. and T. Tucker, F. P. 510535.
9. D. R. P. 202720.
10. Badische Anilin & Soda Fabrik, E. P. 145511; abst. C. A. 1920, **14**, 19, 3154; J. S. C. I. 1921, **40**, 105-A, 144-A; Paper, 1921, **28**, #3, 34; Faser. 1920, **2**, 185; Chem. Met. Eng. 1920, **22**, 989; Textilber. 1921, **2**, 408. D. R. P. 251351; abst. Farben-Ztg. 1912, **17**, 2815.
11. *Ibid.* D. R. P. 284672; abst. C. A. 1916, **10**, 117; J. S. C. I. 1915, **34**, 1048; Chem. Zentr. 1915, II, 111; Chem. Ztg. 1915, **39**, 322; Chem. Ztg. Rep. 1915, **39**, 256; Wag. Jahr. 1915, **61**, II, 367; Zts. ang. Chem. 1915, **28**, II, 351.
12. *Ibid.* F. P. 459006; abst. Chem. Ztg. 1913, **37**, 1186. D. R. P. 406924; abst. J. S. C. I. 1925, **44**, 217-B; Chemicals, 1925, **24**, #17, 47.
13. P. Head, E. P. 299900.
14. A. Knorr, U. S. P. 1780883; abst. C. A. 1931, **25**, 223; J. S. C. I. 1930, **49**, 1164-B.

benindustrie[1], or which the following example is illustrative: 5 parts benzylcellulose is dissolved with the addition of 1.75 parts of an ethylene oxide polymerization product of m. pt. 52°, in benzene and toluene 40 parts each, butyl acetate 9 parts and 6.25 parts ethyl alcohol, a lacquer being formed particularly suitable for application to wood or metal. Diphenylolcyclohexane-formaldehyde resin with cellulose nitrate or acetate, diphenylolpropane or diphenylolcyclohexanone and volatile solvents[2], is advocated as a lacquer formula of wide applicability.

Cyclohexanone with infusible amine aldehyde condensation products[3], and as siccative and binding agents for lacquers[4] has received patent protection, as has the formula for a nitrocellulose brush lacquer combining cyclohexanone or other cyclic ketone with ethyleneglycol monobutyl ether or propyleneglycol monopropyl ether[5]. Ethyl alcohol is the usual diluent in these preparations.

The mechanism of solution of organic substances, as cellulose nitrate, in cyclohexanone, *p*-methylcyclohexanone, fenchone and *m*-xylene has been studied, and the formation of compounds by the solution of cellulose nitrate with these solvents demonstrated[6]. In an investigation of orientation phenomena among the cyclohexanones[7], a number of new compounds has been described of possible future value as solvents, and including 2.2.5-trimethylcyclohexanone, 2.6-dimethylcyclohexanone and its tetrahydropyrone, 2-methyl-6-benzylcyclohexanones, pulegone (2.2.5-trimethylcyclo-

1. E. P. 352042; abst. J. S. C. I. 1931, **50**, 853-B.
2. British Celanese, Ltd., E. P. 344413; abst. C. A. 1931, **25**, 4725.
3. Soc. of Chem. Industry, E. P. 343031. See E. P. 266358, 274501, 284589, 342325, 342326, 342723, 342730, 342767.
4. P. Friesenhahn, D. R. P. 327180; abst. J. S. C. I. 1921, **40**, 459-A; Kunst. 1920, **10**, 197. D. R. P. 334761; abst. J. S. C. I. 1921, **40**, 399-A.
5. H. Finkelstein, U. S. P. 1801340; abst. J. S. C. I. 1932, **51**, 436-B.
6. T. Tomonari, C. Trogus and K. Hess, Z. physik. Chem. 1932, **B17**, 241; abst. C. A. 1932, **26**, 4229.
7. R. Cornubert, R. Humeau, A. Maurel and H. Le Bihan, Bull. Soc. chim. 1931, **49**, 1229, 1238, 1248, 1260; abst. J. S. C. I. 1931, **50**, 1417-A.

hexanone), 3-methyl-2.6-diallylcyclohexanone, 2-methyl-5-propylcyclohexanone and benzylcyclohexanone.

As a solvent for celluloid[1], cellulose acetate[2], cellulose ether[3] and cellulose nitrate gelatinant[4], cyclohexanone has established a permanent position.

Methylcyclohexanone, Sextone B, Methylanon, a colorless oil of peppermint-like odor, sp. gr. 0.925-0.93, b. pt. 165-170°. A powerful nitrocellulose solvent, and an excellent dissolving media for a wide range of cellulose ether types. Methylcyclohexanone is the basic solvent in lacquer processes disclosed by Badische Anilin & Soda Fabrik[5], I. G. Farbenindustrie[6], W. Jenkins[7], and Imperial Chemical Industries, Ltd.[8], the latter associating this solvent with hexalin acetate and butyl propionate. A combination of cyclohexanone, dimethylcyclohexanone, acetylacetone, ethylidene acetone and methyl *o*-phthalate forms the basis of the H. Dreyfus acetylcellulose composition[9].

As a cellulose acetate solvent[10] and liquid fuel ingredient[11] are fields of usefulness in which permanency appears to be established for this solvent.

Cyclopentanol and Cyclohexanol Esters. This series of solvents was first brought to the attention of workers

1. H. Dreyfus, U. S. P. 1363763; abst. C. A. 1921, **15**, 752; J. S. C. I. 1921, **40**, 114-A. U. S. P. 1440006; abst. C. A. 1923, **17**, 1141.
2. U. S. P. 1339728, 1363763, 1395401, 1440006.
3. S. Carroll, U. S. P. 1467101; abst. J. S. C. I. 1923, **42**, 1065-A; Chem. Met. Eng. 1923, **29**, 679.
4. W. Forse, F. Jones and G. Walters, U. S. P. 1468609.
5. D. R. P. 284672; abst. Chem. Zentr. 1915, II, 111. D. R. P. 334871; abst. Chem. Zentr. 1921, II, 1068. E. P. 14042, 1914; abst. C. A. 1915, **9**, 3359; J. S. C. I. 1915, **34**, 956.
6. E. P. 263175; abst. C. A. 1928, **22**, 174.
7. E. P. 310062; abst. C. A. 1930, **24**, 739; J. S. C. I. 1929, **48**, 483-B; British Plastics, 1929, **1**, #2, 72. E. P. 336615; abst. J. S. C. I. 1931, **50**, 72-B.
8. F. P. 683728; abst. C. A. 1930, **24**, 5157.
9. U. S. P. 1363763; abst. C. A. 1921, **15**, 752; J. S. C. I. 1921, **40**, 114-A; Mon. Sci. 1922, (5), **12**, 5; Paper, 1921, **27**, #21, 27. E. P. 131669; abst. C. A. 1920, **14**, 346; J. S. C. I. 1919, **38**, 834-A. See F. P. Addn. 19680 to F. P. 432264.
10. H. Dreyfus, U. S. P. 1395401; abst. J. S. C. I. 1921, **40**, 886-A.
11. T. Midgley, U. S. P. 1491998.

in the cellulose field in 1912 with the patenting of the formates and acetates as high-boiling nitrocellulose solvents, either alone or in conjunction with other volatile solvents or plastifiants. As a class, these esters are relatively high-boiling liquids of good stability, non-toxic and dissolve both the nitrocelluloses and the cellulose ethers.

Formic Esters. Cyclopentanol (cyclopentyl) formate and acetate, cyclohexanol (cyclohexanyl) formate and acetate, *o*-methylcyclohexanol formate and acetate and *b*-methylcyclopentanol acetate have been advocated in conjunction with nitrocellulose[1], or in admixture with camphor, alcohol or castor oil for thermoplastic products. In another method[2] cyclohexanol formate and acetate are used in the proportion of 100-300% with nitrocellulose (12% N), which is then thinned with benzene, and a plasticizer as butyl tartrate added.

Acetic Esters. As cellulose acetate solvents[3], esters obtained by hydrogenation of ketone oils containing alcohol

1. O. Schmidt, G. Lutz, T. Eichler and Badische Anilin & Soda Fabrik, U. S. P. 1045895. E. P. 3869, 1912. D. R. P. 251351 and 255692 being Addns. thereto. Swiss P. 59164, 61611. Holl. P. 103, 1914. D. R. P. 280377 describes lacquers containing resins with cyclohexanol acetate. *o*-Methylcyclohexanol formate is prepared by heating *o*-methylcyclohexanol with formic acid in the presence of calcium chloride. See M. Godchot and F. Taboury, Ann. Chim. Phys. 1912, (8), **26**, 46. *b*-Methylcyclopentanol is a colorless liquid of rather pleasant odor, boiling at 56-58° at 14 mm. The coating composition of G. Padgham (E. P. 347597; abst. C. A. 1932, **26**, 1810) comprises butylcellulose with cyclohexanol acetate, butyl acetate and amyl stearate. E. Clayton (Text. Mfr. 1931, **57**, 455) has described the technical applications of cyclohexanol phthalate, dimethyl-, diethyl-, dibutyl- and di*iso*butyl-phthalate and benzyl benzoate in the manufacture of paper coatings and artificial leather, and cyclohexanol oxalate, methylcyclohexanol oxalate, cyclohexanol and methylcyclohexanol adipate and methyladipate alone, and with ethyl, *iso*propyl adipate and methyladipate, ethyl, propyl and butyl maleate and tartrate in the arts. In Text. Mfr. 1931, **57**, 455, E. Clayton and C. Clark have detailed the physical constants and uses for cyclohexanol and methylcyclohexanol acetates in the dyestuff industry. E. I. du Pont de Nemours & Co. (E. P. 349100; abst. C. A. 1932, **26**, 2072) spraying lacquers in which the binding agent is a vinyl ester polymer with dibutyl-, diethyl-, dicyclohexyl-, cyclohexylbutyl and cyclohexylamyl phthalate.

2. Gross, Sherwood & Heald, Ltd., R. Phillips and H. Thurlow, E. P. 254041; abst. J. S. C. I. 1926, **45**, 760-B.

3. Badische Anilin & Soda Fabrik, D. R. P. 406924. See their D. R. P. 255692.

are mixed with cyclohexanol or cyclohexanol acetate, and lacquers have been described comprising cellulose esters or ethers dissolved in cyclohexyl acetate[1]. The inflammability of the lacquer may be reduced by the addition thereto of ethylene dichloride or tetrachlorethane[2]. Aqueous suspensions of dyestuffs may be mixed with cellulose ethers or esters compatible with water (as methylcellulose)[3], a typical solvent mixture being acetone, butyl alcohol, cyclohexanol, cyclohexyl acetate and butyl acetate.

Cyclohexanyl acetate (Hexalin Acetate, Adronol Acetate, H. A. Solvent) in commercial condition varies considerably in ester content and hence in solvent power. Sp. gr. 0.947-0.98, flash pt. 65-70°, b. pt. 170-180° and contains 80-85% absolute ester. It has a pungent odor somewhat resembling amyl acetate. The technical solvent is a liquid, but in the highly purified condition is a solid. In addition to dissolving cellulose nitrate, acetate and the cellulose ethers, it is a solvent for colophony, dammar, elemi, sandarac, mastic, copal, ester gum, driers and metallic resinates.

Methylcyclohexanyl acetate comprises a mixture of esters resulting from the acetylation of commercial methylcyclohexanol, and in purity depends upon the composition of the latter. The ester content ranges 85-90%. Sextate and Methylhexalin Acetate are trade names. It is neutral. Having a higher boiling point it is more slowly evaporative than cyclohexanyl acetate. Its solvent action for the cellulose ethers is increased by heating, and by the presence of a small amount of benzene, toluene or xylene. It is usually a mixture of the acetated three isomeric hexahydrocresols[4].

Cyclohexyl phenoxyacetate and 2.4.6-trichlorphenoxyacetate have been patented as suitable nitrocellulose sol-

1. I. G. Farbenindustrie, F. P. 671158; abst. C. A. 1930, **24**, 1996.
2. *Ibid.* F. P. 653025; abst. C. A. 1929, **23**, 3821.
3. *Ibid.* Swiss P. 115116; abst. J. S. C. I. 1927, **46**, 305-B.
4. A. Noll, Papierfabr. 1927, **25**, 65.

vents[1], being colorless and odorless and forming films of high transparency. It is used in the proportion of 1 part to 3 parts nitrocellulose. Methyl or ethyl 2.4.6-trichlorphenoxyacetates are soluble in alcohol and gelatinize both nitrocellulose and the cellulose ethers, but their volatility is too great unless hampered by the use of added high-boilers. Films of nitrocellulose with cyclohexyl phenoxyacetate are characterized by great softness and pliability.

Glycollic and Lactic Esters. The Deutsche Hydrierwerke[2] have described methylcyclohexyl lactate (b. pt. 120-130° at 12 mm.), cyclohexyl glycollate (b. pt. 134-135° at 26 mm.) and benzyl lactate as cellulose ester and cellulose ether solvents, while M. Schmidt and J. Voss[3] recommend the addition to cellulose ethers of cyclohexanyl diglycollate or thiodiglycollate or the corresponding diamyl esters.

Oxalic Esters. Dimethylcyclohexanyl oxalate, Barkite, is a colorless, practically odorless liquid of about 85% ester content, sp. gr. 1.034, neutral, anhydrous, water-insoluble, of high stability and pigment wetting power. It dissolves cellulose ethers and nitrocellulose and is miscible without turbidity with the usual lacquer solvents. Dicyclohexyl oxalate, a white crystalline solid, m. pt. 47°, b. pt. 171-172° at 11 mm., of faint odor, forms a solid solution with cellulose nitrate. Dicyclohexyl succinate[4] is likewise a good solvent, b. pt. 212° at 21 mm., forming a softener with cellulose ethers with alcohol-benzene.

Adipic Esters. Cyclohexanol adipate has been recommended as a cellulose ether and cellulose acetate plasticizer by the Tetralin Ges.[5], having m. pt. 35-36°, b. pt. 208-212° at 12 mm. *o*-Methylcyclohexyl adipate boils at 225-260° at 11 mm. and likewise dissolves ethylcellulose and benzylcellulose. They are said to be especially useful in film manu-

1. A. Steindorff and G. Balle, D. R. P. 374322. See D. R. P. 119636.
2. D. R. P. 540902; abst. C. A. 1932, **26**, 2316.
3. D. R. P. 434640; abst. Chem. Zentr. 1927, I, 380.
4. O. Schmidt, T. Eichler, K. Seydel, U. S. P. 1600700; abst. J. S. C. I. 1926, **45**, 1010-B.
5. D. R. P. 406013; abst. J. S. C. I. 1925, **44**, 212-B.

facture, and come into the trade under the name of "Sipalin"[1]. Sipalin A. O. M. is dimethylcyclohexanyl adipate, Sipalin M. O. M. di(methylcyclohexanyl) *b*-methyladipate, and Sipalin A. O. C., dicyclohexanyl adipate. H. Wolff and B. Rosen[2] report that when used with nitrocellulose, Sipalin M. O. M. and Sipalin A. O. M. progressively decrease in viscosity and increase in dilution ratio with toluene resulting in increase with plasticizer content. Cyclohexanyl adipate, succinate and glutarate have been described[3] and their solvent properties detailed.

Phthalic Esters. A group of phthalic acid ester plastizants has been described in which one carboxyl group is esterized with the radical of an aromatic or hydroaromatic alcohol while the other carboxyl is esterized with the radical of an aliphatic or aromatic alcohol, and including benzylcyclohexyl, *iso*amylcyclohexyl, benzyl-*n*-propyl and benzyl-*iso*amyl phthalates. They are also useful as cellulose ether and nitrocellulose plastifiants[4]. They are said to impart unusual flexibility[5]. Mixed cyclohexyl esters of phthalic acid as cyclohexylbutyl phthalate[6] are used as a solvent and modifier for cellulose nitrate. R. Adams and J. Hyde[7] have described the following cyclohexylalkyl phthalates as cellulose ester solvents: 4-methylcyclohexylethyl phthalate, b. pt. 160° at 3 mm.; 4-methylcyclohexylbutyl, b. pt. 183°, 2 mm.; 3-methylcyclohexylethyl, b. pt. 168° at 3.5 mm.; 3-methylcyclohexyl-*n*-butyl, b. pt. 178° at 2 mm.; 2-methylcyclohexylethyl, b. pt. 168° at 3.5 mm.; and 2-methylcyclohexyl-*n*-butyl phthalates, b. pt. 185° at 3 mm.

Acetoacetic and Levulinic Esters. As a cellulose ether

1. W. Schrauth, Farben Ztg. 1929, **34**, 2018; abst. C. A. 1930, **24**, 1234.
2. Farben Ztg. 1929, **34**, 2564; abst. Brit. Plastics, 1929, **1**, 192.
3. Deutsche Hydrierwerke, D. R. P. 524256, Addn. to D. R. P. 406013; abst. C. A. 1931, **25**, 3832.
4. E. Schwabe and I. G. Farbenindustrie, D. R. P. 531642. E. P. 302961.
5. F. Biehler, D. R. P. 367106; abst. Kunst. 1923, **13**, 34.
6. E. Reid and G. Schwartz, U. S. P. 1778567.
7. U. S. P. 1689762; abst. J. S. C. I. 1929, **48**, 511-B.

softener and direct solvent[1], methylcyclohexyl acetoacetate (*b*-ketobutyrate) and methylcyclohexyl levulinate (b. pt. 160-165° at 20 mm.) have been proposed, either alone or in conjunction with ethyl or benzyl acetoacetate or levulinate. Dicyclohexyl acetoacetate and levulinate are also claimed as efficient cellulose ether solvents.

Ethyl Cyclopentanone Carboxylate as a suitable plasticizer for cellulose ethers has been described[2], being used preferably in association which dissolves both the cellulose ether and the plasticizer. Acetone-soluble cellulose acetate is also dissolved.

Vinyl Compounds are derived from the unsaturated alkylenes, C_nH_{2n}, in the same manner as the normal alcohols are obtained from their hydrocarbons. In addition to the general character of alcohols, they possess the property of the olefines to form addition compounds.

Vinyl Alcohol, Vinol, and polymerized vinyl alcohols with urea-formaldehyde condensates have been used with methylcellulose[3] for the production of lacquers and other coatings for absorptive material. J. Davidson[4] has described a lacquer composition comprising cellulose acetate or nitrate, a polymerized olefine derivative and a solvent, suitable polymerized olefines being vinyl acetate or chloride, styrol, divinyl ether and polymerized allylene compounds. J. Walsh, A. Caprio and the Celluloid Corporation combine polymerized[5] or unpolymerized vinyl compounds with cel-

1. Deutsche Hydrierwerke, D. R. P. 535168; abst. Chem. Zentr. 1931, II, 3553.
2. U. S. P. 1880464.
3. I. G. Farbenind. A.-G., E. P. 334567; abst. J. S. C. I. 1930, **49**, 1079-B.
4. Carbide & Carbon Chemicals Corp. and J. Davidson, E. P. 285049; abst. J. S. C. I. 1929, **48**, 219-B. F. P. 640364; abst. C. A. 1929, **23**, 999.
5. E. P. 308658; abst. C. A. 1930, **24**, 499; J. S. C. I. 1930, **49**, 1146-B; Chem. Zentr. 1929, II, 814. Can. P. 300776. The following compounds are used in the admixing of vinyl esters: vinyl halides, carbon tetrachloride, benzoyl peroxide, propionic acid, phthalic acid, calcium lactate, ethyl alcohol, methyl alcohol, butyl alcohol, benzyl alcohol, diacetone alcohol, ethyl acetate, amyl acetate, butyl acetate, ethyl lactate, methyl oxybutyrate, methyl ether of ethylene glycol, benzene, toluene, acetone, methylene dichloride, chloroform, tetra-

tion suitable for film formation. Another recommended composition[1] is a polymer of vinyl chloride or vinyl acetate with di- and tri-benzylin and suitable solvents. H. Scheidemandel[2] disperses a mixture of a polymerized vinyl acetate with a cellulose ether or ester, applies as a lacquer to the surface to be coated, the coating being then heated to produce a coherent film. Another lacquer composition involves bringing a vinyl ester in contact with an aldehyde together with a volatile solvent[3].

Vinyl esters may be produced by the methods of F. Skirrow and G. Morrison[4], H. Plauson[5], and Societe Chimique des Usines du Rhone[6]. The latter treat vinyl esters with a halogen at low temperatures, thereby producing dichlorethyl acetate, dichlorethyl monochloracetate and dibromethyl butyrate. The Chemische Fabrik Griesheim Elektron[7] have described processes for preparing acetalglycerol (acetol-glyceral, acetaldehyde glycerol), vinyl acetate, ethylidene diacetate and dipropionate, and vinyl trichloracetate.

Furan or Furfurane Group. Furfurane, Tetraphenol, Tetrol, Tetrane, Furane, C_4H_4O, a colorless liquid with a peculiar odor somewhat resembling chloroform, insoluble in water and boiling at 32°, and *a*-methylfurane (sylvane) contained in the volatile portion of the tarry oil from *Pinus sylvestris* in which dimethylfurane and higher methylated products are also present, are moderate solvents of the cellulose ethers, more so in the presence of relatively small

1. E. I. du Pont de Nemours & Co., E. P. 349562; abst. C. A. 1932, **26**, 2071.
2. D. R. P. 527445; abst. C. A. 1931, **25**, 4725.
3. Canadian Electro Products Co., Ltd., Can. P. 288642.
4. U. S. P. 1855366, 1855367. Can. P. 288641, 318838, 318839. Patent cites U. S. P. 1638713. A. van Peski, Rec. Trav. Chim. 1921, **40**, 103; abst. Chem. Zentr. 1921, III, 609.
5. U. S. P. 1436288; abst. C. A. 1923, **17**, 564; J. S. C. I. 1923, **42**, 30-A. E. P. 156121; abst. J. S. C. I. 1922, **41**, 483-A.
6. E. P. 325115; abst. C. A. 1930, **24**, 3800. D. R. P. 531336; abst. C. A. 1931, **25**, 5433.
7. E. P. 14246, 1913. See also A. Geuther, Annalen, 1858, **106**, 249. R. Wegscheider and E. Spaeth, Monats. 1909, **30**, 825; abst. Chem. Zentr. 1910, I, 1421. J. Nef, Chem. Zentr. 1904, II, 1282.

lulose ethers[1], having made the interesting observation that vinyl esters are in general, not solvents for cellulose acetate, but gel ethyl- and benzyl-cellulose, and in the presence of an ancillary solvent as ethyl alcohol, dissolve them readily. Vinyl chloride, bromide, acetate, propionate, phthalate or phosphate, or styrene (vinyl benzene) are said to be especially applicable. Plastics are prepared[2] by incorporating likewise cellulose esters as acetylcellulose with the above unpolymerized or partially polymerized vinyl esters and halogen compounds. The British Celanese, Ltd.[3], have increased the compatibility of polymerized vinyl compounds with cellulose esters or methyl-, ethyl- or benzyl-cellulose by incorporating in the compositions synthetic resins harmonious with the cellulose derivatives, such as phenol-furfural resins, acetone-furfuryl resins and aniline-furfuryl resins.

Vinyl Esters. In addition to the esters above named, polyvinyl chloride or acetate[4] or polymerized ethyl acrylate; vinyl chloracetate in ethyl acetate, tetrachlorethane, ethylene dichloride or trichlorethane[5]; or polyvinyl acetate with butyl acetate or vinyl butyrate[6]. For example, 8 parts ethylcellulose are dissolved in a mixture of 25 parts polyvinyl acetate and 100 parts butyl acetate to form a transparent solu-

chlorethane, triphenyl phosphate, tricresyl phosphate, diethyl phthalate, dibutyl tartrate, triacetin, monomethyl-toluene-sulfonamide, thiocarbanilide and urea. Cites E. P. 308657.

1. E. P. 308657; abst. C. A. 1930, **24**, 499; J. S. C. I. 1930, **49**, 943-B; Brit. Plastics, 1930, **2**, #18, 278; Chem. Zentr. 1929, II, 814; Kunst. 1931, **21**, 16. Can. P. 300775. U. S. P. 1873689. Cites E. P. 308658.

2. Celluloid Corp., E. P. 335582; abst. J.S.C.I. 1930, **49**, 1146-B; Brit. Plastics, 1931, **2**, #20, 376; Chem. Zentr. 1932, I, 1316. See also E. P. 308657, 308658.

3. E. P. 345521; abst. C. A. 1932, **26**, 324; J. S. C. I. 1931, **50**, 597-B; Brit. Plastics, 1931, **3**, #28, 63. Compare E. P. 308658, 311657.

4. Roehm & Haas A.-G., E. P. 373947; abst. J. S. C. I. 1932, **51**, 722-B.

5. F. Klatte and A. Rollett, U. S. P. 1241738. E. P. 15271, 1914. F. P. 474086.

6. Consortium für Elektrochemische Industrie G. m. b. H., F. P. 718689. See also F. P. 712590; abst. C. A. 1932, **26**, 2072. W. Haehnel and W. Herrmann, D. R. P. 514435; abst. C. A. 1931, **25**, 1692. Can. P. 298857.

amounts of the lower boiling aliphatic alcohols and acetates, especially methyl acetate.

Furfuraldehyde, Furole, Furfurol, Pyromucic Aldehyde, Furfural, Furfuryl Aldehyde, has been known for many years as occurring in the destructive distillation of sugar. In properties it resembles formaldehyde on one hand, and benzaldehyde on the other, and undergoes many of the same type of chemical reactions that characterize these two aldehydes. It has been in commercial production in the United States since 1922, and is obtainable in two grades of the following specifications:

	Technical	Refined
Boiling point	158–162°	158–162°
Sp. gr. at 20°	1.158–1.16	1.159-1.161
Flash point	55–57°	55–57°
Acidity (as acetic)	0.2% (max.)	0.1% (max.)
Weight per U. S. gallon	9.7 lbs.	9.7 lbs.

Technical furfural, as obtainable on the American market, leaves but 0.03-0.06% residue upon evaporation at 100°. Dehydrated furfural may be decolorized by vacuum distillation, but on exposure to light and air slow resinification appears to take place, and the color changes to a dark amber, this being the most important drawback to its use in the lacquer industry. The addition of 0.06-0.25% of hydroquinone or paraldehyde to freshly vacuum-distilled furfural delays but does not prevent darkening of color.

The physical constants, solubility and dilution ratios of some of these compounds are shown in Tables XXVII, XXVIII and XXIX.

Furfural dissolves readily nearly all types of the cellulose ethers, especially the ethylcelluloses and benzylcelluloses of higher etherification. It is a solvent likewise for pyroxylin and the acetated celluloses, its solvency being augmented by the addition of aliphatic alcohols and esters. As a dissolving body for cellulose acetates[1], one preferred formula prescribes cellulose acetate 1, methyl acetate or

1. P. Goissedet and H. Guinot, F. P. 512850; abst. Chim. et Ind. 1921, **6**, 647; Mon. Sci. 1922, (5), **12**, 38.

Table XXVII. Physical Properties of Furan Compounds

	Boiling Point °C.	Refract. Index n_D	Sp. Gr. 20.4
Furfural	158-162	1.5260	1.1598
Furfuryl Alcohol	165-172	1.4864	1.1351
Tetrahydrofurfuryl Alcohol	172-180	1.4518	1.0514
Methyl furoate	177-184	1.4869	1.1786
Ethyl furoate	188-210	1.4782	1.1774
Propyl furoate	200-215	1.4750	1.0745
Butyl furoate	225-240	1.4740	1.0555
Isoamyl furoate	225-240	1.4720	1.0333
Amylene glycol 1.2	210	1.4413	0.9802
Amylene glycol 1.5	237	1.4499	0.9938
Furane	31	1.4216	0.937
n-Butyl furfuryl ether	190		0.955

Table XXVIII. Solubility of Gums and Resins in Furan Compounds

Product	Congo	Guaiac	Dammar	Coumarone	Ester Gum	Sandarac	Mastic	Kauri	Pontianac	Shellac
Furfural	sw	ss	ss	s	s	ss	ss	ss	sw	ss
Furfuryl alcohol	sw	ss	sw	s	s	s	s	s	s	s
Tetrahydrofurfuryl alcohol	ss	s	sw	s	s	s	s	s	s	s
Methyl furoate	sw	ss	ss	s	s	sw	sw	sw	sw	ss
Ethyl furoate	sw	s	sw	s	s	sw	sw	sw	sw	ss
Propyl furoate	sw	ss	sw	s	s	sw	sw	sw	sw	ss
Butyl furoate	sw	ss	sw	s	s	sw	sw	ss	s	ss
Amyl furoate	sw	ss	sw	s	s	sw	sw	ss	ss	ss

Key: s—soluble; ss—slightly soluble; sw—swells.

Table XXIX. Dilution Ratio of Furan Compounds

Product	Toluene	Gasolene	Water	Butyl Alcohol
Furfural	2.9	0.15•	0.07	2.10
Furfuryl alcohol	2.65	0.05•	0.08	5.0
Tetrahydrofurfuryl alcohol	7.8	0.55•	0.23	>12.5
Methyl furoate	3.1	0.40	..	2.6
Ethyl furoate	3.45	0.65	..	6.15
Propyl furoate	3.9	1.05	...	>12.5
Butyl furoate	3.8	1.35	....	>12.5
Isoamyl furoate	3.2	1.60	.	>12.5

•—forms two layers.

acetone 10, furfural 1. F. Steimmig[1] reports that the solvent action of furfural on acetone-soluble acetylcellulose is not reduced by admixture therewith of ethyl acetate, methyl alcohol, ethyl chloride (which boils too low), benzene or toluene.

The G. Bonwitt formula[2] comprises cellulose acetate 10, furfural 1, alcohol 20, while G. Meunier[3] employs furfural alone or in admixture with alcohol and acetone. The Societe Palewski & Morin[4] combine the solvent powers of furfural with creosote, their prescribed formula being acetylcellulose 75, furfural 25, creosote 25, alcohol 250 and acetone 500.

As a cellulose ether solvent, S. Carroll[5] has described the advantages of furfural in conjunction with methyl or ethyl alcohols, an illustrative formula being water-insoluble ethylcellulose 1, to 5 parts of a mixture of furfural-alcohol 90-50: 10-50 parts. Instead of adding to the furfural a lower monohydroxy aliphatic alcohol, an aromatic alcohol of the type of benzyl alcohol may be employed[6], in which case the inclusion of small amounts of methyl alcohol is alleged to be advantageous. F. Laugel[7] has described cellulose ester varnishes combining furfural and turpentine, and H. Gardner[8] the uses of furfural in cellulose ester enamels and lacquers.

1. D. R. P. 307075; abst. J. S. C. I. 1920, **39**, 153-A; Chem. Zentr. 1919, IV, 913.
2. E. P. 138078; abst. C. A. 1920, **14**, 1762; J. S. C. I. 1920, **39**, 504-A; Chem. Ztg. 1920, **44**, 617; Paper, 1921, **27**, #27, 33. F. P. 519536; abst. Caout. et Gutta. 1921, **18**, 1148. D. R. P. 331285.
3. F. P. 472423; abst. J. S. C. I. 1915, **34**, 500. The use of furfurol has been patented by G. Bonwitt, E. P. 138078; abst. Chem. Met. Eng. 1920, **23**, 35. See also F. P. Addn. 23822 to F. P. 472423; abst. Chim. et Ind. 1922, **8**, 643. Chem. Fabrik. von Heyden A.-G., D. R. P. 302460; abst. J. S. C. I. 1920, **39**, 430-A.
4. F. P. 491490; abst. Chim. et Ind. 1920, **3**, 811; Chem. Ztg. 1919, **43**, 733.
5. U. S. P. 1450716; abst. C. A. 1923, **17**, 1887; J. S. C. I. 1923, **42**, 494-A; Caout. et Gutta. 1924, **21**, 12092; Chem. Zentr. 1923, IV, 164.
6. S. Carroll, U. S. P. 1450714; abst. J. S. C. I. 1923, **42**, 494-A.
7. F. P. 495339; abst. Chim. et Ind. 1920, **4**, 229.
8. Paint Mfrs. Assoc. of U. S., Circ. #209, 1924, 67; abst. C. A. 1924, **18**, 3280.

A. Ward and G. Bray[1] coat surfaces with a phenol as resorcinol in furfural in conjunction with acetated cellulose, and J. Trickey[2] has given tables showing the solubility factors for gums, resins and other products in these compounds. H. Gault[3], C. Ellis[4], B. Brown and C. Bogin[5] and Chemische Fabriken von Heyden[6] have all given details for lacquer manufacture employing furfural as a cellulose ester dissolvant. Furfural bisulfite compounds are said to be used in the shrinking of felts. The admixture of furfural with acetaldehyde and/or paraldehyde offer solvent possibilities that seem about to be recognized.

Furfuryl Alcohol, a colorless, nearly inodorous syrup obtained by the partial hydrogenation of furfural, gives viscous solutions with the cellulose ethers and cellulose esters, being likewise a solvent for pontianac, dammar, elemi, sandarac, ester gum, coumarone and shellac. It is miscible with the usual organic solvents without turbidity[7]. Readily resinifies with dilute mineral acids to form insoluble infusible resins. C. Fawkes[8] has described the preparation of lacquer coatings of cellulose ethers containing furfuryl alcohol (furyl alcohol). British Celanese, Ltd.[9], have described a series of condensation products formed by the reaction of furfural on toluene and xylene sulfonamides, claimed to be compatible with cellulose ether and with cellulose acetate form clear, flexible films upon drying. M. Deschiens[10] has given formulas for acceptable airplane wing dopes in which furfural is incorporated with cellulose esters.

Tetrahydrofurfuryl Alcohol, being a saturated body does not discolor with age as do the unsaturated furfurals, and dissolves both the cellulose esters and ethers, the latter best in conjunction with methyl or ethyl alcohols or ace-

1. E. P. 320649; abst. C. A. 1930, **24**, 2562.
2. J. Ind. Eng. Chem. 1927, **19**, #5, 643.
3. U. S. P. 1394890.
4. U. S. P. 1529056.
5. Can. P. 260927.
6. D. R. P. 302460.
7. P. Goissedet and H. Guinot, F. P. 512850.
8. U. S. P. 1732124.
9. E. P. 307289, 307290, 307291, 313133, 338002, 338024, 340101, 340102, 342458. F. P. 683075. W. Moss and B. White, Can. P. 303697.
10. Chem. Trade J. 1920, **67**, 603.

tates. This alcohol has been granted patent protection as a cellulose nitrate dissolving body[1], and for pyroxylin enamel manufacture[2]. The esters of tetrahydrofurfuryl alcohol are claimed to be water-white and free from objectionable odor[3].

Furfuryl Esters. These are obtained by the direct esterificaion of the alcohol in the presence of a catalyst. Furfuryl acetate has sp. gr. 1.1175 at 20°, b. pt. 175°, and is a direct solvent of cellulose nitrate and some types of the cellulose ethers, the viscosities of which are about the same as with the use of ethyl lactate. It is also a solvent for elemi, sandarac, gamboge, ester gum and coumarone. Tetrahydrofurfuryl acetate has been described by J. Trickey[4] as a desirable nitrocellulose solvent.

As a grease and rust remover, furyl acetate, butyrate and lactate have been recommended[5], and R. Van Schaack[6] has given methods for the preparation of tetrahydrofuryl laurate, oleate, ricinoleate, palmitate and stearate. Furfuryl phthalate, benzoate, and cinnamate have also been proposed as desirable solvents. Likewise glycol and glycerol furoates (pyromucates).

Furoic Esters, Pyromucic Esters. The constants of methyl, ethyl, propyl, butyl and amyl furoate have been given elsewhere. Furoic acid (pyromucic acid) is a latent solvent of both nitrocellulose, ethyl- and benzyl-cellulose, being crystals, m. pt. 132°, and subliming at 100°. Furacrylic acid, m. pt. 135°, is the furan analogue of cinnamic acid.

Sulfones, Sulphones, are not true esters, but compounds characterized by great stability, in which both alcohol radi-

1. J. Trickey, U. S. P. 1703697; abst. C. A. 1929, **23**, 2050; J. S. C. I. 1929, **48**, 566-B.
2. E. I. du Pont de Nemours, E. P. 279520; abst. C. A. 1928, **22**, 3056; J. S. C. I. 1929, **48**, 293-B; Chem. Zentr. 1928, I, 990.
3. J. Trickey, U. S. P. 1756228; abst. J. S. C. I. 1931, **50**, 16-B; Brit. Plastics, 1931, **2**, #21, 159.
4. U. S. P. 1756228.
5. G. Williams, U. S. P. 1496506.
6. U. S. P. 1802623.

cals are linked to sulfur. They cannot be reduced to sulfides. Dimethylsulfone melts at 109° and boils at 238°; diethylsulfone melts at 70° and boils at 248°. H. Clarke[1] has described diethylsulfone in combination with butyl and amyl oxalates, ethyl propionate or butyrate or monochlornaphthalene as a cellulose acetate plastifiant. M. Schmidt[2] has described a group of sulfones containing methyl, ethyl, amyl-phenyl (or -tolyl or -xylyl) sulfone, nine bodies acting as flexilizers with nitro- or acetyl-cellulose. Dioxydiphenylsulfone, phenyloxyethylsulfone, ethyl-*m*-xylylsulfone and ethyl phenylsulfonacetate are included. The alkyl sulfones of H. Clarke[3] for incorporation with nitrocellulose embrace *n*-dibutylsulfone, di*iso*butylsulfone, dimethylsulfone, *n*-dipropylsulfone, di*iso*propylsulfone, di*iso*amylsulfone, methylethylsulfone, diheptylsulfone and ethyl*iso*amylsulfone. For gelatinization of acetylcellulose[4], he prefers the sulfones of dibutyl, di*iso*butyl, dimethyl, diethyl, *n*-dipropyl, di*iso*proply, di*iso*amyl, methylethyl, diheptyl, ethyl*iso*amyl and diphenyl. Acetone or methyl acetate is used as the ancillary solvent in both cases. They all dissolve cellulose ethers[5].

Dioxydiphenylsulfone (dioxysulfobenzide) has been advocated as a camphor substitute in cellulose ester plastics[6]. Dibutylsulfone, a white solid, b. pt. above 250°, may be incorporated 0.5-10 parts with 5 parts cellulose ether and 15-30 parts of a chloroform-alcohol mixture. L. Lilienfeld[7] has described the use of sulfones in connection with viscose coatings.

Sulfoxides. M. Schmidt and J. Voss[8] increase the softness and elasticity of cellulose ether and ester masses by means of dioxydiphenylsulfone (diphenyldisulfoxide) or

1. U. S. P. 1309981.
2. D. R. P. 366116; abst. J. S. C. I. 1923, **42**, 348-A.
3. U. S. P. 1370878; abst. J. S. C. I. 1921, **40**, 296-A.
4. U. S. P. 1370879; abst. J. S. C. I. 1921, **40**, 296-A.
5. H. Clarke, U. S. P. 1357614; abst. C. A. 1921, **15**, 436.
6. Chem. Fabrik Griesheim Elektron, E. P. 15855, 1909; abst. C. A. 1910, **4**, 827. D. R. P. 219918. F. P. 404886.
7. U. S. P. 1355985.
8. D. R. P. 399074; abst. J. S. C. I. 1924, **43**, 905-B; Chem. Zentr. 1924, II, 1644; Kunst. 1925, **15**, 123.

dioxyditolylsulfone (ditolyldisulfoxide), in conjunction with acetone and alcohol. In using as a camphor substitute with nitrocellulose, the mass should be masticated at about 60°. L. Lilienfeld[1] employs sulfoxides, sulfones and mercaptols with viscose for coating wood and paper.

Aromatic Nitro Bodies. The nitro-compounds of benzene, phenol, toluene and xylene have primarily been used in connection with nitrocellulose, the majority of which have proven excellent gelatinants. Many of them are either toxic (nitrobenzene) or impart color to the compositions in which they are incorporated, thus limiting their usefulness.

Nitrobenzene, Mirbane Oil, Mononitrobenzene, has been employed with pyroxylin in insulating compounds[2], to prepare an incombustible cellulose[3], and in modifying the esterification action in the production of cellulose acetate[4] and butyrate[5], or other cellulose esters[6]. Nitrobenzene with ethyl acetate and acetone[7], to which pyridine may be added[8]; or nitrobenzene, nitronaphthalin and volatile solvents[9]; or nitrobenzene and acetone[10], are some of the solvent combinations recommended. A. Nobel[11], W. Wolff and M. von Förster[12], and A. Mai[13] have described processes for the utilization of nitrocellulose, taking advantage of the solvent power of nitrobenzene.

1. E. P. 1378, 1912; abst. C. A. 1913, **7**, 2307.
2. S. Heimann, U. S. P. 547120.
3. J. Schmerber and L. Morane, F. P. 324121; abst. J. S. C. I. 1903, **22**, 569.
4. U. S. P. 623701, 627031, 708459, 790565. D. R. P. 105347, 139669. Belg. P. 137577.
5. C. Weber and C. Cross, U. S. P. 632605. Soc. D'Exploitation des Brevets Dolter, F. P. 375092; abst. J. S. C. I. 1907, **26**, 877.
6. L. Beals, U. S. P. 239424. Soc. D'Exploitation des Brevets Dolter, F. P. 375092; abst. J. S. C. I. 1907, **26**, 877.
7. A. Voswinkel, D. R. P. 74070.
8. A. Luck and C. Cross, D. R. P. 117349.
9. E. Street, D. R. P. 117051. See E. P. 9970, 13724, 1897. D. R. P. 100522, 100523.
10. H. Maxim, D. R. P. 81805.
11. D. R. P. 45712. See D. R. P. 4829, 10232, 36705.
12. D. R. P. 26014.
13. E. P. 200892; abst. C. A. 1924, **18**, 220.

As a diluent or moderator, nitrobenzene has been patented for use in the preparation of cellulose angelate, hexanoate, hypogaete, oleate, stearate, phenylacetate and phenylpropionate[1]. The E. Weston[2] formula combines nitrocellulose, nitrobenzene, naphtha and camphor. The Köln-Rottweil A.-G.[3] dissolve pyroxylin in a mixture of acetone, amyl acetate, nitrobenzene and pyridine, and J. Stevens employs mononitrophenol with or without nitronaphthalin in conjunction with volatile solvents[4]. Nitrochlorbenzene has been specified by H. Dreyfus as a useful acetylcellulose colloidant[17].

Dinitrobenzene, Dinitrobenzol, of which there are three isomers, was described in 1882 by J. Stevens[6] as a desirable camphor substitute in celluloid production, used either alone or with coumarine (coumaric anhydride). G. Trench[7], S. v. Romocki[8], C. Lundholm and J. Sayers[9] and M. Jeschek and J. Jaresch[10] have all recommended nitrocellulose compositions in which dinitrobenzene is an integral part. In producing solutions of "tetranitrocellulose"[11], E. Bronnert combines ethyl acetate with dinitrobenzene, nitronaphthalin, acettoluide and benzanilid, while A. Nobel[12] specifies dinitrobenzene, dinitrotoluene, nitrotoluene, nitrocymene, heavy camphor oil and mono-, di- and tri-acetin.

The H. Güttler formulae for gelatinizing nitrocellulose[13] employ di- or tri-nitrobenzene, di- or tri-nitrotoluene, and mono-, di and tri-nitronaphthalin. Dichlornitrobenzene has been specified by H. Dreyfus[14] as a suitable acetylcel-

1. C. Weber and C. Cross, U. S. P. 632605.
2. U. S. P. 264986, 264987, 264988. E. P. 4458, 1882; abst. Electrician, 1887, **18**, 287.
3. D. R. P. 352905; abst. J. S. C. I. 1922, **41**, 730-A.
4. U. S. P. 583517. See U. S. P. 269342, 517987, 542197, 543692.
5. F. P. 432264. Belg. P. 241251. 6. U. S. P. 269342.
7. E. P. 18472, 1890. See E. P. 18241, 1888.
8. D. R. P. 99875. 9. D. R. P. 53296.
9. D. R. P. 44041.
10. U. S. P. 573132. E. P. 6858, 1896. D. R. P. 93009.
11. E. P. 20234, 1893.
12. D. R. P. 56946; abst. Wag. Jahr. 1891, **37**, 1176; Zts. ang. Chem. 1891, **4**, 436; Bied. Tech. Chem. Jahr. 1891, **92**, 14, 140.
13. F. P. 432264; abst. C. A. 1913, **7**, 3414; J. S. C. I. 1912, **31**, 24.

lulose plastic-inducing body. Nitroproducts from petroleum distillates as substitutes for camphor in thermoplastic nitrocellulose mixtures, have been detailed by L. Edeleanu and G. Filiti[1].

Nitrotoluenes. Dinitrotoluene in the hands of F. Jones[2] and of J. Stevens[3] has been employed in the past to a considerable extent, having high pyroxylin colloiding properties, as also *p*-nitrotoluene in conjunction with camphor or acetanilid[4]. As an activator or gelatinizing accelerator for nitrocellulose, di- and tri-nitrotoluene, nitronaphthalin, dinitrobenzene and nitroxylene (spelled nitrozylene in the patent) have been put forward[5], calcium carbonate being sometimes added with formanilid or formtoluidide. Hydrated cellulose acetate dissolves readily, even in the cold, in *o*-nitrotoluene and alcohol.

Nitroxylenes. Dinitroxylene, camphor and acetanilid forms the pyroxylin thermoplasticizer of J. Stevens[6], while A. Nobel[7] has disclosed methods of gelatinizing nitrocellulose by the use of nitrobenzene, nitrotoluene, nitroxylene, nitrocumene, and nitrocymene. Hudson Maxim[8] in gelatinating and dissolving cellulose nitrates has advocated the use of trinitroanisol or trinitrophenetol, either with or without volatile solvents. For colloiding acetylcellulose, nitro-

1. E. P. 9416, 1902; abst. J. S. C. I. 1903, **22**, 621, 646. See E. P. 2775, 1880.
2. D. R. P. 120201; abst. Zts. ang. Chem. 1901, **14**, 625.
3. U. S. P. 542692, 543108, 552209. See U. S. P. 269342, 517987.
4. J. Stevens, U. S. P. 552209. See U. S. P. 517987.
5. F. Nathan and W. Rintoul, U. S. P. 1302202; abst. J. S. C. I. 1919, **38**, 480-A. W. Rintoul and D. Cross, U. S. P. 1303115; abst. C. A. 1919, **13**, 1930. U. S. P. 1306440; abst. C. A. 1919, **13**, 2130; J. S. C. I. 1919, **38**, 555-A. U. S. P. 1310489; abst. C. A. 1919, **13**, 2449. E. P. 12745, 1912; abst. J. S. C. I. 1913, **32**, 991. W. Rintoul, N. Picton, D. Peacock and Nobel's Explosives Co., E. P. 16692, 1914. W. Rintoul, D. Cross and Nobel's Explosives Co., E. P. 14655, 14656, 1915; abst. C.A. 1919, **13**, 1639; J.S.C.I. 1919, **18**, 340-A. E. P. 126056. W. Rintoul, J. Thomas and Nobel's Explosives, E. P. 128372; abst. J. S. C. I. 1919, **38**, 486-A. W. Rintoul, T. Nolan and Nobel's Explosives, E. P. 131389; abst. C. A. 1920, **14**, 350. See E. P. 12743, 1912; 4940, 4941, 1913.
6. J. Stevens, U. S. P. 553270. See U. S. P. 517987.
7. E. P. 15914, 1894.
8. E. P. 2039, 1910.

p-xylene[1] alone or preferably in the presence of methyl alcohol or ethyl acetate has recently been disclosed. It is a liquid boiling at 239°.

Nitronaphthalin, yellow crystals, readily soluble in alcohol, chloroform, ether and other cellulose ether and ester solvents, m. pt. 56-58°, b. pt. 304-307°, has been used as a gelatinant for nitrocellulose in combination with mono- di- and tri-nitrotoluene, dinitrobenzene and the nitroxylenes[2]; or in conjunction with urethanes or anilids for the same purpose[3]. A mixture of dinitrobenzene and nitronaphthalin (m. pt. 40°)[4], or nitronaphthalin alone, especially in the presence of a small amount of alcohol or ethyl acetate[5], or nitronaphthalin with resinous bodies and volatile solvents[6], have been used to a limited degree in the colloidation of pyroxylin. In the production of celluloid and analogous plastics, nitronaphthalin has been employed to partially replace camphor[7], the volatile solvent portion being denatured alcohol and benzene. In the waterproofing and ornamentation of paper[7], nitrocellulose in conjunction with nitronaphthalin, nitrotoluene, nitro-resin, nitrophenol, nitrocumol and acetone has been advocated, and nitronaphthalin, nitronaphthol, nitrated molasses, nitrosaccharose, nitrophenol and nitrotoluene[9] have been described as useful accompaniments of nitrocellulose in lacquers and other finishing compositions. In films and transparent plastics, the yellow color of nitronaphthalin is a drawback.

1. S. Carroll, U. S. P. 1841313.
2. W. Rintoul and D. Cross, U. S. P. 1306440; abst. C. A. 1919, **13**, 2130.
3. *Ibid.* U. S. P. 1310489; abst. C. A. 1919, **13**, 2449.
4. A. Geserich, D. R. P. 93228; abst. Zts. ang. Chem. 1897, **10**, 641.
5. Societe Neuman, Marx and Desvaux, F. P. 300676; abst. Chem. Ztg. 1900, **24**, 1121; Meyer Jahr. 1900, **10**, 321.
6. B. Gaisenband and G. Piestrak, F. P. 483316; abst. C. A. 1918, **12**, 995.
7. Societe Neumann, Marx and Desvaux, F. P. 300672; abst. Mon. Sci. 1901, **57**, 60.
8. H. Bittner and C. Villedieu, E. P. 7975, 1897; abst. J. S. C. I. 1898, **17**, 469.
9. M. Bielefeldt, D. R. P. 93351; abst. Wag. Jahr. 1897, **43**, 130, 482.

Dinitronaphthalin[1] with ether and alcohol has been combined with nitrocellulose as a brisant.

Amines and Amides. Dimethylamine, trimethylamine and monoethylamine have been called attention to by A. McDaniel[2] as acceptable dissolving and plasticizing agents for cellulose nitrate or acetate, in combination with ethyl acetate, methyl alcohol and acetone, while O. Schmidt[3] has described cellulose ester compounds containing acetyldichlorhexylamine with alcohol, acetone and methylethyl ketone, or *p*-toluénesulfodicyclohexylamine with alcohol alone[4]. These products are odorless, colorless, with low specific gravity, and are said to possess excellent stability against the action of heat and light.

While ethylamine is not a solvent of cellulose esters, butylamine dissolves both acetylcellulose and the cellulose ethers, especially those which, like benzylcellulose, dissolve in benzyl alcohol. Trihydroxytriethylamine (triethanolamine), although one of the weakest organic bases available, has been used in printing pastes containing vats of sulfur colors[5], and for artificial silk printing where water-insoluble anthraquinone compounds are used[6]. (See p. 215, n. 1; 304, n. 8; 937, n. 3.)

As cellulose ether and ester plasticizing compounds, propionamide, succinimide and salicylamide aided by actone have been advocated[7], while formamide[8] has been patented as a cellulose acetate solvent. A combination of for-

1. K. Pflug, D. R. P. 125098; abst. Chem. Zentr. 1901, II, 1140.
2. U. S. P. 1759489; abst. C. A. 1930, **24**, 3646; J. S. C. I. 1931, **50**, 108-B;; Plastics, 1930, **6**, #10, 606; #8, 458.
3. U. S. P. 1200886; abst. C. A. 1916, **10**, 3160; J. S. C. I. 1916, **35**, 1152. E. P. 9270, 1914; abst. J. S. C. I. 1915, **34**, 867. D. R. P. 281225; abst. C. A. 1915, **9**, 2311; Chem. Zentr. 1915, I, 238; Kunst. 1914, **4**, 396; 1915, **5**, 9.
4. See P. Sabatier and J. Senderens, Compt. rend. 1904, **138**, 458.
5. I. G. Farbenindustrie, A.-G., E. P. 324315; abst. J. S. C. I. 1930, **49**, 416-B; J. Soc. Dyers and Col. 1930, **46**, 178.
6. F. van der Grinten, E. P. 330625; abst. J. S. C. I. 1930, **49**, 840-B.
7. S. Carroll, U. S. P. 1844714; abst. C. A. 1932, **26**, 2055.
8. L. Mascart, U. S. P. 1342267; abst. C. A. 1920, **14**, 2247; J. S. C. I. 1920, **39**, 519-A.

mamide, acetamide, chloral, chloral hydrate with methyl, butyl and amyl formates or acetates constitutes the cellulose ester lacquer formula of J. Duclaux[1].

F. Bergstrom, W. Gilkey and P. Lung[2] have determined the solubilities of 288 compounds within a temperature range of 5° to 25° in 12 solvents, and their results are reproduced in Table XXX[3], column 1 being in ethyl alcohol; 2, ethyl ether; 3, methylamine; 4, diethylamine; 5, triethylamine; 6, di-*n*-propylamine; 7, *n*-butylamine; 8, di-*n*-butylamine; 9, tri-*n*-butylamine; 10, *iso*amylamine; 11, tolylamine (methylphenylamine); and 12 in ammonia at —33°. The research is accompanied by a bibliography of 27 citations.

Triethanolamine, a tertiary aliphatic ammonia base consisting of three ethyl groups attached to the ammonia nitrogen atom and having on the outer carbon atom of each ethyl group a hydroxyl group, is a viscous, water-clear, hygroscopic, high-boiling liquid[4]. It is miscible in certain proportions with acetone, alcohols, ethylene chloride, benzene and water. It is a direct solvent for cellulose nitrate, and is a solvent and operates as a good plasticizer for cellulose acetate, dissolved in acetone or methyl alcohol.

Aromatic Amines. The carbocyclic and heterocyclic amines embrace a large number of compounds and deriva-

1. J. Duclaux, E. P. 184197. F. P. 530440. Phot. Abst. 1922, **2**, 95.

2. See Ind. and Eng. Chem. 1932, **24**, 57.

3. The abbreviations used in the Table are as follows: ins, insoluble or extremely slightly soluble; ss, slightly soluble; s, moderately soluble; vs, very soluble; vs+, more than vs; es, extremely soluble; misc, miscible (in methylamine column only); ∞, miscible in all proportions; n, not soluble to an appreciably greater extent in hot solvent; x, more soluble in heated amine, crystallizes on cooling; m, more soluble in heated amine (in some cases because of chemical reaction); p, separates into two liquid phases; r, solute reacts chemically with solvent. Reaction is rapid enough to be apparent. All acidic substances react more or less rapidly with amines. (The letter, r, has been omitted in these cases); a, swells; numerals, numerals appearing in diethylamine column indicate number of grams of solute (or of its reaction product with diethylamine) per 100 cc. of solution.

4. C. Staud and C. Webber, U. S. P. 1880514.

Table XXX. Solubilities of Organic Compounds in Aliphatic Amines *(Continued)*

	1	2	3	4	5	6	7	8	9	10	11	12
Acenaphthene	ssx	..	..	15	sx	..	sx	s	ssx	s	s	ins
Acetaldehyde	..	.	misc	.	..	..	..	..	.	..	..	..
Acetamide	s	..	vs	ssx	ins	..	s	ins	ins	s	s	vs
Acetanilide	vs	ss	..	11	ssx	..	vs	ss	ssx	sx	s	..
Acetic acid	..	..	vs	..	..	..	.	.	.	..	..	..
Acetoacetic ester	∞	..	.	∞	..	.	.	∞	..		..	∞
Acetone	∞	∞	∞	..	..	.		..		.	.	..
Acetophenone	∞	..	..	∞	..	.	∞		∞		.	s
p-Acetophenylene diamine	..	..	..	ins	..		ssx	ssx		ssx		..
p-Acetotoluide	ss	s	..	ss	.		..	.	ssx	ssx	.	ss
Acetylene	s	..	s	..	.	.	..	.		.	.	..
Acetylene tetrabromide	s	∞	.	r	..	.			.	.		s
Acetylsalicylic acid	vs	ss	.	s	s	s	vs	s	ss	vs	s	..
Agar-agar	..	..	..	.	..			.	.	insn	.	ins
Alanine	ss	ins	..	..	..					insn	.	..
Aldol	∞	s	..	∞	..	.	∞	.	..	..	..	.
Alizarin	..	..	s	..	..	..	..		.	.	.	..
Allyl alcohol	∞	∞	..	∞	..	.	.				.	..
1-Aminoanthraquinone	ss	ss		ss	ss	ss	ssm	ss	ssx	ssm	ss	..
p-Aminobenzoic acid	s	ss	..	ins	ins	insn	ss	ins	insn	ss	ssx	..
m-Aminophenol	s	s	.	vs+	ss	.	s	s	ss	vs	s	..
o-Aminophenol	ss	ss	..	vs	ins	s	vs+	sx	ssn	s	s	vs
Aminosulfonic (sulfamic) acid	..	..	..	..	..	.	ssn	..	.	ssx	.	..
Ammonium benzoate	.	..	..	ss	..	..	vsr	.	..	vsr	..	vs
Ammonium citrate	..	..	..	ss	..	..	..	..	..	.	..	..
Amyl alcohol (iso)	∞	∞	.	∞	..		∞	.		..	∞	..
n-Amyl formate	∞	∞	∞	..	..	..	.	..	∞	.	..	..
Anethole	∞	∞	.	∞	.	.	.	.	..	.	..	ss
Anhydroformaldehydeaniline	ss	ss	.	ssn	ssx	ins	ss	ss	ssx	ssx	ssx	..
Aniline blue	..	.		ss	ins	..	ss	ins	ins	ss	ss	..
Anthracene	ss	ss	..	ss	ssx	..	ssx	ss	ssx	ssx	ssx	ins
Anthranilic acid	s	s	..	ss	ins	ssx	s	ss	ss	s	s	..
Anthraquinone	ss	ss	ss	..	..	..	ssx	..	..	ssx	..	ins
Atoxyl	..	..	..	ins	ins	.	ss	ins	ins	ss	ins	.
Azobenzene	ss	s	vs	vs	vsx	vs	vs	vs	s	vs	s	s
Azoxybenzene	s	s	..	es	..	..	..	..	..	es	.	s
Beeswax	..	..	..	s	s	..	s	s	ssm	s	ssm	..
Benzalacetophenone	ss	vs	.	vs	..	.	es	.	ssx	..	..	..
Benzaldehyde	∞	∞	misc	∞	..	.	..	.	.	..	..	es
Benzamide	s	vss	..	ss	ins	s	s	ss	ins	s	s	vs
Benzene	∞	∞	.	∞	..	.	∞	∞	∞	.	∞	s
Benzidine	s	ss	.	ss	ss	.	s	ssx	ins	sx	s	.
Benzil	vs	vs	vs	vs	ss	sx	es	ss	ss	es	es	s
Benzoic acid	vs	vs	vs	ssx	ssx	..	vs	s	ssp	s	sx	vs+
Benzoic sulfinide (Saccharin)	ss	ins	r	.	..	.	.		.	ss	.	..

Benzoin	s	..	..	..	..	..	vs	..	..	..	..	.
Benzophenone	s	s	vs	es	es	..	es	vs+	sx	ss	es	s
Benzyl acetate	∞	∞	..	∞	..	..	..	∞	..	..	∞	s
Benzyl alcohol	∞	∞	..	∞	..	..	..	..	∞	..	..	∞
Borneol	vs	vs	..	es	..	..	..	..	..	..	..	s
o-Bromoacetanilide	..	..	vs	..	..	..	..	..	..	..	..	..
p-Bromoaniline	vs	vs	..	esx	vs+	esx	vs+	vs	ssx	vs	vs+	..
Bromcamphor	s	vs	..	vs+x	s	..	vs+x	vs+	ssx	vs	vs	..
Bromocresol green	..	..	..	ss	ins	..	s	ssn	ins	s	s	..
1-Bromonaphthalene	∞	∞	..	∞	..	..	..	..	∞	..	..	..
p-Bromonitrobenzene	s	s	..	s	..	..	..	..	..	..	..	..
o-Bromotoluene	s	..	..	∞	..	..	..	∞	∞	..	∞	..
p-Bromotoluene	s	s	..	es	..	..	..	es	.	..	..	..
n-Butyl alcohol	∞	..	..	∞	..	..	..	..	..	∞	∞	∞
tert-Butyl alcohol	..	..	∞	.	..	..	..	..	..	..	..	..
n-Butyl cyanide	∞	s	..	∞	..	..	∞	..	..	∞	.	s
n-Butyl ether	∞	∞	..	∞	..	..	∞	∞	∞	∞	..	..
n-Butyl formate	∞	∞	..	∞	..	..	..	∞	..	..	..	..
n-Butyl stearate	..	..	..	∞	..	..	∞	∞	∞	∞	rss	..
Caffeine	ss	ss	..	ss	..	..	ssx	..	..	ssx	..	ss
Calcium acetate	ins	..	..	insn	..	..	..	..	..	..	..	..
n-Calcium butyrate	..	..	..	..	..	..	insn	..	..	.	..	..
Calcium formate	ins	..	..	..	..	..	..	..	..	insn	..	..
d-Camphor	es	vs	.	es	es	..	es	vs	vsx	es	es	vs
Carbon disulfide	∞	∞	..	r	..	..	esr	..	∞	..	..	r
Casein	..	..	..	ins	ins	..	ins	ins	ins	ins	ins	..
Cellulose	ins	ins	..	ins	ins	..	ins	ins	ins	ins	insa	ins
Cellulose acetate	..	..	..	ss	ins	ins	es	ins	ins	s	s	es
Cellulose nitrate	..	..	..	s	ins	..	vs	ss	ins	vs	vs	s
Cerulein	..	..	vs	..	..	..	..	..	..	..	..	..
Cetyl alcohol	s	s	vsx	..	..	..	es	..	s	..	..	ins
Chloroacetic acid (mono)	s	s	..	srx	vsxp	..	sx	ssxr	ssp	vs	ssrm	vs
p-Chlorodiphenyl	s	s	.	vs+	vs+x	..	vs	vs	sx	vs	vs	..
Chloroform	∞	∞	∞r	∞	..	..	..	..	..	..	..	sr
Cholesterol	ssx	s	..	..	..	vs+	..	..	..	vs+	..	ins
Chromotropic salt	..	..	..	..	..	..	insn	..	..	..	..	..
Cinchonine	ss	ss	..	..	..	..	ssn	..	..	ssx	..	ins
Cinnamic acid	s	vs	..	s	ss	..	sx	ss	ssx	s	ssx	s
Coconut oil	..	..	..	∞	∞	..	∞	∞	∞	∞	∞	..
Copal	..	..	..	..	..	..	..	..	..	insn	..	ss
Crystal violet	..	..	..	ins	ins	..	vs	ins	ins	s	s	s
Cyclohexanol	s	s	..	∞	..	..	..	..	..	..	..	..
o-Dianisidine (bianisidine)	s	vs	..	ss	ins	..	sx	ss	ins	s	s	..
Diazoaminobenzene	s	vs	..	vs	..	..	..	..	..	es	..	vs
p-Dibromobenzene	s	..	..	40	vs+x	..	vsx	vs	sx	vs	vs+	ss
2,3-Dibromopropyl alcohol	vs	∞	..	∞	..	..	..	..	..	..	..	..
Dichloramine-T	..	..	..	vsr	sr	..	vsr	ssr	r	vsr	vs+r	r
p-Dichlorobenzene	es	vs	..	53	esx	..	es	ves	vs+x	esx	es	ss
Dichlorogallein	..	..	s	.	..	..	..	..	..	..	..	s
Dichlorohydrin	∞	∞	..	∞	..	..	..	..	..	..	..	

Table XXX. Solubilities of Organic Compounds in Aliphatic Amines *(Continued)*

	1	2	3	4	5	6	7	8	9	10	11	12
2,3-Dihydroxyquinoxaline	..	..	..	..	..	..	insn	..	..	..	..	s
Dimethylaminoazobenzene	x	..	..	sx	ssx	ssx	sx	s	ss	s	s	..
p-Dimethylaminobenzaldehyde	c	s	..	..	..	..	sx	..	..	..	..	..
Dimethylaniline	s	∞	..	∞	..	..	..	..	..	..	..	ss
Dimethylethylcarbinol	c	s	..	∞	..	..	..	∞	..	∞	∞	..
Dimethylglyoxime	vs	vs	..	ssx	s	ssx	vs	ss	ssx	vs	s	.
2,6-Dimethylquinoline	vs	vs	..	vs	..	..	..	..	..	..	..	..
2,2-Dinaphthylamine	ss	..	..	ssx	ssx	ssx	sx	ssx	ssx	s	ss	..
2,4-Dinitroaniline	ss	..	vs	..	..	..	..	..	..	..	..	..
m-Dinitrobenzene	ssx	..	vs	9.3	ss	..	s	ss	ssx	s	s	..
3,5-Dinitrobenzoic acid	vs	ss	..	ss	ss	ssx	s	ss	ssx	vs	sm	..
4,4'-Dinitrodiphenyl	ss	vs	..	ss	ss	..	ssx	ssx	ssx	ssx	ssx	..
2,4-Dinitro-1-naphthol-7-sulfonic acid	..	..	..	ss	..	..	..	..	..	..	..	..
2,4-Dinitrophenol	ss	vs	..	ss	..	..	sx	..	ssn	vs	..	vs
2,4-Dinitrotoluene	ss	..	vs	sx	..	..	sx	ssx	ssx	..	..	ss
Diphenyl	ss	s	..	41	s	..	vs	s	sx	vs	vs	ss
Diphenylamine	vs	vs	..	cs	vs	cs.	cs	vs	sx	cs	cs	..
Diphenylbenzamide	..	..	..	ss	..	..	..	..	..	ssx	..	..
Diphenylguanidine	..	..	..	ss	ins	..	vs	s	ssx	vs	s	..
Diphenyl ketoxime	..	..	vs	..	..	..	..	..	..	..	..	..
Diphenyl sulfone (phenyl sulfone)	ss	s	..	ssx	ssx	..	ssx	ss	ssx	ssx	sx	..
Diphenylurea (sym.)	s	s	..	ss	ins	..	ss	ss	ssx	s	ssx	s
4,4'-Dipyridyl (bipyridine)	vs	..	..	..	..	..	vsx	..	..	sx	..	vs
Di-p-tolylselenide	..	..	..	..	..	..	cs	..	..	..	..	..
Eosin	s	..	..	ss	ins	..	vs	ss	ins	vs	s	s
Ethyl alcohol	∞	∞	..	..	..	..	..	∞	..	..	∞	..
Ethyl carbonate	s	..	..	ssr	..	..	∞	..	..	..	∞	sr
Ethyl cyanoacetate	∞	∞	..	∞	..	..	..	..	..	..	..	..
Ethylene dibromide	s	∞	spr	∞	.	..	..	∞	..	..	∞	..
Ethylene glycol	∞	ss	..	∞	..	∞	..	..	..	∞	..	..
Ethyl iodide	s	s	..	∞	..	..	..	..	∞	..	csr	s
Ethyl malonate	∞	∞	..	∞	..	..	..	∞	..	∞	..	..
Ethyl oxalate	s.	..	..	∞	..	..	..	∞	..	..	ssr	..
Ethyl sulfate	..	..	..	r	..	..	..	rs	..	..	..	..
Fluorene	ss	vs	..	13	ssx	sx	s	s	ssx	s	s	ins
Fluorescein	vs	ss	..	ss	ins	..	s	ins	ins	s	s	s
Galactose	ss	..	vs	..	..	..	..	..	..	..	..	..
Gallein	..	..	ss	..	..	..	..	..	..	..	..	..
Gallic acid	s	ss	..	insn	insn	..	s	insx	insn	s	ssm	s
Gelatin	..	..	..	ins	ins	..	insn	ins	ins	ins	ins	..
Glucose	ss	ins	vs	ss	ins	ssn	vs+	ins	ins	s	s	vs
β-Glucose pentaacetate	ss	ss	..	..	..	..	cs	..	..	..	..	..
Glycerol	∞	ins	vs	..	..	..	..	..	..	..	..	..
Guaiacol	∞	∞	..	∞	..	..	..	..	..	..	..	.
Guanidine nitrate	..	..	..	ss	..	..	..	..	..	..	..	vs

Gum arabic	..	..	..	insn	ins	..	ins	ins	ins	esn	es?	..
H acid	ss	ss	..	..	..	..	insn	..	..	..	..	..
Hemoglobin	..	..	.	ins	..	..	insn	..	..	.	..	ss
Hexaethylbenzene	s	vs	..	..	.	..	ssx	.	.	ssx	..	..
Hexamethylenetetramine	ss	ins	..	ssn	.	..	ssn	..	..	..	.	..
Hippuric acid	ss	vss	vs	ssx	..	..	..	..	..	vs	.	vs
Hydrazine sulfate	ins	..	..	ins	..	..	..	..	..	..	.	insi
Hydroquinone	vs	vs	vs	35	ss	s	s	s	ss	s	ssx	vs
Hydroxylamine hydrochloride	s	ins	vs	..	.	..	..	..	.	..	..	..
Indigotin	ins	ins	vs	ins	ins	..	ss	ss	ss	ins	ss	ss
Indole	vs	vs	..	es	.	..	es	..	..	..	..	vs
Isatin	s	ss	..	..	.	..	vs	..	.	..	..	s
Isoquinoline	∞	∞	..	∞	..	..	..	∞	.	∞	..	s
Lactose	ss	ins	..	ss	ss	..	ss	ins	ins	ss	ins	vs
Lanolin	..	..	..	es	es	..	es	es	es	es	es	..
Linseed oil, raw	..	..	..	∞	∞	..	∞	∞	∞	∞	∞	..
Lysol	..	..	..	∞	..	..	..	..	..	..	..	..
Maleic acid	s	ss	..	ins	ins	..	ssn	ins	ins	ssx	insm	
Malic acid	vs	ss	..	ins	ins	ins	ssn	ins	ins	ssn	ssx	ss
Malonic acid	s	ss	..	ins	insn	insx	ss	ins	ss?	ss	ins	ins
Mannite	ss	ins	..	ss	ins	..	ss	ins	ins	ssn	ins	ss
d-Menthol	vs	vs	..	es	es	es	es	es	es	es	es	es
Mercuric acetate	ss	..	..	insr	ins	s	vs	ss	ins	ss	ins	s
Mercuric cyanide	s	.	vs	..	..	..	es	..	ssn	..	..	vs
Mercury diphenyl	ss	..	..	ss	ins	ss	ss	ss	ins	ss	ins	..
Mercury di-*p*-tolyl	..	..	..	.	.	..	ssx	..	ssx	ssx	..	..
Methanol	∞	∞	∞	..	..	..	∞	..	∞	..	..	..
meso-Methyl acridine	vs	vs	..	..	..	..	..	.	..	es	..	..
Methylene aminoacetonitrile	..	..	..	ss	ss	..	ss	ins	ssx	ss	ins	.
Methylene dianiline	..	..	..	insn	ss	..	ss	ss	insx	ss	ss	..
Methyl orange	ss	ins	ss	ins	ins	ins	ssn	ins	ins	ss	ss	..
Mucic acid	ins	..	..	ins	ins	insn	ss	ins	ins	ss	ins	s
Naphthalene	ss	vs	..	27	sx	..	vsx	s	sx	vs	sx	ss
Naphthionic acid	ss	ins	..	ss	ins	..	s	ins	ins	s	ss	..
1-Naphthol	vs	vs	vs	..	..	..	..	..	..	..	..	..
2-Naphthol	vs	vs	vs	es	vs+	..	es	es	vs	es	es	ss
Naphthol yellow	..	..	..	ins	ins	..	ss	ins	ins	ins	ins	..
Night blue	..	..	..	s	s	..	s	s	s	s	s	..
p-Nitroacetanilide	s	ss	..	ss	..	..	..	..	..	..	..	..
m-Nitroaniline	s	ss	..	sx	ssx	..	s	ss	ssx	s	s	s
p-Nitroaniline red	..	..	..	ss	ss	..	s	ssx	ssx	s	s	..
m-Nitrobenzaldehyde	vs	vs	vs	..	..	..	..	..	..	..	..	..
Nitrobenzene	∞	∞	∞	..	..	..	∞	..	∞	..	..	vs
m-Nitrobenzenesulfonamide	..	..	vs	..	..	..	..	..	..	..	..	..
o-Nitrobenzoic acid	s	s	vs	..	..	..	..	..	..	..	..	..
p-Nitrobenzoic Acid	ss	ss	..	ssx	insn	ssx	vsx	ss	ss	s	sx	ss
p-Nitrobromobenzene	ss	..	..	ss	ss	ssx	sx	ss	ssx	s	sx	..
o-Nitrophenol	vs	vs	vs	..	..	..	..	..	..	..	..	..
p-Nitrophenol	vs	s	..	13	ss	ssx	vs	ss	ssm	vs	s	s
p-Nitrophenylhydrazine	..	..	..	..	..	..	vs	..	ssx	..	..	..

Table XXX. Solubilities of Organic Compounds in Aliphatic Amines *(Continued)*

	1	2	3	4	5	6	7	8	9	10	11	12
o-Nitrotoluene	∞	∞	vs	..	..	..	..	..	..	..	..	..
p-Nitrotoluene	s	s	..	vs+x	..	..	..	..	sx	vsx	..	..
3-Nitro-4-toluidine	vs	..	..	sx	..	..	vsx	..	ssx	..	..	s
Nitrourea	vs	vs	..	ins	..	..	..	..	..	..	..	vs
Oleic acid	∞	∞	..	∞	∞	..	∞	∞	∞	∞	∞	ins
Olive oil	..	..	..	∞	∞	..	∞	∞	∞	∞	∞	..
Orange IV	..	..	..	ss	ins	..	ss	ss	ins	ssn	ss	..
Oxalic acid.2H₂O	s	ss	..	ins	ins	..	insn	insn	ins	ins	ins	ins
Oxanilide	ss	ss	..	0.5	..	..	..	..	..	..	..	..
Palmitic acid	ss	..	vs	..	..	..	..	..	..	..	..	..
Paraffin	..	..	..	ss	sx	..	s	sm	sx	s	ssx	ins
Paraffin oil	.	..	..	∞	..	..	∞	..	∞	..	..	..
n-Pentane	∞	..	∞	..	..	..	..	..	..	..	..	..
2-Pentene	..	..	..	∞	..	..	..	..	..	..	..	..
Penacetin	ss	ss	.	ss	ins	ssx	s	ss	ssx	s	ss	..
Phenanthrene	ss	s	.	s	..	..	..	..	..	..	vs	ins
Phenol	∞	∞	vs	es	..	..	..	..	..	es	..	vs
Phenolphthalein	s	ss	vs	s	ss	..	s	ss	ss	s	s	..
Phenylacetic acid	es	vs	vs	..	..	..	vsx	..	..	..	..	..
meso-Phenyl acridine	ss	s	..	..	..	..	..	..	..	ssx	..	..
Phenylazo-1-naphthylamine	..	..	..	..	..	..	..	..	ssx	s	..	..
o-Phenylenediamine	vs	vs	..	..	..	..	sx	..	..	sx	..	vs
Phenylglucosazone	ss	.	.	..	..	..	sx	..	..	vs	..	vs
Phenylhydrazine	∞	∞	∞	..	..	..	..	..	..	..	..	..
Phenylmercuric bromide	..	.	..	.	..	..	ssx	..	..	ssx	..	..
2-Phenylquinoline	vs	vs	..	vs	..	..	vs	..	..	s	..	..
Phenyl-p-tolyl sulfone	.	..	.	6 3	ins	ins	ss	ss	ssx	ssx	ss	..
Phenyl urea	vs	vs	.	ss	ss	ssn	s	ss	ssx	vs	s	s
Phthalic acid	s	ss	ins	ins	ins	..	ins	ins	insx	..	ssx	ins
Phthalic anhydride	s	ss	ins	sm	ss	..	s	ss	ins	s	ssm	..
Phthalimide	s	ss	.	s	ss	ss	s	sx	ssm	s	s	vs
Picric acid	s	ss	vs	ssp	ss	vs	vs+	s	ssx	vs	s	es
Potassium amide	r	ins	.	ins	.	..	insn	..	..	..	..	vs
Potassium ethyl sulfate	..	..	..	ins	..	..	..	..	..	..	..	vs
Potassium quinaldine	r	vs	..	..	..	..	vs	..	..	..	..	es
Potassium triphenylmethyl	r	s	..	.	..	..	s	..	..	..	..	.
Pyridine	∞	∞	∞	..	..	..	..	.	..	..	..	∞
Pyrogallol	vs+	vs+	vs	ssm	ss	.	s	s	ss	s	sm	es
Pyrrole	vs	vs	..	∞	..	..	.	..	..	..	.	..
Quinaldine	vs	vs	..	∞	..	..	∞	..	∞	∞	.	s
Quinaldine picrate	ss	..	..	es	..	..	es	vsx	ss	..	..	..
Quinine	es	vs+	..	s	ssm	s	vs	ssm	ss	vs	s	insol
Quinoline	s	..	..	∞	..	..	∞	∞	∞	..	∞	∞
Quinoline methiodide	..	..	..	..	..	..	vsx	..	..	vs	.	vs
Quinoline yellow (water soluble)	..	..	..	ins	ins	..	ss	ss	ins	ssn	ss	..
Quinone	vs	vs	sr	vsr	..	..	..	..	..	..	..	..
Resorcinol	es	vs	vs	s	..	..	vs	..	..	..	..	es
Rosaniline	s	ins	vs	ins	ins	..	ss	ins	ins	ss	ss	s
Rosin	vs	vs	..	s	s	..	vs	vs	ins	s	s	insr
Rosolic acid	ss	s	.	ss	ss	..	s	ss	ss	s	s	ss

Rubber, vulcanized	ins	ins	..	s	s	..	s	s	s	s	ins	ins
Salicylic acid	vs	vs	..	vs	sp	sx	vs+	ss	ssm	es	s	..
Selenium	ins	ins	.	ins	ins	.	ins	ins	ins	ins	ins	ins
Shellac, white	.	..	.	ins	ins	..	ins	ins	ins	insn	ins	..
Skatole	s	..	..	es	..	..	..	..	es	..	..	s
Soap	..	..	..	.	..	..	ins	..	..	ins	..	ins
Sodium alizarin sulfonate	..	..	..	ss	ins	..	s	ss	ins	s	s	ins
Sodium benzoate	ss	..	..	insn	..	..	insn	..	..	..	.	..
Sodium indigo sulfonate	..	..	.	ins	ins	..	ss	ins	ins	ss	ss	.
Sodium-*p*-nitrophenylantidiazotate	..	..	.	..	..	..	vs	..	..	..	..	s
Starch (corn)	ins	ins	..	ins	ins	..	ins	ins	ins	ins	ins	insa
Stearic acid, tech.	es	s	.	es	vs+	es	es	vs+	vs	vs	ssx	ins
Strychnine	ins	ins	..	..	..	..	ss	..	..	..	..	..
Succinic acid	s	ss	ins	insn	ss	ssx	ins	ins	ins	ins	ssx	..
Succinimide	s	..	..	ss	ins	s	vsx	ss	ssx	sx	ss	.
Sucrose	ss	..	vs	ss	ss	..	vs	ins	ins	s	vs	vs
Sulfanilic acid	ss	ss	..	ssn	ss	..	s	ss	ss	s	ss	vs
Sulfonal	ss	ss	..	..	..	..	ssx	..	..	ssx	.	s
Sulfur, rhombic	ins	ins	..	s	s	..	vs	ss	ssx	s	s	s
Tallow	..	..	..	vsx	..	..	..	..	..	es	..	..
Tannic acid	ss	ss	..	ss	ins	insn	ss	ins	ins	ss	ss	ss
Tartaric acid	s	ss	ins	ins	ins	..	ss	ss	insn	ss	ssx	ins
Tetraethylammonium iodide	..	..	..	ins	ins	..	ins	ins	insn	ins	ins	ss
Tetraethyl lead	∞	∞	..	∞	..	.	∞	..	..	..	..	.
Tetrahydronaphthalene	vs	vs	..	∞	..	..	∞	..	∞	..	..	.
Tetramethyldiaminobenzophenone	vs	vs	..	0.6	ss	ssx	ss	ss	ssx	ssx	ssx	ss
Tetraphenyl lead	..	..	..	..	..	..	ssx	..	..	ssx	..	..
Tetraphenylmethane	..	..	..	ss	ss	ss	ssx	ssx	ssx	ssx	ssx	ss
Thymol	vs	vs	vs	es	es	es	es	es	vs	es	es	vs
***o*-Tolidine**	vs	..	..	s	ss	ssx	s	ss	ssx	s	s	vs
Toluene	∞	∞	∞	..	..	..	..	.	∞	..	.	
***p*-Toluenesulfonamide**	..	..	..	vs	ss	vs	vs+	s	ssx	vs	s	s
***p*-Toluidine**	s	s	..	es	vs+	..	es	vs+	sx	es	es	vs
Trichlorogallein	..	..	ss	..	..	..	..	..	..	..	.	.
2,4,6-Trinitroaniline	ins	..	es	..	..	..	..	..	..	..		..
1,3,5-Trinitrobenzene	ss	vs	..	es	ss	sp	s	ss	ss	s	s	vs
2,4,6-Trinitrotoluene	ss	vs	..	s	ss	sp	vs	ss	ss	s	s	s
Triphenylmethane	ss	vs	..	25	s	sx	s	s	ss	s	s	..
Triphenylselenonium iodide	..	..	..	..	..	..	ssn	..	..	ssn	..	.
Tyrosine	ins	ins	..	ss	ins	ins	ss	ins	ins	ss	ins	..
Urea	ss	ss	vs	ins	ins	..	ss	ins	ins	ss	ss	s
Uric acid	ins	ins	ins	..	..	..	..	..	insn	insn	..	ins
Wax, carnauba	..	..	..	ss	..	..	..	..	..	..	..	..
Wax, Japan	..	..	..	vs	..	..	..	..	..	..	..	..
***m*-Xylene**	vs	vs	∞	..	..	..	..	.	..	..	..	
1,3,5-Xylenol	s	..	..	es	vs+	..	es	vs	vs	es	es	..
Xylose (crude)	ins	ins	..	es	..	..	s+	..	..	s	..	..
Zinc stearate	..	..	..	ss	ins	ss	vs?	ss	ins	s?	s	..

tives prepared therefrom which exercise a solvent or gelatinizing function upon the cellulose esters and cellulose ethers. And reasoning from analogy, many of those found applicable in the older and more firmly established pyroxylin and acetylcellulose arts, will be found equally applicable when combined with the etherified celluloses.

As a suitable plasticizing group for both ethylcellulose and acetylcellulose, G. Schneider and C. Dreyfus[1] have described acetyl-, propionyl- and butyryl-chlor(or brom)aniline, while benzylaniline with triphenylguanidine or carbazole has been detailed by L. Rosenthal, E. Messmer and R. Hebermehl[2]. Chloraniline, chloracetanilid, methyl-, ethyl- and benzyl-aniline, or -*o*-toluidine or -naphthylamine, monoethylaniline and the group formyl-, ethoxyallyl-, acetyl- and benzoyl-ethylaniline form the mono- or poly-halogen derivatives of primary amines and their acyl compounds put forward by Chemische Fabrik Weiler-ter-Meer[3], who include also specially purified acetyldiphenylamine and acetylmethylaniline[4], which is claimed to be substantially inodorous and unaffected by light. As supple-inducing components for cellulose esters[5], diphenylamine, butylaniline, *m*-nitraniline, and *m*-nitro-*p*-toluidine have been specified.

Acid derivatives of primary aromatic amines have proven useful camphor substitutes in the plastic industry[6], such as acetyldiphenylamine, acetylphenyltolylamine and

1. Can. P. 317330.
2. D. R. P. 538110; abst. C. A. 1932, **26**, 1782; Chem. Zentr. 1932, I, 1010.
3. E. P. 15435, 1904; abst. J. S. C. I. 1905, **24**, 686. E. P. 16271, 1906; J. S. C. I. 1907, **26**, 989. F. P. 341556; J. S. C. I. 1904, **23**, 880. F. P. 377671; C. A. 1907, **1**, 2831; J. S. C. I. 1907, **26**, 1064; Mon. Sci. 1908, (4), **68**, 145. Can. P. 103036. Belg. P. 194836. See E. P. 12863, 22662, 1901; 2817, 1905.
4. Chemische Fabrik vorm. Weiler-ter-Meer, F. P. 341556, 377671.
5. W. Baldsiefen and T. Rogers, U. S. P. 1675631; abst. Plastics, 1928, **4**, #12, 688.
6. Deutsche Celluloidfabr., E. P. 12863, 1902; abst. J. S. C. I. 1902, **21**, 494. F. P. 312086, 312087; Mon. Sci. 1902, **58**, 194. D. R. P. 80776; abst. Jahr. Chem. 1895, **48**, 1361; Wag. Jahr. 1895, **41**, 1058. D. R. P. 132371; abst. Mon. Sci. 1902, **58**, 194; Wag. Jahr. 1902, **48**, II, 594; Jahr. Chem. 1902, **55**, 1057. See E. P. 16271, 1906.

acetylphenylnaphthylamine. Ethylaniline in alcohol is a ready solvent for acetylcellulose and ethyl- and benzyl-cellulose. As a cellulose ester stabilizer, *m*-amidobenzenesulfoazodiphenylamine and the sodium salt thereof have been patented[1]. The Compagnie Francaise du Celluloid[2], taking monoacetylethylaniline as a type, have described a series of 60 compounds in which acetyl is replaced by propionyl, butyryl and valeryl, the ethyl is substituted by methyl, propyl, butyl and amyl, and the aniline by toluidine or xylidine as cellulose ester thermoplasticizers. *o*-Toluylenemethenylamidine, ethylethenyltrichloramidine and methylethenyltrichloramidine[3] are representatives of amidines derivable from *o*-diamido-compounds of the aromatic series. The above three gelatinize nitrocellulose, and the first member (and probably the other two) dissolves the cellulose ethers in alcoholic solution.

Certain amidines from *o*-diamines as *o*-toluylenemethylenediamine, ethylethenyl- and methylethenyl-trichloramidine are claimed to be efficient colloidants for cellulose esters[4] and to be practically inodorous. Alkyl derivatives of aromatic amines as formanilid m. pt. 46°, *o*-acetphenetidin m. pt. 70°, *o*-acettoluid m. pt. 107°, *p*-acetphenetidin m. pt. 133°, *p*-acettoluid m. pt. 147°, and benzanilid m. pt. 161° constitute another series of plastifiers, which include also their brom- and nitro- substituents, as brombenzanilid or nitrobenzanilid[5]. Aniline, toluidine and

1. E. Lajoanio, F. P. 452154.
2. F. P. 427804; abst. C. A. 1912, **6**, 2315; J. S. C. I. 1911, **30**, 1051; Mon. Sci. 1913, **79**, 32; 1913, **78**, 392; Chem. Ztg. Rep. 1912, **36**, 111; Kunst. 1911, **1**, 398. F. P. 440955; abst. J. S. C. I. 1912, **31**, 812; Mon. Sci. 1914, **81**, 14; Kunst. 1912, **2**, 355.
3. C. Schraube and E. Laudien, U. S. P. 892899; abst. J. S. C. I. 1908, **27**, 828.
4. Badische Anilin und Soda-Fabrik, E. P. 10228, 1906; abst. C. A. 1907, **1**, 801; J. S. C. I. 1906, **25**, 866. E. P. 10228-A, 1906; abst. J. S. C. I. 1906, **25**, 1064. F. P. 366106; abst. C. A. 1907, **1**, 2960; J. S. C. I. 1906, **25**, 1001. D. R. P. 180126; abst. C. A. 1907, **1**, 2203; J. S. C. I. 1907, **26**, 1064; J. C. S. 1907, **92**, i, 973; Zts. ang. Chem. 1907, **20**, 1541; Chem. Zentr. 1907, I, 1473; Jahr. Chem. 1905-08, II, 991; Chem. Ztg. Rep. 1907, **31**, 77; Wag. Jahr. 1907, **53**, II, 562. Aust. P. 32175. See D. R. P. 80776, 176474.
5. R. Schüpphaus, E. P. 21331, 1894. D. R. P. 80776.

xylidine all dissolve acetone-soluble acetylcellulose directly, the solvent avidity decreasing with increasing molecular magnitude. Dimethylaniline alone is valueless for acetyl-, ethyl- or benzyl-cellulose solutions. Aniline oil[1], dimethylaniline[2], acetyldiphenylamine and tricresyl phosphate[3], aniline, toluidine, dimethylaniline, cresol and pyridine[4], and diacetylaniline or formylacetyl-*o*-toluidine[5] are employed as plasticizers primarily with the acetylcelluloses.

Formylethylacetanilid[6] with nitrocellulose is said to lower the water-sensitivity and raise the crystal-turbidity of a lacquer prepared therefrom, while chloraniline assisted by tritolyl phosphate[7] constitutes the thermoplastic composition of G. Schneider. Diphenylamine dissolved in acetone and combined with acetylcellulose represents the plastic of W. Lindsay[8]; while E. Farrow lowers the viscosity of a cellulose ether solution by the addition thereto of this same amine[9]. For instance, the addition of 1/70th of the weight of diphenylamine to methyl acetate produces an ethylcellulose in which the viscosity lowers 15-20% on standing. The viscosity of a cellulose ether solution may be similarly attenuated by the addition thereof of tribenzylamine in about the same proportion[10]. A mixture of dibenzylamine and methyl acetate will dissolve at least 20% of its weight of water-insoluble ethylcellulose[11]. Analogous

1. Commercial Products Co., Aust. P. 45594.
2. J. Walter, Zts. ang. Chem. 1911, **24**, 62; abst; Zts. Chem. Ind. Koll, 1912, **10**, 110.
3. E. Franquet, F. P. 312817; abst. J. S. C. I. 1902, **21**, 134; Mon. Sci. 1903, (4), **59**, 12.
4. Imperial Chemical Industries, Ltd., F. P. 681177; abst. Chim. et Ind. 1932, **27**, #3, 653; Chem. Zentr. 1930, II, 802.
5. G. Racky, D. R. P. 391873; abst. J. S. C. I. 1924, **43**, 553-B; Plastics, 1925, **1**, 26.
6. Chemische Fabriken vorm. Weiler-ter-Meer, D. R. P. 343182; abst. Chem. Zentr. 1922, II, 101.
7. Can. P. 317330; abst. C. A. 1932, **26**, 1406.
8. U. S. P. 1199798; abst. C. A. 1916, **10**, 3159; J. S. C. I. 1916, **35**, 1215.
9. U. S. P. 1494475; abst. C. A. 1924, **18**, 2249; J. S. C. I. 1924, **43**, 593-B; Chem. Zentr. 1924, II, 2623; Kunst. 1925, **15**, 164.
10. E. Farrow, U. S. P. 1494473; abst. C. A. 1924, **18**, 2249; J. S. C. I. 1924, **43**, 593-B; Chem. Zentr. 1924, II, 2304; Kunst. 1925, **15**, 164.

in action are the di- and tri-benzylin of W. Triggs[1] (see p. 203, n. 1).

Benzamide in methyl acetate or methyl alcohol[2] both dissolves and lowers the viscosity of an ethylcellulose solution. Ethylbenzylaniline[3] which alone is practically devoid of solvency for the cellulose ethers, in the presence of methyl alcohol or methyl acetate, will dissolve from 20-25% of its weight of highly etherified ethylcellulose. Dimethylaniline in the presence of methyl or ethyl alcohols or acetates will dissolve on heating up to 35% of its weight of a low viscosity ethylcellulose non-swellable in water[4], while benzylaniline aided by acetone[5] performs an analogous function with the higher esterified, partially hydrated acetylcelluloses. Acetylchloraniline, propionyl- or butyryl-chloraniline with arylsulfonamides or arylsulfonanilids[6] colloid methyl-ethyl- and benzyl-cellulose, and in addition reduce the inflammability.

2.3-Oxynaphthoic acid anilid, a weakly yellowish substance of m. pt. 241°, is a direct cellulose acetate plasticizer, difficultly soluble in alcohols and esters, but readily so in ketones. In the use of aniline and its homologues in the fabrication of celluloid substitutes[7], and to dissolve cellulose ethers[8] and esters[9], it must be remembered that the vapors are decidedly toxic, and that the effect upon the human organism is cumulative. Ethyl-, methylacetyl-, acetylbenzoyl-, ethylbenzoyl-*o*-toluidine, diethyl-, methylben-

11. S. Carroll, U. S. P. 1467092; abst. J. S. C. I. 1923, **42**, 1065-A; Chem. Met. Eng. 1923, **29**, 679.

1. E. P. 349562; abst. Brit. Plastics, 1931, **3**, #30, 271.

2. E. Farrow, U. S. P. 1494471; abst. C. A. 1924, **18**, 2249; J. S. C. I. 1924, **43**, 593-B; Chem. Zentr. 1924, II, 2100; Kunst. 1925, **15**, 164.

3. S. Carroll, U. S. P. 1467096; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.

4. *Ibid.* U. S. P. 1467094; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.

5. T. Murray and C. Staud, U. S. P. 1880465.

6. British Celanese, Ltd., E. P. 312609; abst. C. A. 1930, **24**, 960; J. S. C. I. 1930, **49**, 1023-B; Brit. Plastics, 1930, **2**, #19, 322.

7. U. S. P. 1134527, 1217027, 1245984.

8. U. S. P. 1217027, 1217028, 1389084.

9. U. S. P. 1389084, 1390252.

zoyltrichlor-acetanilid, phthalimide, *b*-naphthyl acetate, benzylideneacetoacetic ester (benzylidene acetoacetate), phenoxy acetate, and chloral hydrate[1] form a group characterized by comparatively low melting points and non-disagreeable odors.

Acetyl-, propionyl-, butyryl-, and valeryl-methyl (or ethyl-, propyl-, butyl- or amyl) aniline represent a group of 20 plastifiants, the lowest member being acetylmethylaniline[2]. Aniline, aniline oil and aniline resinate[3], phthalimide[4], and a series of bodies evolved by the Badische Anilin & Soda Fabrik[5] indicate the importance and potentialities of this group of solvents, extensifiers, and colloiding agents. This group comprehends the use of *as*-trichlorbenzene,

1. P. Benrath, E. Damm and O. Stephani, U. S. P. 1031616; abst. C. A. 1912, **6**, 2687; J. S. C. I. 1912, **31**, 770. Farbenf. vorm. F. Bayer & Co., E. P. 11354, 1909; abst. C. A. 1911, **5**, 1843; J. S. C. I. 1910, **29**, 752, 1096; Chem. Ztg. Rep. 1910, **34**, 562; Mon. Sci. 1913, **78**, 392; J. Soc. Dyers Col. 1910, **26**, 218. E. P. 18193, 1909; abst. J. S. C. I. 1910, **29**, 575; Mon. Sci. 1913, **78**, 392. E. P. 13100, 1910; abst. C. A. 1911, **5**, 3165; J. S. C. I. 1911, **30**, 533; Mon. Sci. 1913, **78**, 392; J. Soc. Dyers Col. 1911, **27**, 161. F. P. 408370; abst. J. S. C. I. 1910, **29**, 624; Mon. Sci. 1913, **78**, 392; J. Soc. Dyers Col. 1910, **26**, 96, 226, 242. First Addn. 12469 to F. P. 408370; abst. J. S. C. I. 1910, **29**, 1299. Second Addn. 12755 to F. P. 408370; abst. J. S. C. I. 1910, **29**, 1371. F. P. 415048; abst. J. S. C. I. 1910, **29**, 1247; J. Soc. Dyers Col. 1910, **26**, 226. F. P. 417027; abst. J. S. C. I. 1910, **29**, 1373; Mon. Sci. 1913, **79**, 20; J. Soc. Dyers Col. 1910, **26**, 242. D. R. P. 227238; abst. Zts. ang. Chem. 1917, **30**, I, 76. D. R. P. 235357; abst. C. A. 1911, **5**, 3129; 1912, **6**, 1960; Zts. ang. Chem. 1911, **24**, 1435; Chem. Zentr. 1911, II, 171; Chem. Ztg. Rep. 1911, **35**, 348; Wag. Jahr. 1911, **57**, II, 97. D. R. P. 235381; abst. C. A. 1912, **6**, 1855; Chem. Ztg. Rep. 1911, **35**, 324; Wag. Jahr. 1911, **57**, II, 533. D. R. P. 240188; abst. C. A. 1912, **6**, 2178; Zts. ang. Chem. 1911, **24**, 2336; Chem. Zentr. 1911, II, 1563; Chem. Ztg. Rep. 1911, **35**, 576; Wag. Jahr. 1911, **57**, II, 468; Chem. Zts. 1911, **10**, No. 2590. D. R. P. 243068; abst. C. A. 1912, **6**, 2310; Zts. ang. Chem. 1912, **25**, 560; Chem. Zentr. 1912, I, 534; Chem. Ztg. Rep. 1912, **36**, 110; Wag. Jahr. 1912, **58**, II, 502; Chem. Zts. 1912, **11**, No. 2739. D. R. P. 248946; abst. C. A. 1912, **6**, 2850; Zts. ang. Chem. 1912, **25**, 1758; Chem. Zentr. 1912, II, 296; Chem. Ztg. Rep. 1912, **36**, 439; Wag. Jahr. 1912, **58**, II, 502. Belg. P. 220225. Swiss P. 48975, 52903, 53888; abst. Chem. Ztg. 1912, **36**, 327. Aust. P. Appl. 4642 of 1910; abst. Chem. Ztg. 1910, **34**, 1362.

2. Cie. Franc. du Celluloid, F. P. 427804; abst. Kunst. 1911, **1**, 398; Chem. Ztg. Rep. 1912, **36**, 111.

3. L. Berend, U. S. P. 952724; abst. J. S. C. I. 1910, **29**, 503.

4. Farbenfabriken vorm. F. Bayer & Co., E. P. 13100, 1910; abst. J. S. C. I. 1911, **30**, 533.

5. E. P. 10228, 1906. F. P. 365297, 366106.

v-tetrachlorbenzene, tri- and tetra-chloramidines, acetyltrichlor-*o*-phenylenediamine (m. pt. 200°), methenyl-, formyl-, methylmethenyl-, and ethylethenyl-trichloramidine and ethylethenyltrichloramidine acetate (m. pt. 98-99°), ethenyltetrachloramidine, and ethyl- and benzyl-ethenyltetrachloramidine, with benzenyl- or methylethenyl-trichloramidine.

A cellulose ether composition has been described by T. Murray and C. Staud[1] in which *p*-anisidine (methoxyaniline, aminoanisole, methoxyaminobenzene, methoxyoxyaniline) is used as a plasticizer affiliated with a low boiling solvent such as acetone. *p*-Anisidine, white crystals, is soluble in alcohol and the usual cellulose ether solvents, melts at 58°, boils 245°, sp. gr. 1.071. It is particularly compatible with cellulose acetate.

Anilids. Carbocyclic and heterocyclic amido and imido compounds have long been favorably employed as gelatinants in the nitrocellulose industry, especially on account of their alkaline character they sometimes act as ant-acids in addition to a well developed plasticizing function. With many of this class, they exhibit their solvency to the maximum only when in the molten condition or when in solution in ethyl alcohol or other low-boiling solvent.

Acetanilid, Phenylacetamide, Antifebrin, Acetanil, Acetylamidobenzene, odorless, crystalline scales, soluble in 190 parts water, 3.4 of alcohol, 17 of ether, 3.7 of chloroform, 4 of acetone and in 47 parts benzene, melts at 113-115° and boils at 295°. It has been used as a solvent for celluloid[2], cellulose ether[3], cellulose nitrate[4], ethylcellulose[5], ethyl starch[6], for manufacture of acetylcellulose varnish[7],

1. U. S. P. 1826668. See p. 295, n. 2.
2. J. McClellan, U. S. P. 1408816.
3. L. Lilienfeld, U. S. P. 1217027, 1217028.
4. W. Rintoul, T. Nolan and O. Strickland, U. S. P. 1392851.
5. L. Lilienfeld, U. S. P. 1188376, 1217027, 1217028.
6. *Ibid.* U. S. P. 1350820.
7. J. Goldsmith, U. S. P. 1298199; abst. C. A. 1919, **13**, 1771; J. S. C. I. 1919, **38**, 472-A. E. P. 124515; abst. J. S. C. I. 1919, **38**, 378-A.

and phonograph record blanks[1]. Acetanilid alone produces an unduly brittle celluloid[2] but in conjunction with urea or substituted ureas, the elasticity is somewhat increased. Acetanilid with phenol, creosote or guaiacol[3], with triacetin, with benzene and alcohol[4], or joined with ethylacetanilid[5] forms stable pyroxylin gelatinants and stabilizers which meet commercial specifications.

A. Romain prepares celluloid-like masses from cellulose ethers by means of an alcoholic solution of acetanilid[6], the cellulose ether solvent composition of E. Farrow[7] being acetanilid with methyl alcohol and acetate, the viscosity of a cellulose ether being lowered by about 15-20% due to the presence of the anilid. The J. Stevens pyroxylin plastifiant is acetanilid in the molten condition[8], or a mixture of acetanilid with one of the *m*-dinitroxylols[9]. Acetanilid, triacetin and triphenyl phosphate is the colloiding combination of K. Wegner[10].

Of the halogen-substituted derivatives[11], acetyl-4-brommethylanilid, acetyl 2.4- or acetyl-3.4-dibromanilid, acetyl-2.4.6-(or -2.4.5-)tribromanilid, diacetyl-2.4.6-tribromanilid, acetyl-2.4.6-tribromomethylanilid, diacetyl-3.5-dibrom-2-toluidide, diacetyl-1.3.6-tribrom-*b*-naphthalid and benzoyl-2.4.6-tribromanilid have been specified. It must be

1. T. Edison, U. S. P. 1158659, 1158660.
2. K. Atsuki, J. Faculty Eng. Tokyo Imp. Univ. 1925, **15**, 291; abst. C. A. 1925, **19**, 1626.
3. H. Cathelineau and A. Fleury, D. R. P. 185240; abst. C. A. 1908, **2**, 349; Mon. Sci. 1910, **73**, 80; 1913, **79**, 392; Chem. Zentr. 1907, II, 1037; Chem. Ztg. Rep. 1907, **31**, 361; Zts. ang. Chem. 1907, **20**, 2177.
4. R. Mitchell, U. S. P. 1398239; abst. C. A. 1922, **16**, 831; J. S. C. I. 1922, **41**, 53-A; Chem. Tech. Ueber. 1922, **46**, 334.
5. Rheinische Gummi-u. Celluloid Fabrik, E. P. 277626.
6. E. P. 238253; abst. J. S. C. I. 1926, **45**, 580-B; Chem. Zentr. 1926, I, 1075.
7. U. S. P. 1548938; abst. C. A. 1925, **19**, 3018; J. S. C. I. 1925, **44**, 843-B; Chem. Zentr. 1926, I, 795; Caout. et Gutta. 1926, **23**, 13315.
8. U. S. P. 510617; abst. J. A. C. S. 1894, **16**, 68.
9. J. Stevens, U. S. P. 553270. See U. S. P. 517987.
10. F. P. 644011; abst. C. A. 1929, **23**, 2569; Chem. Zentr. 1929, I, 1636.
11. Brit. Celanese, Ltd., and A. Daly, E. P. 319073.

remembered that bromine substituted anilids are prone to discolor with age and atmospheric influences. Aniline chloride or acetate and *p*-aminoacetanilid form another combination extolled as especially suitable for nitrocellulose lacquers[1]. A class of nitrocellulose stabilizers especially useful for explosives containing the higher nitrated celluloses[2], nitromannite or nitrostarch, includes formanilid, acet-*o*-toluidid, acet-*p*-anisidid, acet-*b*-naphthalid , benz-*o*-anisidid, phenylacetanilid, ethyl-acet-*b*-naphthalid and phenylacet-*a*-naphthalid. Ethylanilid cresoxyacetate and methyl-*o*-toluidid cresoxyacetate[3], acettoluidid or *p*-acetphenetidin[4], and methylenebenzoyltrichloranilid, *sym*-monomethyltrichloranilid, methylacetyltrichloranilid, monoethyltrichloraniline, monobenzyltrichloraniline, ethylacetyltrichloranilid or benzylacetyltrichloranilid are other analogous bodies which have been proposed which are stated to have innocuous odors, a high stability and to be unaffected by light[5]. *s*-Methyl, *s*-ethyl, *s*-benzyl- and *s*-ethylbenzoyl-acetylchloranilids, m. pt. 89-90°, 50-51°, 61°, and 127° respectively; *as*-methyl-, *as*-ethyl, *s*-benzyl-acetyltetrachloranilid, m. pt. 73°, 96° and 97° respectively, or benzoylbenzyltetrachloranilid constitute the range of nitrogen-containing gelatinants of another process[6]. Acet-*o*- (and *m*-)xylid, although only

1. W. Lams and J. Wyler, U. S. P. 1833526.
2. F. Nathan, W. Rintoul and F. Baker, E. P. 12746, 1912. F. P. 459540. Australian P. 9238, 9239, 9240, 9241.
3. G. Racky, D. R. P. 395703; abst. J. S. C. I. 1925, **44**, 68-B.
4. R. Schüpphaus, U. S. P. 528812. E. P. 21331, 1894; abst. J. S. C. I. 1894, **13**, 1248; Jahr. Chem. 1896, **49**, 1031; Chem. Ztg. 1896, **20**, 330; Ber. 1896, **29**, 452. D. R. P. 80776; abst. Wag. Jahr. 1895, **41**, 1088; Zts. ang. Chem. 1895, **8**, 397; Jahr. Chem. 1895, 1361; Meyer Jahr. 1895, **5**, 341.
5. Badische Anilin & Soda-Fabrik, F. P. 365297. D. R. P. 180208; abst. Chem. Zentr. 1907, I, 1474; J. S. C. I. 1907, **26**, 1064; Zts. ang. Chem. 1907, **20**, 461; Wag. Jahr.. 1907, II, 562. Swiss P. 64710. See D. R. P. 180203.
6. *Ibid.* F. P. 363846; abst. C. A. 1908, **1**, 2957; J. S. C. I. 1906, **25**, 1064. F. P. Addn. 6292 to F. P. 363846. E. P. 8077, 1906; abst. J. S. C. I. 1906, **25**, 608. D. R. P. 176474; abst. C. A. 1907, **1**, 1350; Chem. Zentr. 1907, I, 142; Zts. ang. Chem. 1907, **20**, 369; Chem. Tech. Rep. 1906, **30**, 375; Wag. Jahr. 1906, II, 527. Aust. P. 32175. Swiss P. 59164. Belg. P. 191531. See F. P. 366106.

sparingly soluble in alcohol or acetone, dissolve freely in wood spirit, in which pyroxylin is also soluble[1].

Ethylacettoluide with ethyl lactate or salicylate[2], acetyltrichloranilid or acetyltrichlornitranilid, m. pt. 194°, formyltrichlornitranilid, m. pt. 164°, methylformyltrichlornitroanilid, m. pt. 124-135°, ethylacetyltrichlornitranilid, m. pt. 87-89°, acetyltetrachlornitranilid, m. pt. 201-202°, benzylethenyltetrachloramidine, m. pt. 176-177°, benzoyltrichlornitranilid, m. pt. 205-207°, ethenylethenyltrichloramidine and methylethenyltrichloramidine represent the series which have proven useful gelatinants for nitrocellulose with the amidines derived from aromatic *o*-diamines.

Methylacetanilid, Exalgin, is claimed by J. Schmerber as a partial or complete succedaneum for camphor in the manufacture of celluloid[3], or ethylacetanilid, in the presence of low boiling aliphatic esters[4]. W. Lindsay has recommended a mixture of methyl- or ethyl-acetanilid with ethyl-*p*-toluenesulfonamide[5]; diacetanilid with diphenylamine, borneol or salol (phenyl salicylate)[6]; ethylacetanilid with ethyltoluenesulfonamide[7]; methyl-, ethyl- or tetrachlorethyl-acetanilid in the presence of *p*-ethyltoluenesulfonamide[8]; a mixture of acetanilid with trichlormethylacetanilid[9]; or tetrachlorethyl- or trichlormethyl-acetanilid

1. J. Stevens, U. S. P. 564343.
2. J. Stockhausen, F. P. 428468. D. R. P. 281262. Aust. P. 3192; abst. Kunst. 1912, **2**, 460.
3. F. P. 340266; abst. J. S. C. I. 1904, **23**, 758. J. Schmerber and L. Morane, F. P. 348618; abst. J. S. C. I. 1905, **24**, 512.
4. A. Menger, U. S. P. 1798097; abst. C. A. 1931, **25**, 2823; J. S. C. I. 1932, **51**, 35-B. E. P. 295366; abst. Chem. Zentr. 1928, I, 2770.
5. U. S. P. 1244348; abst. C. A. 1918, **12**, 424; Chem. Zentr. 1918, **42**, 118. See U. S. P. 1041113.
6. W. Lindsay, U. S. P. 1388472; abst. C. A. 1921, **15**, 3950; J. S. C. I. 1921, **40**, 732-A. See U. S. P. 1050065, 1067785.
7. *Ibid.* U. S. P. 1244347; abst. C. A. 1918, **12**, 424; J. S. C. I. 1917, **36**, 1269; Chem. Zentr. 1918, **42**, 118.
8. *Ibid.* U. S. P. 1229487; abst. C. A. 1917, **11**, 2276; J. S. C. I. 1917, **36**, 869.
9. *Ibid.* U. S. P. 1216581; abst. C. A. 1917, **11**, 1301; J. S. C. I. 1917, **36**, 1269; Chem. Ztg. 1918, **42**, 118.
506; Mon. Sci. 1915, **82**, 215.

in conjunction with methyl alcohol[1], all for the production of acetylcellulose plastics.

Ethylacetanilid, Mannol, Manol, in conjunction with tetrahydronaphthol acetate or dibutyl carbonate forms the thermoplasticizing medium of the I. G. Farbenindustrie[2], and methylacetanilid (acetylmethylaniline) with naphthyl acetate[3], the acetylcellulose solubilizing mixture of A. Eichengrün. S. Carroll[4] dissolves the cellulose ethers in general and water-insoluble ethylcellulose in particular, by means of ethylacetanilid conjointly with methyl alcohol and acetate.

Alkyl ethers of acidylated aminophenols form the subject matter of a disclosure of British Celanese, Ltd., for use with methyl- and ethyl-cellulose, comprising acetyl-, propionyl- or butyryl-phenetidin or -anisidin, or propyloxy- or butyloxy-acetanilid[5]. Methylacetanilid, ethylacetanilid, propylacetanilid, butylacetanilid, a liquid solvent of low volatility, and amylacetanilid, a liquid slowly dissolving the cellulose esters[6], comprehends the series of anilids, particulars of which are embodied in the J. Stevens patent. Ethylacetanilid (acetethylanilid) with ethyl ether and benzene[7], and methyl- or ethyl-acetanilid with borneol or isoborneol[8] are other camphor substitute compositions utilizable with the pyroxylins, either alone or associated with the series including dioxydiphenyldimethylmethane, dioxydiphenyl-

1. W. Lindsay, U.S.P. 1041117; abst. C.A. 1912, **6**, 3518; J.S.C.I. 1912, **31**, 1075; Mon. Sci. 1913, **79**, 110; Chem. Ztg. 1912, **36**, 1475.
2. E. P. 300924; abst. C. A. 1929, **23**, 4031; Chem. Zentr. 1929, I, 1529.
3. E. P. 27258, 1910; abst. C. A. 1912, **6**, 1526; J. S. C. I. 1911, **30**, 1112.
4. U. S. P. 1552794; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Caout. et Gutta. 1926, **23**, 13316; Chem. Zentr. 1926, I, 541.
5. E. P. 312606; abst. C. A. 1930, **24**, 960; J. S. C. I. 1930, **49**, 943-B; Silk J. 1929, **6**, #64, 68; Brit. Plastics, 1930, **2**, 278; Chem. Zentr. 1930, II, 2722.
6. J. Stevens, U. S. P. 551456. See U. S. P. 517987.
7. C. F. Boehringer & Soehne, E. P. 354957; abst. J. S. C. I. 1931, **50**, 936-B; Chem. Zentr. 1931, II, 3062.
8. W. Beatty, E. P. 18822, 1912; abst. J. S. C. I. 1913, **32**, 907. F. P. 447645.

methylethylmethane, dioxydiphenyldiethylmethane and dioxyditolyldimethylmethane.

Ethyl- or trichlorethyl-acetanilid with dimethyl phthalate or triacetin[1], trional (diethylsulfonmethylethylmethane), sulfobenzid (diphenylsulfone), sulfonal (diethylsulfondimethylmethane) and sulfocarbanilid (*s*-diphenylthiocarbamide) have been recommended as converting agents for the thermoplasticization of the cellulose nitrates[2]. The cellulose ether film of J. Donohue[3] combines methylacetanilid, acetyl-*p*-phenetidin, diethylcarbanilid, aniline acetate, phenylurea, diphenylethylenediamine, phenylnaphthylamine, benzanilid and *p*-dimethylaminophenyl acetate, preferably in association with methyl alcohol or acetate. Phenylaceto-2-naphthalid[4], thiocarbanilid with diethyl phthalate and chlornaphthalene[5]; and a series embracing benzenesulfonanilid, benzenesulfonmethylanilid, dibenzenesulfonanilid, toluene- and *p*-toluene-sulfoanilid, toluenedisulfonanilid with xylenesulfonamides, all are claimed to dissolve, soften or gelatinize the cellulose ethers, especially ethylcellulose[6].

Antipyrin, Phenazone, Dimethyloxyquinizine, Phenyldimethylpyrazolon, Analgesine, Metozine, Parodyne, Phenylone, Anodynine, Phenylene, Antipyreticum, Oxydimethylquinizine, Pyrazine, Pyrazoline, Sedatine, has been used as a nitrocellulose stabilizer[7] and for the coating of smokeless powder[8].

p-Toluenesulfanilid, Mittel P. I., Abracol, is a white, crystalline solid, m. pt. 103°, readily dissolvable in alcohol,

1. P. Balke and G. Leysieffer, E. P. 154157; abst. C. A. 1921, **15**, 1092. U. S. P. 1468222; abst. C. A. 1923, **17**, 3789.
2. J. Stevens, U. S. P. 572135.
3. U. S. P. 1460097; abst. C. A. 1923, **17**, 2957; J. S. C. I. 1923, **42**, 925-A; Ann. Rep. S. C. I. 1923, **8**, 151; Kunst. 1925, **15**, 43; Faser. 1924, **6**, 11; Chem. Zentr. 1924, I, 267.
4. H. Ryan and J. Drumm, Proc. Roy. Irish Acad. 1918, **34**, 165; abst. J. S. C. I. 1919, **38**, 741-A; J. C. S. 1919, **116**, i, 324.
5. British Celanese, Ltd., E. P. 296675.
6. *Ibid.* E. P. 308708; abst. C. A. 1930, **24**, 498; Chem. Zentr. 1929, II, 1104; Silk J. 1929, **6**, #62, 72.
7. T. Davis, U. S. P. 1439505.
8. E. Ricard, U. S. P. 1440176.

acetone and ether, and is employed as an acetylcellulose softener[1]. Methyl-*p*-toluenesulfanilid melts at 95°. Propyl-, butyl- and amyl-toluenesulfanilids have too high melting points and a limited solubility.

Methylbenzyltrichloraniline and methylbenzoyltrichloraniline[2], trichloraniline[3] and the nitranilines[4], are substituted anilids which have been advanced as specific acetylcellulose colloidants, most of them having previously been patented as nitrocellulose plastic-inducing bodies. The Compagnie Francaise du Celluloid[5] has protected by patent issuance a series of 20 compounds which may be regarded as ethylacetanilid in which ethyl may be replaced by methyl,

1. W. Forse, F. Jones and G. Walters, E. P. 192108; abst. J. S. C. I. 1923, **42**, 305-A. Farbwerke vorm. Meister, Lucius & Brüning, D. R. P. 122272; abst. Chem. Zentr. 1901, II, 328.

2. U. S. P. 1031616; abst. J. S. C. I. 1912, **31**, 770; C. A. 1912, **6**, 2687. E. P. 11354, 1909; abst. J. S. C. I. 1910, **29**, 752. E. P. 18193, 1909; abst. J. S. C. I. 1910, **29**, 575. E. P. 13100, 1910; abst. J. S. C. I. 1911, **30**, 533. F. P. 408370; abst. J. S. C. I. 1910, **29**, 624. First Addn. 12469, dated April 13, 1910, to F. P. 408370; abst. J. S. C. I. 1910, **29**, 1299. Second Addn. dated June 11, 1910, to F. P. 408370; abst. J. S. C. I. 1910, **29**, 1371. Aust. P. 29B, 4642-10, June 21, 1909.

3. A. Eichengruen, U. S. P. 1015156; abst. Mon. Sci. 1912. **77**, 163. E. P. 1441, 1910; abst. J. S. C. I. 1910, **29**, 1005; Chem. Tech. Rep. 1911, **35**, 340. E. P. 18076, 1910; abst. J. S. C. I. 1910, **29**, 1199; first Addn. to E. P. 1441, 1910. F. P. 412797; abst. J. S. C. I. 1910, **29**, 1005; Rev. Chim. Ind. 1910, **21**, 257. First Addn. 12388, dated Mar. 19, 1910, to F. P. 412797; abst. J. S. C. I. 1910, **29**, 1199. D. R. P. 238348; abst. Chem. Ind. 1911, **34**, 637; Chem. Tech. Rep. 1911, **35**, 520; Wag. Jahr. 1911, II, 552; C. A. 1912, **6**, 1672; Chem. Zentr. 1911, II, 1085. Aust. P. 47899. Swiss P. 52115; abst. Kunst. 1912, **2**, 99. Can. P. 129265.

4. E. Knoevenagel, U. S. P. 961241; abst. J. S. C. I. 1910, **29**, 876; Mon. Sci. 1910, (4), **73**, 135. U. S. P. 979966; abst. J. S. C. I. 1911, **30**, 206; Mon. Sci. 1912, **77**, 30. U. S. P. 981574, 1002408; abst. J. S. C. I. 1911, **30**, 126, 1157; Mon. Sci. 1912, **77**, 29. E. P. 24284, 1907; abst. J. S. C. I. 1908, **27**, 1150; Mon. Sci. 1911, (5), **74**, 92. F. P. 383636; abst. J. S. C. I. 1908, **27**, 332. First Addn. dated April 5, 1909, to F. P. 383636; abst. J. S. C. I. 1909, **28**, 1199. E. P. 7743, 1909; abst. J. S. C. I. 1910, **29**, 209. D. R. P. 198008; abst. Chem. Zts. 1908, **7**, 865; Wag. Jahr. 1908, II, 409; Zts. ang. Chem. 1908, **21**, 1471; Chem. Zentr. 1908, I, 1809; Chem. Tech. Rep. 1908, **32**, 379; Bull. Soc. Chim. 1909, (4), **6**, 557. D. R. P. 199559; abst. Zts. ang. Chem. 1908, **21**, 1810; Chem. Zentr. 1908, II, 271; Bull. Soc. Chim. 1909, (4), **6**, 557. D. R. P. 234028; abst. Zts. ang. Chem. 1911, **24**, 1151; Wag. Jahr. 1911, II, 422.

5. F. P. 427804; abst. C. A. 1912, **6**, 2315; J. S. C. I. 1911, **30**, 1051; Chem. Tech. Rep. 1912, **36**, 111.

propyl, butyl and amyl, and the acet has been substituted by propionyl, butyl or valeryl radicals, the solvent efficiency being augmented by dilution with acetone.

Ureas. Urea, the substituted urea esters have been employed primarily in the pyroxylin industry, fulfilling the double function of stabilizer by virtue of the ant-acid properties coupled with a colloiding and dissolving action. They have been used less frequently in connection with the plasticization and stabilization of the cellulose acetates. Recent investigations as yet unpublished, indicate that this class of bodies is destined to play an important role in connection with development of technical applications of the cellulose ethers, by virtue of the fact that they combine solvency in combination with the aliphatic alcohols and esters simultaneously with a well defined preservative function.

Urea, Carbamide, Carbonyldiamide, white crystals, m. pt. 131-133°, sp. gr. 1.32-1.33 at 4°. As a stabilizer and colloiding agent for pyroxylin, urea with triacetin[1], camphor and *sec*-butyl acetate, propionate, caproate; methyl acetone and methylethyl ketone[2]; urea and alcohol[3]; urea, boric acid, methyl acetone and triphenyl phosphate[4]; and urea with acetanilid[5] indicates the range of supplementary bodies incorporated with the urea.

In connection with plasticizing and stabilizing acetylcellulose, W. Lindsay has recommended triphenyl phosphate, urea and acetylene tetrachloride[6]; urea and diphenylamine[7]; urea, trichlorphenol, diacetic ether, benzoic ether and acetodichlorhydrin[8]; urea, triphenyl phos-

1. J. Kessler, U. S. P. 1456782; abst. C. A. 1923, **17**, 2505; J. S. C. I. 1923, **42**, 712-A.
2. W. Lindsay, U. S. P. 1538861; abst. Chem. Zentr. 1926, I, 2267.
3. R. Schüpphaus, U. S. P. 514838. E. P. 22384, 1893.
4. W. Doerflinger, U. S. P. 1315216; abst. C. A. 1919, **13**, 3028; J. S. C. I. 1919, **38**, 834-A.
5. K. Atsuki, J. Fac. Eng. Tokyo, 1925, **15**, 291.
6. U. S. P. 1133385. E. P. 10795, 1910. F. P. 415518.
7. W. Lindsay, U. S. P. 1199798; abst. C. A. 1916, **10**, 3159; J. S. C. I. 1916, **35**, 1215.
8. *Ibid.* U. S. P. 1319229; abst. C. A. 1920, **14**, 223; J. S. C. I. 1920, **39**, 14-A.

phate and dichlorhydrin[1]; urea, phenyl salicylate (salol), ethyl acetate, diacetic ether and trichlorphenol[2]; urea and triphenyl phosphate[3]; and urea with tricresyl phosphate, diphenylamine, trichlorphenol and chloroform[4]. For molding purposes H. Dreyfus[5] unites urea, methylurea, with xylenealkylsulfonamides, and H. Clarke[6] urea with butyl oxalate, dibutyl sulfone, monochlornaphthalene and fusel oil; or[7] urea and amyl oxalate (diamyl oxalate), butyl or amyl acetate, ethyl propionate or butyrate. Urea, aniline, pyridine, quinoline, glycocoll, quinaldine; urea, phenol, acetone oil, benzyl alcohol, acetate or benzoate, furfural, eugenol, phenol, cresol[8]; urea and triacetin free from lower acetins[9]; urea, with methyl, ethyl, phenyl, *a*- or *b*-naphthyl formyl(or acetyl, or propionyl or benzoyl) salicylates[10]; urea and benzyl benzoate[11]; and urea plus triphenyl phosphate and low boiling solvents synopsizes the main processes which have been advocated from time to time[12]. To prevent shrinkage of acetylcellulose films in develop-

1. W. Lindsay, U. S. P. 1386576; abst. C. A. 1921, **15**, 3906; J. S. C. I. 1921, **40**, 689-A.
2. *Ibid.* U. S. P. 1245476; abst. C. A. 1918, **12**, 424; J. S. C. I. 1918, **37**, 27-A.
3. *Ibid.* U. S. P. 1050065; abst. C. A. 1912, **6**, 889; J. S. C. I. 1913, **32**, 133; Chem. Ztg. 1913, **37**, 228; Chem. Ztg. Rep. 1913, **37**, 195; Kunst. 1913, **3**, 218; Oil, Paint and Drug. Rep. 1913, Jan. 13, 25. F. P. 415517; abst. J. S. C. I. 1910, **29**, 1299; Mon. Sci. 1912, **77**, 9; 1913, **78**, 392; Kunst. 1911, **1**, 73. E. P. 10794, 1910; abst. C. A. 1911, **5**, 3156; J. S. C. I. 1911, **30**, 679; Kunst. 1911, **1**, 356. See also Celluloid Co., D. R. P. 263056.
4. *Ibid.* U. S. P. 1067785; abst. C. A. 1913, **7**, 3025; J. S. C. I. 1913, **32**, 823.
5. E. P. 179208; abst. C. A. 1922, **16**, 3370; J. S. C. I. 1922, **41**, 542-A. F. P. 542740; abst. Chem. Zentr. 1923, II, 1066. U. S. P. 1528291; abst. C. A. 1925, **19**, 1497; J. S. C. I. 1925, **44**, 312-B.
6. U. S. P. 1309981; abst. C. A. 1919, **13**, 2443.
7. H. Clarke, U. S. P. 1309980; abst. C. A. 1919, **13**, 2443.
8. H. Gault, U. S. P. 1394890; abst. C. A. 1922, **16**, 502.
9. J. Kessler, U. S. P. 1360759; abst. J. S. C. I. 1921, **40**, 42-A. E. P. 165439; abst. J. S. C. I. 1922, **41**, 855-A.
10. *Ibid.* U. S. P. 1408095; abst. Caout. et Gutta. 1922, **19**, 11653.
11. W. Lindsay, U. S. P. 1027619; abst. C. A. 1912, **6**, 1989; J. S. C. I. 1912, **31**, 584.
12. *Ibid.* U. S. P. 1045990; abst. C. A. 1913, **7**, 699; J. S. C. I. 1913, **32**, 19; Mon. Sci. 1913, **79**, 110; Chem. Ztg. 1913, **37**, 188; Chem. Ztg. Rep. 1913, **37**, 347. E. P. 10795, 1910; abst. J. S. C. I. 1911, **30**, 205; Mon. Sci. 1913, **79**, 392; Kunst. 1911, **1**, 215. F. P.

ing[1], they are immersed 12-48 hours in water, the process being accelerated by adding to the water a small amount of urea, trimethylamine, aniline, acetamide, phenylacetamide (acetanilid), pyridine, hexamethylenetetramine or benzidine.

Urea, glycerol and methyl phthalate[2]; or urea, thiourea, guanidine, dimethylthiourea, diethylurea or monomethylguanide[3] are two processes involving the stabilization and colloidization of the cellulose ethers, specifically methyl-, ethyl- and benzylcellulose. The Farbenfabriken vorm. F. Bayer & Co.[4] stabilize acetylcellulose solutions in glycerol- and monochlor-hydrins by the addition of relatively small quantities of urea, aliphatic aminoacids, aniline or pyridine.

Urea Esters. Urea acetate[5], benzoate[6], butyrate, formate, nitrate[7], propionate, salicylate[8], valerate, naphthoate and sulfate[9] have been protected by patent issuance as desirable pyroxylin stabilizing and colloidizing bodies, always in conjunction with low boiling active solvents[10]. J. Hamilton[11] recommends the use of urea oxalate.

415518; abst. J. S. C. I. 1910, **29**, 1299; Mon. Sci. 1912, **77**, 9; 1913, **79**, 392; Chem. Ztg. 1910, **34**, 889; Kunst. 1911, **1**, 73. See also Celluloid Co., D. R. P. 263056.

1. L. Weston, E. P. 293269; abst. Chem. Zentr. 1928, II, 2090.
2. M. Paquin and I. G. Farbenindustrie A.-G., D. R. P. 549194; abst. C. A. 1932, **26**, 3919.
3. H. Dreyfus, F. P. 657764. E. P. 315766; abst. C. A. 1930, **24**, 1740; J. S. C. I. 1930, **49**, 1147-B; Brit. Plastics, 1931, **2**, #20, 146; Cellulose, 1930, **1**, #5, 150.
4. E. P. 243722; abst. J. S. C. I. 1926, **45**, 796-B; Rayon, 1926, **2**, #4, 15; Caout. et Gutta. 1926, **23**, 13314.
5. J. Stevens, U. S. P. 589870, 622293, 622294. F. P. 328658, 427804, 440955.
6. *Ibid.* U. S. P. 617450.
7. *Ibid.* U. S. P. 589870, 605931, 612531, 621433, 621434, 622290, 622291. E. P. 9799, 1888. F. P. 199375.
8. *Ibid.* U. S. P. 617450, 621382.
9. *Ibid.* U. S. P. 593787.
10. For other processes employing urea in conjunction with cellulose esters, see U. S. P. 507279, 514838, 589870, 605931, 610615, 610953, 612531, 613400, 614514, 621433, 621434, 622291, 622292, 622293, 622294, 623963, 625684, 996274, 1114981.
11. E. P. 22162, 1896; abst. J. S. C. I. 1896, **15**, 764; 1897, **16**, 716, 825; Chem. Ztg. 1898, **22**, 189; Mon. Sci. 1898, **52**, 178.

Substituted Ureas. Mono- di- and tri-methylurea and -triethylurea in conjunction with nitrocellulose, methyl- or ethyl-cellulose[1], cellulose acetate[2], benzylcellulose[3], or ethylcellulose alone[4], have been described by H. Dreyfus as acceptable plasticizing components, especially in conjunction with benzenemethylethyl-, *o*- and *p*-toluenedimethyl-, *o*- and *p*-methylethyl-, *o*- and *p*-toluenediethyl-, xylenediethyl-, xylenemethylethyl-sulfonamides. Cellulose acetate, methyl or ethyl acetates and the above sulfonamides, to which triphenyl phosphate or tricresyl phosphate may be added[5], or triacetin with the above, indicate some of the solvent permutations possible. Phenyl-, methylphenyl-, methyldiphenyl-, benzyl-, methylbenzyl-, dimethylbenzyl-, naphthyl-, methylnaphthyl-, dinaphthyl-, phenanthryl-, methylphenanthryl-, and dimethylphenanthryl-ureas[6]; benzoylurea[7], diethylmalonylurea (diethylbarbituric acid)[8], substituted urea with urethanes and esters of carbamic acid[9], guanidine, tetraethyl -and trimethyl-am-

1. H. Dreyfus, U. S. P. 1454961; abst. C. A. 1923, **17**, 2362; J. S. C. I. 1923, **42**, 600-A; Chem. Zentr. 1923, IV, 1018; Kunst. 1924, **14**, 43. E. P. 164386; abst. Chem. Zentr. 1921, IV, 883. F. P. 527756; abst. Chem. Zentr. 1922, II, 595.

2. *Ibid.* U. S. P. 1353384; abst. C. A. 1920, **14**, 3792; J. S. C. I. 1920, **39**, 745-A. E. P. 132283; abst. C. A. 1920, **14**, 346; J. S. C. I. 1919, **38**, 896-A. See also E. P. 114304.

3. *Ibid.* U. S. P. 1454960; abst. Chem. Zentr. 1923, IV, 1018. E. P. 164385; abst. Chem. Zentr. 1921, IV, 883. F. P. 527737; abst. Chem. Zentr. 1922, II, 595.

4. *Ibid.* U. S. P. 1454959; abst. Chem. Zentr. 1923, IV, 1018. E. P. 164384; abst. Chem. Zentr. 1921, IV, 883. F. P. 527736; abst. Chem. Zentr. 1922, II, 595. See E. P. 132383, 133353, 154334, 164374.

5. *Ibid.* U. S. P. 1353385; abst. C. A. 1920, **14**, 3793; J. S. C. I. 1920, **39**, 745-A. E. P. 133353; abst. J. S. C. I. 1920, **39**, 14-A. See also E. P. 154334. U. S. P. 1501206, 1508928, 1528291, 1530987.

6. F. Nathan, W. Rintoul and F. Baker, E. P. 12745, 1912.

7. J. Hanns, U. S. P. 1355834.

8. The acetylation of urea to an acetate does not increase the solvent power for hydrated cellulose acetate, nor is urea acetate an auxiliary solvent in conjunction with acetone or tetrachlorethane. Some of the substituted ureas, however, are energetic solvents, specifically diethylmalonyl urea (veronal, diethylbarbituric acid), a white, crystalline powder, m. pt. 191°, and soluble in about 150 parts cold and 12 parts boiling water. Veronal is readily soluble in acetone, and such solutions make useful additions to acetate plastics.

9. W. Rintoul, D. Cross and Nobel's Explosives Co., E. P. 126056; abst. C. A. 1919, **13**, 2280; J. S. C. I. 1919, **38**, 513-A. See E. P. 14655, 14656, 1915.

monium hydroxide and thioureas[1], indicate other similar compounds which have been described as useful combined with the cellulose ethers and esters. The condensate obtained by action of urea with formaldehyde is used with cellulose esters for heavy lacquers and enamels[2], acetylurea and benzoylurea being formed in the reaction. *s*-Bis(hydroxymethyl)urea has been used as a celluloid substitute in admixture with cellulose esters[3], and for incorporation in urea-formaldehyde condensates[4]. Dicyanodiamide with pyroxylin and camphor is said to produce an easily workable thermoplastic body[5].

C. Claessen has described diethyldiphenyl urea and tetraphenyl urea[6]—two bodies which find extensive use as plastifiers and stabilizers. The first is known in the trade as Centralite I or Mollit I, and the second as Centralite II and Mollit II. He has also detailed ethylmethyldiphenylurea. *s*-Diethyldiphenylurea melts at 79°, *as*-diethyldiphenylurea at 54° and tetraphenylurea at 183°. All are insoluble in water but dissolve readily in the usual range of cellulose ether solvents. O. Thieme[7] partially substitutes camphor in celluloids by means of one or more of these bodies. Dimethylphenyltolylurea[8], dimethylurea or diethylurea[9], diethylphenyltolylurea and methylethylphenyl-

1. L. Lilienfeld, U. S. P. 1771460, 1771461, 1771462; abst. C. A. 1930, **24**, 4630.
2. Badische Anilin and Soda Fabrik, D. R. P. 404024; abst. Chem. Zentr. 1925, I, 908. See U. S. P. 1355834.
3. J. Hanns, U. S. P. 1355834.
4. F. Pollak, U. S. P. 1458543. E. P. 171094; abst. Chem. Zentr. 1922, II, 749. F. Pollak and K. Ripper, U. S. P. 1507624; abst. Chem. Zentr. 1925, I, 1455. Swiss P. 104339. F. P. 562320; abst. Chem. Zentr. 1924, II, 1282.
5. Canadian Explosives, Ltd., Can. P. 213268. See U. S. P. 1358653.
6. E. P. 20037, 21493, 1906; 13100, 1910; 24839, 1913; 155778. F. P. 364804, 369797, 410239. U. S. P. 701591, 825143. D. R. P. 163668, 172941, 172966, 172967, 178133, 191454. Belg. P. 190920, 194658. Aust. P. 27060.
7. U. S. P. 831488; abst. C. A. 1907, **1**, 239, 255; Mon. Sci. 1907, **67**, 54.
8. L. Clement and C. Riviere, F. P. 505087; abst. Chim. et Ind. 1921, **6**, 89.
9. T. Davis, U. S. P. 1654114, dedicated to the public; abst. Plastics, 1928, **4**, 438.

tolylurea[1], either alone or accompanied by benzophenone are other analogously acting bodies. Diethyldiphenyl urea alone or with form-*o*-toluide, phenylurethane or phenyl oxamate[2] is alleged to be an especially useful softener for cellulose acetate phonograph records. A. Menger has described a luting in which acetylcellulose is jointly colloidized by diethyldiphenylurea and acetanilid[3], F. Hefti[4] has dilated on the advantages of diethylbromacetylurea as a softening body for the esterified celluloses, and B. Flürscheim[5] has described guanidine nitrate, biguanide nitrate and biguanide. Diurea methylaniline[6], methylurea nitrate[7] and dicyanodiamidine nitrate[8] are other bodies which have been proposed for this purpose.

Pyridine, Quinoline, Acridine. Pyridine is benzene in which one CH has been replaced by N. Quinoline stands in the same relationship to naphthalene, and acridine to anthracene, as does pyridine to benzene. Pyridine and quinoline are liquids, acridine a solid. These bodies and their homologues and analogues are highly basic bodies and combine a weak solvent action with a stabilizing function.

Pyridine has been used by L. Malone[9] as a combined solvent for mixtures of cellulose ethers and esters, and by P. Seel[10] to reduce the viscosity of pyroxylin solutions. L. Lilienfeld[11] has described ethylcellulose and other cellulose ethers dissolvable by pyridine, quinoline and picoline, and

1. J. Desmaroux, Mem. Poudres, 1923, **20**, 70; abst. J. S. C. I. 1923, **42**, 686-A.
2. Columbia Graphophone Co., Ltd., W. Forse, F. Jones, G. Walters, E. P. 192108; abst. C. A. 1923, **17**, 3253.
3. D. R. P. 469189; abst. C. A. 1929, **23**, 1190.
4. E. P. 13433, 1913; abst. J. S. C. I. 1913, **32**, 959.
5. E. P. 24702, 1913; abst. J. S. C. I. 1915, **34**, 818. See E. P. 138371.
6. J. Wallers, Zts. ang. Chem. 1911, **24**, 62.
7. H. Backer, Verslag. Akad. Wetensch. **22**, 770; Rec. trav. chim. Pays-Bas. 1915, **34**, 187; abst. C. A. 1914, **8**, 2346; 1915, **9**, 2383.
8. A. Marin, E. P. 121294; abst. J. S. C. I. 1919, **38**, 698-A. Cf. Cyani. Ges. m. b. H., E. P. 27515, 1903; abst. Arms & Explos. 1905, **13**, 10.
9. U. S. P. 1429153; abst. C. A. 1922, **16**, 3758.
10. U. S. P. 1648509; abst. C. A. 1928, **22**, 500.
11. U. S. P. 1217027; abst. C. A. 1917, **11**, 1545.

also a cellulose ether insulating composition of the above composition[1] with benzylcresyl ether added. The T. Tesse airplane lacquer utilizes cellulose acetate with pyridine, carvol, eugenol, isoeugenol, carvacrol and benzyl alcohol[2], and L. Collardon[3] combines acetylcellulose with casein by means of a solvent mixture of pyridine, aniline or methyl- or dimethyl-aniline.

Pyridine with tetrachlorethane, diphenylamine, dicresyline or benzyl alcohol[4]; or with aniline, quinoline and chlorhydrins[5]; or with tetrachlorethane[6] indicate some of the preferred formulas for placing the cellulose esters in solution. Benzene and methyl alcohol added to pyridine and nitrobenzene[7] is said to be an excellent nitrocellulose dissolvant. J. Chevalet[8] admixes pyridine and ureas with volatile solvent for hydrocellulose acetate lacquers, and A. Dubosc uses pyridine in nitrobenzene as a cellulose formate dissolving body[9]. In the dyeing of cellulose acetate[10] P. Rabe has described processes in which pyridine, methylpyridine (picoline) and low boiling solvents are utilized.

C. Cross and E. Bevan have described cellulose formates readily dissolvable in pyridine and nitrobenzene[11], whereas the cellulose formate of H. Deming was but slightly soluble in pyridine[12]. The nitrocellulose explosive of A. Luck and C. Cross[13] used pyridine as an antacid and gelatinizant. In the production of cellulose acetate[14] and cel-

1. U. S. P. 1563205; abst. C. A. 1926, **20**, 465.
2. U. S. P. 1521056; abst. C. A. 1925, **19**, 739. E. P. 124763; abst. J. S. C. I. 1919, **38**, 319-A.
3. U. S. P. 830493. F. P. 359073. E. P. 22525, 1905.
4. J. See, U. S. P. 1431845; abst. C. A. 1922, **16**, 4308.
5. Farbenfabriken vorm. F. Bayer & Co., E. P. 243722.
6. Debauge et Cie, F. P. 418347; abst. J. S. C. I. 1911, **30**, 96.
7. Köln-Rottweil, D. R. P. 352905.
8. E. P. 266300; abst. C. A. 1928, **22**, 499. D. R. P. 516462; abst. C. A. 1931, **25**, 1993.
9. Caout. et Gutta. 1913, **10**, 6897; abst. C. A. 1913, **7**, 2682.
10. U. S. P. 1517581; abst. C. A. 1925, **19**, 404.
11. J. C. S. 1911, **99**, 1450; abst. C. A. 1911, **5**, 3568; J. S. C. I. 1911, **30**, 1008.
12. J. A. C. S. 1911, **33**, 1519; abst. C. A. 1911, **5**, 3678.
13. D. R. P. 117349; abst. Wag. Jahr. 1901, **47**, I, 492.
14. P. Goissedet, U. S. P. 1357450; abst. C. A. 1921, **15**, 436.

lulose carbamate[1], as well as in the fabrication of celluloid substitutes[2], pyridine has ben utilized to a limited extent. The homologues of pyridine, picoline, lutidine and collidine have been used little, if at all.

Quinoline, Chinoline, Leucoline, has been described as a desirable cellulose ether solvent[3], and for dissolving ethylcellulose and starch ether[4]. Its b. pt. of 232-237° is unduly high compared to its feeble dissolving power. The salts of quinoline, especially the chloride, salicylate, sulfate and sulfocyanide have been tried by us for their solvency with ethylcellulose and benzylcellulose, and found wanting.

Acridine has been patented as a neutralizant in the acetylation of cellulose[5].

Piperidine (hexahydropyridine), a liquid of strongly basic properties boiling at 106°, has been proposed as a solvent and colloiding agent for cellulose acetate[6], in association with acetone. It also is a solvent for methyl-, ethyl- and benzyl-cellulose in this combination.

Toluenesulfonate Compounds. Recently a number of esters and allied compounds of benzene-, toluene- and xylene-sulfonates have been utilized primarily as acetylcellulose plasticizing agents, some of which, at least, form excellent colloidants for the cellulose ethers, especially in association with monohydroxy aliphatic alcohols and their corresponding acetates. A. Schmidt and Farbwerke vorm. Meister, Lucius & Brüning[7] have described such a comprehensive series, embracing the phenyl, tolyl, xylyl, naphthyl, nitronaphthyl, nitrotolyl and alkoxyphenyl (as methyl-, ethyl-, propyl-oxyphenyl) sulfonates of methyl, ethyl, pro-

1. J. Zdanowich, U. S. P. 1445382; abst. C. A. 1923, **17**, 1549.
2. L. Lilienfeld, U. S. P. 1217027. S. Catow, U. S. P. 1245975, 1245984, 1280862.
3. *Ibid.* U. S. P. 1217027, 1217028.
4. *Ibid.* U. S. P. 1188376, 1350820, 1563205.
5. Debauge et Cie, F. P. 418347 and Addn. 15217; abst. J. S. C. I. 1911, **30**, 96; 1912, **31**, 651.
6. T. Murray and C. Staud, U. S. P. 1826667; abst. J. S. C. I. 1932, **51**, 719-B.
7. U. S. P. 758335; abst. J. S. C. I. 1904, **23**, 558. E. P. 25434, 1899; abst. J. S. C. I. 1901, **20**, 62. D. R. P. 122272; abst. Chem. Zentr. 1901, II, 328; Wag. Jahr. 1901, II, 609. Belg. P. 148560.

pyl, phenol, naphthol, cresol, resorcinol and dioxydiphenylmethane, an example being methyl phenylsulfonate. This series of 72 compounds has been found efficient cellulose nitrate and hydrated acetylcellulose plasticizing bodies, usually in conjunction with low boiling solvents. They also have described glyceryl *p*-toluenesulfonate and *p*-toluenesulfamide (*p*-toluenesulfonamide) as especially desirable with cellulose esters for photographic film formation[1]. The latter is known as Camphrosol.

The S. Carroll[2] acetylcellulose composition involves the use of *o*-cresyl *p*-toluenesulfonate, Mittel K P, a brown oil nearly inodorous, a suitable formula being cellulose acetate 100, acetone 400-500, cresyl toluenesulfonate 5-30. Phenyl *p*-toluenesulfonate, Agent P O, a white substance crystallizing in needles and readily soluble in the usual organic solvents, has been combined with acetylcellulose and triphenyl phosphate as a plasticized body[3]. It melts at 93°, with an ester number of 220.

Aqueous methanesulfonic acid[4] at 10-20° is said to be an excellent cellulose solvent. Di- or tri-acetyl-*o,o'*-dimethylol-*p*-cresol *p*-toluenesulfonate[5], m. pt. 63°, has been patented as an efficient acetylcellulose thermoplastic-inducing body. Ethyl *p*-toluenesulfonate, Mittel A. E. F, said to be slightly toxic, is insoluble in water, and plasticizes the higher benzylated celluloses. Ethyl *p*-toluenesulfonate, Agent A E P, melts at 32°, of pleasant odor and readily soluble in the usual organic solvents, has a strong swelling power for the cellulose ethers and for acetylcellulose.

A composition of ethylcellulose with aminonaphthalenesulfonic acid-formaldehyde condensate has been put for-

1. E. P. 25434, 1899; abst. J. S. C. I. 1901, **20**, 62. F. P. 295592.
2. U. S. P. 1560542; abst. C. A. 1926, **20**, 111; J. S. C. I. 1926, **45**, 48-B.
3. G. Schneider, Can. P. 302648; abst. C. A. 1930, **24**, 4597; J. S. C. I. 1930, **49**, 985-B.
4. Soc. des Usines Chim. Rhone-Poulenc, E. P. 326579; abst. J. S. C. I. 1930, **49**, 504-B.
5. Farbwerbe vorm. Meister Lucius & Brüning, D. R. P. 395704; abst. J. S. C. I. 1925, **44**, 68-B; Ann. Rep. S. C. I. 1925, **10**, 155; Chem. Zentr. 1924, II, 2623; Kunst. 1925, **15**, 122.

ward as an efficient component of lacquers[1], and benzenesulfonic acid as a desirable cellulose acetate[2] and cellulose acetonitrate[3] colloiding agent. It has been used in varnish remover formulas[4]. Sulfonated oleic acid[5] may be incorporated with artificial masses to combine plasticity and suppleness, and sodium *iso*propyl or butyl naphthalenesulfonates[6] associated with the cellulose ethers is alleged to impart softness, or these compounds may be used for the pre-treatment of cellulose prior to etherification to increase chemical reactivity. Phenol and naphthol sulfonates[7], and methyl *p*-toluenesulfonate[8] have likewise been recommended for this purpose.

It must be remembered that the amount usable in conjunction with cellulose derivatives is limited on account of proneness to crystallization upon long standing.

Sulfonamides. The sulfonamides, first-cousin to saccharin (*o*-benzoylsulfonamide) are a product of the last decade, developed primarily in an endeavor to impart to the organic cellulose esters the enviable properties conferred by camphor upon the corresponding inorganic esterified celluloses. As a group, they probably are the most important acetylcellulose thermoplasticizing bodies known, and some of the members have proven useful as colloidants and softeners in connection with the etherified celluloses.

The effect of incorporating various arylsulfonamides as plasticizers on some commercially important properties of cellulose acetate lacquers has been examined by T. Cars-

1. L. Lilienfeld, U. S. P. 1505044; abst. C. A. 1924, **18**, 3279.
2. H. Bassett, U. S. P. 1466329; abst. C. A. 1923, **17**, 3789.
3. L. Clement and C. Riviere, U. S. P. 1168164; abst. J. S. C. I. 1916, **35**, 251. See F. P. 449253; abst. J. S. C. I. 1913, **32**, 482.
4. C. Ellis, U. S. P. 1147849.
5. I. G. Farbenindustrie, A.-G., E. P. 336250; abst. J. S. C. I. 1931, **50**, 16-B.
6. *Ibid.* F. P. 642220; abst. C. A. 1929, **23**, 1266.
7. W. Merckens and H. Manissadjian, F. P. 413657; abst. J. S. C. I. 1910, **29**, 1101.
8. A. Eichengrün and T. Becker, U. S. P. 738533; abst. J. S. C. I. 1903, **22**, 1100.

well[1], no relationship being observable between the chemical constitution of these compounds and their "retentivity" in cellulose acetate, but *p*-toluenemethylenesulfonamide has a significantly high value. Replacement of methyl by ethyl tends to increase the elongation and decrease the tensile strength of the films produced. With increasing numbers of methyl groups in the nucleus the tensile strength of the films increases without notable effect on elongation. With the phenyl group attached to nitrogen there is a marked decrease in tensile strength. *p*-Toluenemethylenesulfonamide produced the highest tensile strength of the derivatives examined, which are given in the Table below. Toluenesulfonamide derivatives produced films of greater fastness to light than the corresponding benzene or xylene compounds, but an *N*-phenyl group markedly decreases fastness. The best results in this connection were obtained with *p*-toluenemethylenesulfonamide. Relationships between chemical constitution of the plasticizer, the resistance of films to outdoor exposure were indefinite, except that the sulfonmethyleneamide is superior to simple alkyl derivatives.

Table XXXI. Sulfonamide Derivatives

Derivative	Melting Point		Solubility in		
	Pure Product	Comml. Product	Benzene	Acetone	Alcohol
p-Toluenesulfonamide	137°	137°			
Benzene methylsulfonamide	30-31°	About 30°	Slight	Fair	Slight
Benzene ethylsulfonamide	57-58°	About 45°	All		
p-Toluenemethylsulfonamide	78-79°	About 40°		others	
p-Toluene-ethylsulfonamide	63.2°	About 45°			good
Xylenemethylsulfonamide	.....	Liquid			
p-Toluenesulfonanilid	103°	101-102°			
p-Toluene methylenesulfonamide	.....	70-75°			

Disclosures of Lindsay. The first reference in patent literature to the sulfonamide group is found in a patent granted to W. Lindsay[2], applied for Nov. 6, 1911, and issued

1. Ind. Eng. Chem. 1929, **21**, 1176; abst. C. A. 1930, **24**, 738; J. S. C. I. 1930, **49**, 857-B; Brit. Plastics, 1930, **2**, 100; Rayon Record, 1930, **4**, #5, 283.

2. U. S. P. 1041113; abst. C. A. 1912, **6**, 3517; J. S. C. I. 1912, **31**, 1075.

the year following, in which he listed as nitrocellulose solvents which become active when melted or when dissolved in methyl or ethyl alcohol, toluenesulfonamide, ethyl-*p*-toluenesulfamide, benzenesulfonamide, alone or in conjunction with methyl- or ethyl-acetanilid. He filed an application in 1912 covering the use of *p*-ethyltoluenesulfonamide with triphenyl phosphate to produce plastics of the desired toughness and moldability[1]. *p*-Ethyltoluenesulfonamide with chloroform and methyl or ethyl alcohols[2]; or methyl alcohol and methyl acetate with *p*-ethyltoluenesulfonamide[3]; or with methyl- or tetrachlorethyl-acetanilid[4]; or associated with triphenyl phosphate. Alcohol and benzene[5] are some of the modifications disclosed in order to produce the maximum desirable plasticizing effect with various acetylcelluloses. Ethyl acetate and methyl alcohol[6]; benzene, methyl alcohol and water[7]; epichlorhydrin and ethyl alcohol[8]; methyl alcohol, benzene and water[9]; methyl acetate and methyl alcohol[10]; triphenyl phosphate, epichlorhydrin and methyl alcohol[11][12] chloroform and alcohol[12]; and alcohol and chloroform[13], *all* in association with *p*-ethyl-

1. W. Lindsay, U. S. P. 1188797; abst. C. A. 1916, **10**, 2146; J. S. C. I. 1916, **35**, 887; Chem. Ztg. 1916, **40**, 805.
2. *Ibid.* U. S. P. 1188798; abst. J. S. C. I. 1916, **35**, 887.
3. *Ibid.* U. S. P. 1188799; abst. C. A. 1916, **10**, 2145; J. S. C. I. 1916, **35**, 887.
4. *Ibid.* U. S. P. 1188800; abst. C. A. 1916, **10**, 2145; J. S. C. I. 1916, **35**, 887.
5. *Ibid.* U. S. P. 1199395; abst. C. A. 1916, **10**, 3158; J. S. C. I. 1916, **35**, 1215; Chem. Ztg. 1916, **40**, 1054.
6. *Ibid.* U. S. P. 1203756; abst. C. A. 1917, **11**, 99; J. S. C. I. 1916, **35**, 1256.
7. *Ibid.* U. S. P. 1226339; abst. C. A. 1917, **11**, 2153; J. S. C. I. 1917, **36**, 707.
8. *Ibid.* U. S. P. 1226340; abst. C. A. 1917, **11**, 2153; J. S. C. I. 1917, **36**, 707.
9. *Ibid.* U. S. P. 1226341; abst. C. A. 1917, **11**, 2157; J. S. C. I. 1917, **36**, 707.
10. *Ibid.* U. S. P. 1226342; abst. C. A. 1917, **11**, 2157; Kunst. 1918, **8**, 9.
11. *Ibid.* U. S. P. 1226343; abst. C. A. 1917, **11**, 2157.
12. *Ibid.* U. S. P. 1229485, 1229486; abst. C. A. 1917, **11**, 2276; J. S. C. I. 1917, **36**, 869.
13. *Ibid.* U. S. P. 1244107; abst. C. A. 1918, **12**, 424; J. S. C. I. 1917, **36**, 1269.

toluenesulfonamide for gelatinizing and plasticizing acetylcellulose.

In order to produce cellulose acetate solutions of the desired flowability[1], Lindsay found alcohol 7 parts to chloroform 3, or[2] ethylene chloride and propyl, butyl or amyl alcohols, in conjunction with *p*-ethyltoluenesulfonamide, produced plastics of permanent plasticity and easy of manipulation.

Celanese Researches. H. Dreyfus, on an application filed in 1919, disclosed a process for the manufacture of non-inflammable celluloid using acetylcellulose[3], with mixtures of isomeric xylenemonomethylsulfonamides, xylenedimethylsulfonamides and xylenemonoethylsulfonamides, and described their properties. The same day (April 15, 1919)[4], he published his process for the incorporation of cellulose acetate with low-carbon toluenealkylsulfonamides which are liquid at ordinary temperatures, with monomethylurea, dimethylurea, trimethylurea, monoethylurea, diethylurea and triethylurea. He has described the following compounds[5] as especially suitable for colloidants, by incorporation with the cellulose ethers, especially methyl- and ethyl-cellulose:

Benzenemonomethylsulfonamide. This substance boils at about 180° under 1-2 mm. pressure, is liquid at ordinary temperature and forms a clear, soft jelly at —15°.

Benzenemethylethylsulfonamide. Boils at about 170-

1. W. Lindsay, U. S. P. 1244108; abst. J.S.C.I. 1917, **36**, 1269; Chem. Ztg. 1918, **42**, 178. U. S. P. 1244347, 1244348, 1244349; abst. C. A. 1918, **12**, 424.

2. *Ibid.* U. S. P. 1265217; abst. C. A. 1918, **12**, 1700; J. S. C. I. 1918, **37**, 461-A; Chem. Ztg. 1918, **42**, 494. Cites U. S. P. 1027616.

3. U. S. P. 1353384. E. P. 132283. W. Moss and B. White, U. S. P. 1881219.

4. U. S. P. 1353385; abst. C. A. 1920, **14**, 3793; J. S. C. I. 1920, **39**, 745-A. E. P. 133353; abst. J. S. C. I. 1920, **39**, 14-A.

5. H. Dreyfus, U. S. P. 1454959; abst. C. A. 1923, **17**, 2362; J. S. C. I. 1923, **42**, 600-A; Chem. Zentr. 1923, IV, 1018. E. P. 164384, 164386; abst. C. A. 1922, **16**, 494; J. S. C. I. 1921, **40**, 540-A; Chem. Met. Eng. 1921, **25**, 715; Ann. Rep. S. C. I. 1921, **6**, 139; Chim. et Ind. 1922, **8**, 1081; Chem. Zentr. 1921, IV, 883.

175° under 1-2 mm. pressure, is liquid at ordinary temperature and forms a soft turbid jelly at —25°.

Mixtures of *o*- and *p*-toluenedimethylsulfonamides. Such mixtures boil at about 133-137°, under 1 mm. pressure, are liquid at ordinary temperature, form slightly turbid jelly at —15° and a firm turbid jelly at —20°.

Mixtures of *o*- and *p*-toluenemethylethylsulfonamides. Such mixtures boil at about 188-189° under 1 mm., are liquid at ordinary temperature, form soft, clear jellies at —15° and form clear jellies at —20°.

Mixtures of *o*- and *p*-toluenediethylsulfonamides. Such mixtures boil at about 136-142° under 1 mm., are liquid at ordinary temperature, form soft, clear jelly at —10° and a firm, clear mass at —20°.

o-Toluenedimethylsulfonamide. This substance boils at about 148-152° under 2 mm., is liquid at ordinary temperature, forms a soft, clear jelly at —10° and a firm, clear jelly at —20°.

o-Toluenediethylsulfonamide. This substance boils at about 152-155° under 2 mm., is liquid at ordinary temperature, forms a soft, clear jelly at —5° and a firm, clear jelly at —20°.

Mixtures of isomeric xylenediethylsulfonamides. Such mixtures boil at about 148-154° under 1 mm. pressure, are liquid at ordinary temperature, and form a soft, clear jelly at —5° and a firm, clear jelly at —20°.

Mixtures of isomeric xylenemethylethylsulfonamides. Such mixtures boil at about 155-156° under 1 mm., are liquid at ordinary temperature, form clear, soft jellies at —14° and slightly harder jellies at —20°.

The above toluenesulfonamide compounds have also been patented as benzylcellulose plasticizing bodies[1]. For making celluloid-like materials, it is directed to mix 100

1. H. Dreyfus, U. S. P. 1454960; abst. C. A. 1923, **17**, 2362; J. S. C. I. 1923, **42**, 600-A; Chem. Zentr. 1923, IV, 1018. E. P. 164385; abst. J. S. C. I. 1921, **40**, 540-A; Ann. Rep. S. C. I. 1921, **6**, 139; Chim. et Ind. 1922, **8**, 1081; Chem. Zentr. 1921, IV, 883. Cites U. S. P. 1353384, 1353385. E. P. 154334, 164375, 164377.

parts benzylcellulose with 25 parts benzenemonomethyl-, toluene-*o*-monoethyl-, xylenemonomethyl- or xylenemonoethyl-sulfonamides and about 12 parts triphenyl or tricresyl phosphates, with a low boiling benzylcellulose solvent as benzene, are mixed, rolled and pressed until a homogeneous mass results. The above proportions give a relatively hard, incombustible celluloid-like material, the hardness of which may be increased by reducing the quantity of sulfonamide used. To produce a soft celluloid, it is recommended to use equal weights of benzylcellulose and sulfonamide.

For films and varnishes an 8-10% solution is made of benzylcellulose in benzene, and 10% of one or more of the above sulfonamides dissolved therein. Benzylethylcellulose acts similarly with the sulfonamides. As a nitrocellulose plasticizer, H. Dreyfus has given formulas for incorporation of sulfonamides as above, with pyroxylin in various proportions, with the addition of a nitrogenous compound as methylamine, ethylamine, and mono-, di- and tri-methyl (or ethyl) urea[1]. For plasticizing cellulose acetates[2], it is advised to incorporate mixed isomeric monoethyl- or monomethyl-xylenesulfonamides or *o*- and *p*-monomethyl (or ethyl) toluenesulfonamides with methyl or ethyl, alcohols, and dissolve the cellulose acetate or gelatinize the ester in this mixture. Liquid benzenemonoethylsulfonamide or benzenemethylethylsulfonamide with cellulose acetate is said to produce a soft and readily manipulated plastic body[3],

1. H. Dreyfus, U.S.P. 1454961; abst. C.A. 1923, **17**, 2362; J. S. C. I. 1923, **42**, 600-A; Chem. Zentr. 1923, IV, 1018; Kunst. 1924, **14**, 43.

2. *Ibid.* U. S. P. 1466819; abst. C. A. 1923, **17**, 3789; J. S. C. I. 1923, **42**, 1017-A. E. P. 160225; abst. J. S. C. I. 1921, **40**, 243-A, 296-A; Kunst. 1922, **12**, 7. F. P. 538993; abst. Caout. et Gutta. 1923, **20**, 11686; Chem. Ztg. 1922, **46**, 709. Ital. P. 233180.

3. *Ibid.* U. S. P. 1501206; abst. C. A. 1924, **18**, 2809; J. S. C. I. 1924, **43**, 743-B. E. P. 154334; abst. C. A. 1921, **15**, 1075; Chem. Met. Eng. 1921, **24**, 708; J. S. C. I. 1920, **39**, 839-A; 1921, **40**, 42-A; Chem. Zentr. 1921, II, 575. F. P. 521370; abst. Caout. et Gutta. 1922, **19**, 11194; Chem. Zentr. 1921, IV, 826; Rev. Prod. Chim. 1921, **24**, 712. Ital. P. 220640. See also E. P. 132283, 133353. U. S. P. 1353384, 1353385.

as does mixtures of *o*- and *p*-toluenedimethyl (methylethyl or diethyl) sulfonamide[1].

If the cellulose ester or cellulose ether be finely divided[2], a mixture of toluenesulfonamide with methyl, ethyl, propyl or butyl phthalates is said to produce a celluloid easily manipulable and of high stability.

C. Dreyfus[3] associates cellulose acetate with *p*-toluenesulfonamide in the presence of triacetin, or isomeric xylenemonomethylsulfonamides, while W. Dickie and E. Greenwood[4] treat methyl-, ethyl- and benzyl-cellulose with monomethylxylenesulfonamide (mono oil) camphor, acetone or methyl or ethyl ketone and alkyl acetates. The plastic composition as evolved by G. Schneider[5] involves the addition to acetylcellulose of acetyl-*o*-anisidine, acetyl-, propionyl- or butyryl-anisidine or -phenetidine, to which stearanilid may be added. Combination of methyl-, ethyl- or benzylcellulose in the presence of artificial resins for lacquer manufacture is the eventuation of a patented process granted British Celanese, Ltd.[6], employing monomethylxylenesulfonamide, ethyltoluenesulfonamide, diphenylolpropane and triacetin. They form artificial resins[7] by acting upon these sulfonamide derivatives with formaldehyde, which resins are readily incorporable with the cellulose ethers in the formation of heavy lacquers and varnishes.

The following are illustrations of preferred incorporation of the alkylcelluloses with sulfonamides, as recommended by British Celanese, Ltd.[8]:

1. H. Dreyfus, U.S.P. 1508928; abst. C. A. 1924, **18**, 3719; J. S. C. I. 1924, **43**, 864-B. E. P. 154334; abst. J. S. C. I. 1921, **40**, 42-A. Belg. P. 360796.
2. *Ibid.* E. P. 354860, 354861; abst. J. S. C. I. 1931, **50**, 936-B; Chem. Zentr. 1931, II, 3691.
3. U. S. P. 1595506; abst. C. A. 1926, **20**, 3349; Chem. Zentr. 1927, I, 207. E. P. 215823; abst. C. A. 1924, **18**, 3458; Kunst. 1925, **15**, 144. See F. P. 631344. India P. 13467. Swiss P. 127755.
4. E. P. 360896. Cites E. P. 274841, 314396.
5. Can. P. 317329; abst. C. A. 1932, **26**, 1406.
6. E. P. 359387; abst. Brit. Plastics, 1932, **3**, 482.
7. British Celanese, Ltd., E. P. 315807, 315808.
8. E. P. 312688; abst. C. A. 1930, **24**, 960; Silk J. 1929, **6**, #64, 68; J. S. C. I. 1930, **49**, 985-B; Chem. Zentr. 1930, II, 2722.

1. Ethylcellulose 100 parts ground to 100 mesh, 20-50 parts *p*-toluene-ethylsulfonate (m. pt. 33°), masticated together, the combined powder being directly usable or with effect materials for molding into finished articles.

2. 100 parts ethylcellulose, ground to 100 mesh, are incorporated with 20-50 parts benzenephenylsulfonate, and the powders mixed until homogeneous.

3. 100 parts ethylcellulose are mixed for 2-3 hrs. with 100 parts acetone-alcohol-benzene 2:1:1, and 20-40 parts *p*-toluenephenylsulfonate dissolved in a mixture of acetone and alcohol are then added together with 10-15 parts triphenyl phosphate and the whole kneaded to an indistinguishable mass.

The W. Moss lacquer[1] starts with a methyl-, ethyl- or benzyl-cellulose base to which one or more natural or semi-synthetic resins as manila, acaroid, pontianac, kauri, dammar, rosin or shellac are added, the whole mixed and monomethyltoluenesulfonamide, diphenylol-propane, triacetin and volatile solvents admixed to a flowable solution. Or[2], monomethylxylenesulfonamide or ethyltoluenesulfonamide may be utilized.

Methyl, ethyl and propyl *p*-toluenesulfonates, *p*-toluenesulfamide and *p*-toluenedimethyl(or ethyl or propyl)-amide[3]; ethyl-*p*-toluenesulfonamide[4]; acetyldicyclohexylamine and dicyclohexyltoluenesulfonamide[5]; *p*-toluenesulfamide[6], and the processes of the Celluloid Corporation[7] and A. Caprio[8] show the trend of development in this

1. W. Moss and British Celanese, Ltd., E. P. 307292; abst. C. A. 1929, **23**, 5338; Chem. Zentr. 1929, I, 3152.
2. W. Moss, B. White and British Celanese, Ltd., E. P. 317454; abst. C. A. 1930, **24**, 2292.
3. Cie Paris de Couleurs d'Anilin, F. P. 295592; abst. Mon. Sci. 1901, **57**, 32; Rev. de Chim. Ind. 1900, **11**, 186; Chem. Ztg. 1901, **25**, 139.
4. Cello Products, Inc., Can. P. 264990; abst. Chem. Zentr. 1927, II, 352.
5. Badische Anilin und Soda Fabrik, E. P. 9270, 1914; abst. C. A. 1915, **9**, 2980; J. S. C. I. 1915, **34**, 867.
6. A. Eichengruen and T. Becker, U. S. P. 738533; abst. J. A. C. S. 1904, **26**, 193; Mon. Sci. 1904, **61**, 9.
7. E. P. 368457; abst. J. S. C. I. 1932, **51**, 519-B.
8. U. S. P. 1848158.

class of compounds. In the Caprio invention, *p*-ethyltoluenesulfamide is admixed with cellulose ethers as ethylcellulose, oxanilid, dibutyl tartrate and camphor.

p-Toluenesulfonamide (*p*-Toluenesulfamide, Neucamphrosal, Abracal 789) is readily soluble in acetone, chloroform, ether, ethyl, propyl, butyl and amyl alcohols and acetates, being soluble 20% in water at 9°. The Farbwerke vorm. Meister, Lucius & Brüning[1] have described a

1. E. P. 25434, 1899; abst. J. S. C. I. 1901, **20**, 62. U. S. P. 758335. D. R. P. 122272; abst. Zts. ang. Chem. 1901, **14**, 788; Chem. Zentr. 1902, II, 328; Wag. Jahr. 1901, **47**, I, 609; Mon. Sci. 1901, (4), **57**, 292. Belg. P. 148560 have evolved a series of camphor substitutes in which aromatic sulfo acids of the general type $R\text{-}SO_2A$ are used to partially or wholly replace the camphor. In this formula, R represents an aromatic radical or its substitution product—such, for instance, as phenyl, tolyl, xylyl, naphthyl, nitrophenyl, nitrotolyl, alkyloxyphenyl, etc.—and A indicates either an aliphatic or aromatic ether residue, such as oxyalkyl or residue of mono or polyvalent alcohol—for instance, methyl, ethyl, benzyl, cinnamyl alcohols, etc.—and oxyalphyl or residue of a monovalent or polyvalent phenol, such as phenol, naphthol, cresol, resorcinol, dioxydiphenylmethane, etc., or amido group, which, non-substituted, may be substituted once or twice. This is an exceedingly important group known under the general name of Plastol. The members constituting it are of more interest at the present time than when they were patented, due to the fact that several have been found to be latent solvents of acetylhydrocelluloses and acetyloxycelluloses. The most important of this group are as follows: benzenesulfamid, *p*-toluenesulfamid, *p*-chlorsulfamid, benzenesulfoethylamid, benzene sulfdiethylamid, *p*-toluenesulfoethylamid, *p*-toluenesulfodiethylamid, acetbenzenesulfoamid, acet-*p*-toluenesulfamid, *p*-chlorbenzenesulfanilid, dibenzyl-*p*-chlorbenzenesulfamid, dibenzyl-*p*-toluenesulfamid, dibenzyl-*p*-toluenesulfoimid, benzenesulfanilid, *p*-chlorbenzene sulfanilid, dibenzyl-*p*-chlorbenzenesulfanilid, *p*-toluenesulfoanilid, dibenzyl-*p*-toluenesulfoanilid. Benzenesulfo-methylanilid, -ethylanilid, -*o*-toluid, -*o*-chloranilid, -*o*-phenetidin, -*p*-phenetidin, α-naphthylamin, β-naphthylamin and benzenesulfodiphenylamin, *p*-toluenesulfo-methylanilid, -ethylanilid, -*o*-toluid, -*p*-toluid, -*m*-xylidid, -*p*-chloranilid, -*o*-phenetidin, -*p*-phenetidin, -α-naphthylamin, β-naphthylamin, -diphenylamin, -phenylhydrazin, -acidphenylether, -cresol, -β-naphthol, -α-naphthol, -acidethylester. Benzenesulfoacidphenylether, -*p*-cresol, -β-naphthol; dibenzenesulfo-2.7-dioxynaphthalin, *p*-chlorbenzenesulfo-β-naphthol, di-*p*-sulfo-2.7-dioxynaphthalin, *p*-chlorbenzenesulfanilid, *p*-toluensulfamido acetic acid, *p*-toluenesulfamido ethyl ester; *o*-, *p*-, *m*-amidosulfbenzoic acid; *o*-, *p*-, *m*-sulfamidoethylester. The melting points of these sixty-three compounds are within the range of pyroxylin decomposition with but few exceptions, and the melting point may be materially lowered in a number of instances by mixing two or more in various proportions, as for instance, a mixture of *p*-toluenesulfamid (m. pt. 137°) and *p*-toluenesulfomonoethylamid (m. pt. 58°) gives a series of melting points at any degree between these two extremes.

group of camphor substitutes which contain many members extensively used at the present time, the group embracing substituted aromatic sulfonic acids.

Essential Oils. Terpenes. Many of the natural volatile oils employed in the perfume industry are excellent direct solvents and colloidants of the cellulose ethers, as they have long since been found to gelatinize the nitrocelluloses and cellulose acetates, but their cost is often high and the supply limited from the viewpoint of commercial consumption. However, the point should not be lost sight of that their presence in comparatively low amounts often increases the solvent capacity of the mixture in which they are contained, many times over what is necessary for perfect solvency if the essential oil was not present, and in this fact, their possible interest resides.

J. Stevens[1] found a distinct dissolving propensity for pyroxylin with oils of caraway seed, hyssop, sage, tansy, cloves, wintergreen; acetal, amyl nitrite or nitrate, oils of chamomile, valerian, golden rod, sassafras, anise, cumin, cynae ether, dill, elecampane, fennel seed, eucalyptus, fennel chaff, wormseed, myrtle, laurel, marjoram, peppermint, rue, cinnamon leaves, palmarosa, rosemary, erigeron, or heavy oil of wine[2]. C. Borgmeyer[3] specified synthetic cassia oil, lemongrass oil diluted with amyl acetate[4], and J. Jarvis[5] lavender or clove oil with dammar, mastic and guaiac for nitrocellulose lacquer fabrication.

In conjunction with acetone and methyl or ethyl acetates[6], oil of chamomile, fennel seed, palmarosa or wormseed have also been specified on account of the dissolving power of the esters contained therein. Oils of spearmint, cassia, cherry laurel, melissa (balm), pennyroyal and birch tar[7] have also been included. W. McCaine[8] makes a latent

1. U. S. P. 269341; abst. J. A. C. S. 1892, **14**, 289.
2. J. Stevens, U. S. P. 269345.
3. U. S. P. 502921; abst. J. A. C. S. 1893, **15**, 477.
4. C. Borgmeyer, U. S. P. 502546; abst. J. A. C. S. 1893, **15**, 477.
5. U. S. P. 329313; abst. J. A. C. S. 1885, **7**, 254.
6. J. Stevens, U. S. P. 269343; abst. J. A. C. S. 1892, **14**, 289.
7. *Ibid.* U. S. P. 269340.
8. U. S. P. 262077.

pyroxylin solvent of alcohol with benzene or toluene, then adds sufficient oil of cassia or cinnamon to just clear up the solution. J. Stevens wets the nitrocellulose with oil of caraway seed, hyssop, sage, tansy, cloves or wintergreen, and after standing 12 hours for the solvent latency to develop to the maximum, applies heat and pressure to insure colloiding in the absence of but small amounts of volatile solvents. In a series of patented processes issued to Harvel Corporation[1], oil of acajou nut shells is detailed. Wood oil[2], pinene or camphene[3], turpentine oil[4], Canada balsam[5], camphor oil[6], juniper oil[7], caraway chaff oil[8], cedar leaf oil[9], clove buds oil[10], and oils of tansy, peppermint, red thyme or sassafras with fusel oil[11], form the basis of other cellulose ester solvent processes.

Caraway seed oil "ozonized" to increase its drying powers[12], thymol[13], carvacrol, eugenol and isoeugenol[14], juniper oil[15], terpineol, terpinolene, terpinene and dipentene[16],

1. U. S. P. 1838070, 1838071, 1838072, 1838073, 1838074, 1838075, 1838076, 1838077. E. P. 275574; abst. Chem. Zentr. 1927, II, 2720. D. R. P. 534834; abst. C. A. 1932, **26**, 1119; Chem. Zentr. 1927, II, 2720.
2. W. Haller, D. R. P. 114400. E. P. 24224, 1895.
3. E. Callenberg, F. P. 288640, 1899; 322946, 1902; Addn. Oct. 28, 1902; abst. J. S. C. I. 1903, **22**, 380, 760; Mon. Sci. 1900, **56**, 63; Rev. Chim. Ind. 1899, **10**, 299. D. R. P. 108402. Belg. P. 145542, 1899; abst. Chem. Zentr. 1900, I, 1150; Chem. Tech. Rep. 1900, **39**, 326; Tech. Chem. Jahr. 1899, **22**, 144; Jahr. Chem. 1900, **53**, 614; Meyer Jahr. Chem. 1900, **10**, 322; Wag. Jahr. 1900, **46**, I, 401.
4. G. Kasse, D. R. P. 106334; abst. Chem. Zentr. 1900, I, 698.
5. H. Koller, D. R. P. 66055; abst. Wag. Jahr. 1893, **39**, 1118. G. Koller, Belg. P. 243162.
6. H. Kolf, D. R. P. 62159; abst. Wag. Jahr. 1892, **38**, 377.
7. F. Lehner, U. S. P. 559392. D. R. P. 58508; abst. Wag. Jahr. 1891, **37**, 1112.
8. C. Borgmeyer, U. S. P. 503401; abst. J. A. C. S. 1893, **15**, 477.
9. *Ibid.* U. S. P. 502547; abst. J. A. C. S. 1893, **15**, 447.
10. *Ibid.* U. S. P. 503402; abst. J. A. C. S. 1893, **15**, 477.
11. *Ibid.* U. S. P. 504905; abst. J. A. C. S. 1893, **15**, 593.
12. L. Paget, U. S. P. 507749.
13. F. Gunther, U. S. P. 1412937.
14. T. Tesse, U. S. P. 1521056; abst. J. S. C. I. 1925, **44**, 95-B.
15. A. Christiansen, E. P. 29026, 1913; abst. J. S. C. I. 1914, **33**, 547.
16. A. Tixier and L. Rambaud, E. P. 17135, 1903; abst. J. S. C. I. 1904, **23**, 990. P. Genvresse, Compt. rend. 1901, **132**, 637; abst.

pine oil[1], fenchone[2], dimethylamino-*b*-methylcoumarin[3] and "essence of turpentine"[4], show the expenditure of time and thought which have been expended in the direction of combining these products in usable cellulose ester compositions. Borneol and isoborneol[5], chlorinated turpentine[6], camphor oil[7], and benzyleugenol ether and benzylisoeugenol ether[8], about round out the list.

Borneol, isoborneol, terpineol formate, acetate, butyrate, oxalate, phthalate or salicylate (total 18) have been proposed as cellulose ether solvents. Where the bodies are solid as borneol phthalate, oxalate or salicylate, a volatile solvent is employed therewith, otherwise they are preferably used without dilution[9].

Benzyl or naphthyl dihydrocarvone, the latter boiling at 182-183° at 10 mm., has been described as producing desirable celluloid-like masses with the cellulose esters[10], to which the addition of cyclohexanone, carvone or pulegone in some instances is said to be especially useful. Borneol or isoborneol with benzyl alcohol or butyl phthalate has been

J. S. C. I. 1901, **20**, 503. Compt. rend. 1902, **134**, 360; abst. J. S. C. I. 1902, **21**, 424.

1. I. Humphrey, U. S. P. 1746895; abst. C. A. 1930, **24**, 1753.
2. C. Claessen, E. P. 11365, 1910; abst. J. S. C. I. 1910, **29**, 1084. D. R. P. 163668; abst. Chem. Zentr. 1905, II, 1568.
3. T. Schopper, Gummi-Zeit, 1915, **29**, 1250. Zts. ang. Chem. 1915, **28**, 644; abst. J. S. C. I. 1916, **35**, 356. See also F. Lehmann, F. P. 469925.
4. A. Meygret, U. S. P. 756176; abst. J. S. C. I. 1904, **23**, 445. U. S. P. 776192; abst. J. A. C. S. 1905, **27**-R, 441; Centr. Akk. Techn. 1905, **4**, 199. U. S. P. 776480; abst. J. A. C. S. 1905, **27**-R, 442; J. S. C. I. 1904, **23**, 1223. U. S. P. 779553; abst. J. S. C. I. 1905, **24**, 139; J. A. C. S. 1905, **27**-R, 541. E. P. 1676, 1903; abst. J. S. C. I. 1904, **23**, 119. D. R. P. 152630; abst. Zts. ang. Chem. 1904, **17**, 1215; Jahr. Chem. 1904, **17**, 239.
5. A. Béhal, E. P. 11512, 1905; abst. J. S. C. I. 1905, **24**, 855.
6. E. Callenberg, F. P. 322506; abst. J. S. C. I. 1903, **22**, 377.
7. H. Dreyfus, F. P. 432264; abst. J. S. C. I. 1912, **31**, 24.
8. F. Ach, U. S. P. 487167, 487205; abst. J. A. C. S. 1892, **14**, 390.
9. J. Schindelmeiser, E. P. 283619; abst. J. S. C. I. 1928, **47**, 237-B.
10. B. Szelinski, D. R. P. 202720; abst. Chem. Zentr. 1908, II, 1837; Zts. ang. 1908, **21**, 2428; Chem. Tech. Rep. 1908, **32**, 594; Wag. Jahr. 1908, II, 540.

advocated as a useful cellulose ether solvent combination[1], as shown by the following illustrative formulas:

1. 3 kilos of shredded ethylcellulose are kneaded with 500 gms. benzene, 260 gms. 98% ethyl alcohol and 500 gms. isoborneol for 16 hrs. at 30° in a closed container, sheeted, and after seasoning and pulverizing are pressed into plastic masses at 125-127°.

2. 3 kilos shredded ethylcellulose are mixed with 500 gms. spent oil from camphor manufacture containing chiefly borneol and fenchol and 200 gms. alcohol with 300 gms. benzene. The mass is kneaded in a closed container for 48 hrs. at ordinary temperature, then plasticized in a block press at 115° and cut into sheets at 100°.

Cinnamene or styrolene[2], fenchone[3], terpinene[4], camphene hydrochlorate with acetone[5], a mixture of borneol and isoborneol[6], turpene or camphene chlorides[7], warm terpine hydrate[8], a mixture of fenchol, borneol and acetone[9], bornyl formate, acetate, stearate or phenate[10], borneol alone[11] or with camphor[12], dipentene[13], or a mixture of α-terpineol, terpine hydrate, fenchyl alcohol and camphor[14],

1. I. G. Farbenindustrie, A.-G., Aust. P. 118635; abst. Chem. Zentr. 1930, II, 2854; Kunst. 1931, **21**, 93.
2. F. Matthews, E. P. 16278, 1911; abst. J. S. C. I. 1912, **31**, 694.
3. C. Claessen, U. S. P. 979431; abst. J. S. C. I. 1910, **29**, 1084. E. P. 11365, 1910; abst. C. A. 1911, **5**, 2333; J. S. C. I. 1910, **29**, 1084. F. P. 415737. Can. P. 127966.
4. K. Ohno, E. P. 16978, 1913; abst. J. S. C. I. 1914, **33**, 614.
5. J. Stevens, U. S. P. 552934. See U. S. P. 542692, 543197.
6. A. Behal, U. S. P. 831028; abst. C. A. 1907, **1**, 254; J. S. C. I. 1906, **25**, 1064. E. P. 11512, 1905. F. P. 249970. Belg. P. 184896.
7. O. Nagel, U. S. P. 596662.
8. Cold terpine hydrate is not a solvent of cellulose acetate.
9. I. G. Farbenindustrie, A.-G., E. P. 295940; abst. C. A. 1929, **23**, 2293; J. S. C. I. 1930, **49**, 99-B; Chem. Zentr. 1928, II, 2760. F. P. 659116; abst. C. A. 1929, **23**, 5283.
10. O. Dubosc, F. P. 383478.
11. A. Behal, P. Magnier and C. Tissier, F. P. 349970; abst. J. S. C. I. 1905, **24**, 984. See E. P. 11512, 1905.
12. J. Basler & Co., D. R. P. 185808, 1905; abst. C. A. 1908, **2**, 351.
13. I. Humphrey, U. S. P. 1817561; abst. J. S. C. I. 1932, **51**, 518-B.
14. W. Fermazin, Chem. Ztg. 1931, **55**, 613; abst. Brit. Plastics, 1932, **3**, #32, 102.

are other bodies which have been made the basis of critical study and patent issuance.

The J. Donohue cellulose ether composition combines carvone[1], the chief component of caraway, dill and spearmint oils, with water-insoluble ethylcellulose in the presence of a lower monohydroxy aliphatic alcohol as methyl or ethyl alcohols.

Thymol (1-methyl-4-*iso*propyl-3-hydroxybenzene) has been used as a colloiding agent in combination with cellulose acetate[2], and as a plastic with casein and acetylcellulose[3]. Coumarin (1.2-benzypyrone, *o*-hydroxycinnamic lactone) has been patented as a cellulose nitrate plastic-inducing body[4]. The Farbenfabriken vorm. F. Bayer & Co.[5] has described the preparation of ethoxyacetylborneol, ethoxyacetylsantalol and methoxyacetyl-borneol and -santalol, possible cellulose ether colloidants of value.

Camphor, whose solvent functions laid the basis of the celluloid industry, and which is still "Chairman of the Board" and doyen of plasticizers insofar as nitrocellulose is concerned, has not been equalled in the cellulose acetate industry or in the manipulation of cellulose ether plastics, notwithstanding the feverish thumbing over of the pages of Beilstein for the past double decade, and the reduction to laboratory experimentation of the numberless mental psychoses of those who *dream* and *work* in this industry. The complete answer is still in the future.

The utilization of camphor[6] as a cellulose ether sol-

1. U. S. P. 1552802; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, I, 795; Caout. et Gutta. 1926, **23**, 13316.

2. W. Walker, U. S. P. 774713; abst. J. S. C. I. 1904, **23**, 1159; Mon. Sci. 1905, (4), **62**, 50.

3. H. Cathelineau and A. Fleury, D. R. P. 185241, Addn. to D. R. P. 185240; abst. Mon. Sci. 1910, (4), **72**, 76; Chem. Zentr. 1907, II, 1819; Chem. Ztg. Rep. 1907, **31**, 396; Wag. Jahr. 1907, 563.

4. J. Stevens, U. S. P. 269342. 5. F. P. 367057.

6. U. S. P. 91377, 97454, 105338, 136953, 209570, 246891, 265337, 267343, 304229, 311203, 375952, 410204, 417202, 428654, 463039, 471422, 478543, 517987, 542692, 543197, 552209, 552934, 552935, 553270, 555596, 561624, 564343, 566349, 568106, 572135, 595355, 596662, 597144, 602797, 607554, 612066, 612067, 612553, 615319, 631295, 697790, 729990,

vent[1] and plasticizer[2], especially for the plasticization of ethylcellulose[3], for recent celluloid manufacturing processes[4] and celluloid substitute formulas[5], for the dissolving[6] and colloiding[7] of cellulose acetate and cellulose nitrate[8], has found extensive use. In the production of films[9], es-

738533, 831028, 831488, 952724, 996191, 999490, 1012887, 1015155, 1015156, 1027614, 1027615, 1027616, 1041115, 1041116, 1045895, 1076215, 1076216, 1148908, 1153596, 1161063, 1188356, 1188798, 1195040. E. P. 3984, 1868; 3102, 1869; 1865, 1866, 1879; 3072, 1882; 466, 1883; 15121, 1884; 5791, 1887; 10393, 1889; 9315, 1890; 3345, 1891; 2568, 1896; 11927, 1898; 8063, 26075, 1901; 7088, 1902; 4863, 15696, 1903; 12278, 1905; 28376, 1904; 3450, 1906; 4390, 9313, 1908; 4145, 12976, 26657, 27102, 1909; 6519, 10320, 12406, 14586, 29246, 1910; 2145, 15945, 25449, 1911; 3869, 22623, 1912; 2425, 6387, 12804, 16940, 18499, 1913; 2326, 3370, 1914. F. P. 132495, 184548, 319542, 317008, 319724, 319926, 320133, 322506, 324121, 324718, 326576, 328054, 328658, 331819, 352853, 354292, 354942, 360912, 363592, 364690, 365297, 372018, 388097, 402028, 409196, 411126, 415945, 421010, 421843, 421854, 423774, 422819, 459048, 467991. D. R. P. 10210, 17089, 68356, 80776, 86740, 180203, 180204, 180489, 207868, 210519, 220228, 221081, 238348, 249348, 249535, 255692, 281373, 368476, 404024. Aust. P. 17684, 34908, 47890, 47899, 51094, 54512, 72493. Swiss P. 51952, 59164.

1. U. S. P. 1217027, 1217028, 1290794, 1405487, 1431905, 1450714, 1450715, 1450716, 1467091, 1467092, 1467093, 1467094, 1467095, 1467096, 1467097, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105, 1469812, 1469813, 1469816, 1469825, 1469826, 1469862, 1469863.

2. U. S. P. 1389084, 1418413, 1425173, 1429153, 1429188, 1450714, 1450715, 1450716, 1473217, 1473218, 1473219.

3. U. S. P. 1188376, 1217027, 1217028, 1405449, 1405487, 1425173, 1429169, 1432373, 1432374, 1434426, 1434427, 1434432, 1434465, 1437792, 1441143, 1441181, 1444331, 1444406, 1450714, 1450715, 1450716, 1460097, 1460690, 1464169, 1464170, 1467071, 1467091, 1467092, 1467093, 1467094, 1467095, 1467096, 1467097, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105, 1469812, 1469813, 1469816, 1469825, 1469826, 1469862, 1469863, 1473217, 1473218, 1473219.

4. U. S. P. 1233374, 1234450, 1240616, 1370853, 1468820, 1508457, 1508483, 1508484.

5. U. S. P. 1153596, 1156969, 1160063, 1175425, 1185074, 1188356, 1188798, 1188800, 1195040, 1217027, 1234381, 1241738, 1242783, 1331127, 1350820.

6. U. S. P. 1128468, 1244107, 1244108, 1244347, 1244348, 1244349, 1265217, 1290794, 1308803, 1309980, 1463864.

7. U. S. P. 1132384, 1188798, 1188800, 1199800, 1388472, 1408095, 1434634, 1453764.

8. U. S. P. 1128468, 1136248, 1139112, 1173337, 1244107, 1244108, 1244347, 1244348, 1244349, 1290794, 1308803, 1309981, 1321611, 1358653, 1431900, 1432368, 1434453, 1463864, 1510739.

9. U. S. P. 1217027, 1241738, 1242783, 1275063, 1405487, 1425173, 1429153, 1429169, 1434426, 1434427, 1434432, 1437792, 1441181, 1450714, 1450715, 1450716, 1460097, 1473217, 1473218,

pecially for photographic uses[1], as well as in lacquer[2], general plastic[3] and varnish production[4], the commercial utilization of the cellulose esters and to a lesser degree those of the cellulose ethers, are inseparably linked with the application of some form of camphor or utilized in conjunction with ancillary or modifying solvents, extensifiers or softening bodies.

The camphor *substitutes* which have been made the basis of patent application and acceptance for use in conjunction with cellulose esters and ethers, and which have been issued more recently, are grouped in the following list with the respective United States patent number following the name of the product to which patent protection has been granted:

Benzohydrol 1181860
Benzoyloxystearic acid esters 1357876
Benzoylricinoleic acid esters 1357876
Benzyl alcohols 1181860
Benzyl methyl ether 1181859
Butyl aceto-acetate 1437952
Butyl acetyloxystearate 1357876
Butyl acetylricinoleate 1357876
Butyl acetylsalicylate 1408095
Butyl alcohol 1469815
Butyl benzoyloxystearate 1357876
Butyl benzoylricinoleate 1357876
Butyl benzoylsalicylate 1408095
Butyl formyloxystearate 1357876
Butyl formylricinoleate 1357876
Butyl formylsalicylate 1408095
Butyl propionyloxystearate 1357876

1473219, 1479955, 1494469, 1494470, 1494471, 1494472, 1494473, 1494474, 1494475, 1494476, 1505044, 1514283.

1. U. S. P. 1188798, 1188800, 1199799, 1199800, 1229485, 1229486, 1229487, 1342601, 1388472, 1394505, 1405449, 1411708, 1415059, 1429188, 1431900, 1431905, 1432368, 1432373, 1432374, 1434453, 1434454, 1434465, 1441143, 1441181, 1441185, 1450714, 1450715, 1450716, 1467091, 1467092, 1467093, 1467094, 1467095, 1467096, 1467097, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105, 1496198, 1500366, 1518417, 1519659.

2. U. S. P. 1188798, 1188800, 1195673, 1229485, 1229486, 1229487, 1234381, 1241738, 1242592, 1242593, 1350820, 1377677, 1496198, 1505043.

3. U. S. P. 1175425, 1185074, 1188798, 1188800, 1194201, 1199800, 1229485, 1229486, 1229487, 1234381, 1241738, 1317721, 1331127, 1350820, 1367886, 1388472, 1389084, 1402969, 1405487, 1425173, 1437792, 1450714, 1450715, 1450716, 1467091, 1467092, 1467093, 1467094, 1467095, 1467096, 1467097, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105, 1474830, 1505044.

4. U. S. P. 1188789, 1188800, 1195673, 1229485, 1229486, 1229487, 1234381, 1242592, 1242593, 1242783, 1350820, 1429169, 1441181, 1467092, 1467093, 1467094, 1467095, 1467096, 1467097, 1467098, 1467099, 1467100, 1467101, 1467102, 1467103, 1467104, 1467105, 1481485, 1505043.

Butyl propionylricinoleate 1357876
Butyl propionylsalicylate 1408095
Chloral 1508483; 1508484
Chloral alcoholate 1195040; 1508483; 1508484
Chloral hydrate 1195040; 1508483; 1508484
Chlor-benzohydrol 1181860
m-Chlorbenzyl alcohol 1181860
o-Chlorbenzyl alcohol 1181860
p-Chlorbenzyl alcohol 1181860
Chlornaphthalene 1469815
Cresyl benzoate 1160063
Cresyl chlorbenzoate 1160063
Cresyl chlortoluate 1160063
Cresyl diphenyl phosphate 1462306
Cresyl hydroxybenzoate 1160063
Cresyl toluate 1160063
Diethoxy-benzene 1181859
1.2-Diethoxy-benzene 1181859
Dimethoxy-benzene 1181859
Ethoxy-benzyl alcohol 1181860
1-Ethoxy-naphthalene 1181859
2-Ethoxy-naphthalene 1181859
Ethyl aceto-acetate 1437952
Ethyl acetyloxystearate 1357876
Ethyl acetylricinoleate 1357876
Ethyl acetylsalicylate 1408095
Ethyl benzoyloxystearate 1357876
Ethyl benzoylricinoleate 1357876
Ethyl benzoylsalicylate 1408095
Ethyl diacetyloxystearate 1357876
Ethyl dibenzoyloxystearate 1357876
Ethyl diformyloxystearate 1357876
Ethyl dipropionyloxystearate 1357876
Ethyl formyloxystearate 1357876
Ethyl formylricinoleate 1357876
Ethyl formylsalicylate 1408095
Ethyl propionyloxystearate 1357876
Ethyl propionylricinoleate 1357876
Ethyl propionylsalicylate 1408095
Ethyl triacetyloxystearate 1357876
Ethyl tribenzoyloxystearate 1357876
Ethyl triformyloxystearate 1357876
Ethyl tripropionyloxystearate 1357876
Formyloxystearic acid esters 1357876
Formylricinoleic acid esters 1357876
Glyceryl acetyloxystearate 1357876
Glyceryl acetylricinoleate 1357876
Glyceryl benzoyloxystearate 1357876
Glyceryl benzoylricinoleate 1357876
Glyceryl diacetyloxystearate 1357876
Glyceryl dibenzoyloxystearate 1357876
Glyceryl diformyloxystearate 1357876
Glyceryl dipropionyloxystearate 1357876
Glyceryl formyloxystearate 1357876
Glyceryl formylricinoleate 1357876
Glyceryl propionyloxystearate 1357876
Glyceryl propionylricinoleate 1357876
Glyceryl triacetyloxystearate 1357876
Glyceryl tribenzoyloxystearate 1357876
Glyceryl triformyloxystearate 1357876
Glyceryl tripropionyloxystearate 1357876
Manol 1181860
Methoxy-benzyl alcohol 1181860
1-Methoxy-naphthalene 1181859
2-Methoxy-naphthalene 1181859
Methyl acetanilide 1181860
Methyl aceto-acetate 1437952
Methyl acetyloxystearate 1357876
Methyl acetylricinoleate 1357876
Methyl acetylsalicylate 1408095
Methyl benzoyloxystearate 1357876
Methyl benzoylsalicylate 1408095
Methyl diacetyloxystearate 1357876
Methyl dibenzoyloxystearate 1357876
Methyl diformyloxystearate 1357876
Methyl dipropionyloxystearate 1357876
Methyl ethyl aceto-acetate 1437952
Methyl formyloxystearate 1357876
Methyl formylricinoleate 1357876
Methyl formylsalicylate 1408095
Methyl propionyloxystearate 1357876
Methyl propionylricinoleate 1357876
Methyl propionylsalicylate 1408095

3-Methyl-5-*iso*-propyl-cyclohexanone 1477691
3-Methyl-5-*iso*-propyl-△-2-cyclohexanone 1477691
Methyl triacetyloxystearate 1357876
Methyl tribenzoyloxystearate 1357876
Methyl triformyloxystearate 1357876
Methyltripropionyloxystearate 1357876
a-Naphthyl acetyloxystearate 1357876
b-Naphthyl acetyloxystearate 1357876
a-Naphthyl acetylricinoleate 1357876
b-Naphthyl acetylricinoleate 1357876
a-Naphthyl acetylsalicylate 1408095
b-Naphthyl acetylsalicylate 1408095
a-Naphthylbenzoyloxystearate 1357876
b-Naphthyl benzoyloxystearate 1357876
a-Naphthyl benzoylricinoleate 1357876
b-Naphthyl benzoylricinoleate 1357876
a-Naphthyl benzoylsalicylate 1408095
b-Naphthyl benzoylsalicylate 1408095
a-Naphthyl formyloxystearate 1357876
b-Naphthyl formyloxystearate 1357876
a-Naphthyl formylricinoleate 1357876
b-Naphthyl formylricinoleate 1357876
a-Naphthyl formylsalicylate 1408095
b-Naphthyl formylsalicylate 1408095
a-Naphthyl propionyloxystearate 1357876
b-Naphthyl propionyloxystearate 1357876
a-Naphthyl propionylricinoleate 1357876
b-Naphthyl propionylricinoleate 1357876
a-Naphthyl propionylsalicylate 1408095
b-Naphthylpropionylsalicylate 1408095
Norcamphor 1169316
Paracoumarone 1191801
Paraindene 1191801
Phenetole 1181859
Phenols, ethers of 1181860
Phenones 1181860
Phenoxy-benzyl alcohol 1181860
Phenyl acetyloxystearate 1357876
Phenyl acetylricinoleate 1357876
Phenyl acetyl salicylate 1408095
Phenyl benzoate 1160063
Phenyl benzoyloxystearate 1357876
Phenyl benzoylricinoleate 1357876
Phenyl benzoylsalicylate 1408095
Phenyl chlorbenzoate 1160063
Phenyl chlortoluate 1160063
Phenyl ether 1181859
Phenyl formyloxystearate 1357876
Phenyl formylricinoleate 1357876
Phenyl formylsalicylate 1408095
Phenyl hydroxybenzoate 1160063
Phenyl propionyloxystearate 1357876
Phenyl propionylricinoleate 1357876
Phenyl propionylsalicylate 1408095
Phenyl salicylate 1193178
Phenyl toluate 1160063
Propionyloxystearic acid esters 1357876
Propionylricinoleic acid esters 1357876
Propyl aceto-acetate 1437952
1-*iso*-Propyl cyclohexan-3-one 1477691
Safrol 1181859
iso-Safrol 1181859
Sodium benzoate 1477691
Sodium *m*-hydroxybenzoate 1477691
Sodium salicylate 1477691
Tribenzyl phosphate 1370853
Triphenyl phosphate 1181860; 1193178; 1469815

Resins and Waxes. Of the cellulose derivatives, all are insoluble in natural and synthetic resins, insofar as aware, except the cellulose ethers of a high degree of etherification.

As direct solvents neither the resins nor waxy bodies exercise an important function in the exploitation of etherized celluloses. Wool fat or lanolin, used by A. Kennedy[1] as a waterproof material, is claimed as a direct dissolvant of ethylcellulose (see p. 19), also a useful adjunct in cellulose ester compositions[2]. Rosin[3], resin and castor oil[4], polymers of coumarone and indene[5], kauri and dammar resins[6], glycerol-phthalic anhydride condensates[7], ceresin, Japan wax, carnauba wax, beeswax[8], ketone-phenol-aldehyde resins[9] and congo copal benzyl ester[10] are a few of the combinations which have been incorporated with cellulose esters and ethers. Shellac, mastic and acaroid[11], benzene-, toluene- and xylene-sulfonamide-formaldehyde resins[12], dammar with linseed oil[13], butyl, amyl and methylamyl ricinoleate, abietate and laurate[14]; glyceryl, sorbitol and pentaerythritol succinate, maleate, adipate, diglycollate and oxalate[15]; aromatic dibasic condensates with hydroxyalkyl ethers[16], copal[17], glycerol-phthalic anhydride tung oil resins[18] are synoptical of the range involved.

1. U. S. P. 587096.
2. See U. S. P. 587096, 587097, 1217027. E. P. 17602, 1897; 127615, 127678.
3. C. Gillet, F. P. 352853; abst. C. A. 1907, **1**, 1497.
4. *Ibid.* F. P. 382350; abst. J. S. C. I. 1908, **27**, 244.
5. F. Lehmann, U. S. P. 1191801.
6. J. McClelland, U. S. P. 366231.
7. British Thomson-Houston Co., Ltd., H. Warren and A. Ward, E. P. 303915; abst. C. A. 1929, **23**, 4582. Allgemeine Elektrizitats, E. P. 312923; abst. C. A. 1930, **24**, 980.
8. Wolff & Co., R. Weingand and F. Spiecker, E. P. 309017; abst. C. A. 1930, **24**, 515.
9. British Celanese, Ltd., E. P. 299781; abst. J. S. C. I. 1930, **49**, 571-B.
10. J. Alles, D. R. P. 513541; abst. C. A. 1931, **25**, 1993.
11. Zuehl & Eisemann, D. R. P. 177778. See also D. R. P. 128956, 139589.
12. British Celanese, Ltd., E. P. 342144; abst. J. S. C. I. 1931, **50**, 357-B.
13. L. Blumer, Chem. Fabr., D. R. P. 504018; abst. C. A. 1930, **24**, 5517.
14. I. G. Farbenind., A.-G., E. P. 330910; abst. C. A. 1930, **24**, 6040.
15. *Ibid.* E. P. 330909; abst. C. A. 1930, **24**, 6040.
16. *Ibid.* E. P. 322466, 322537, 322538, 322539, 322540, 322541, 322542; abst. J. S. C. I. 1930, **49**, 157-B.
17. J. Bonnaud, E. P. 8063, 1901; abst. J. S. C. I. 1902, **21**, 487.
18. H. Weber, U. S. P. 1690515; abst. J. S. C. I. 1929, **48**, 168-B.

Ethylcellulose with the resin from glycerol and phthalic acid or glyceryl mono- or di-linoleate or ricinoleate, or colophony glyceride with hydroxyethyl linoleate, or benzylcellulose with glyceryl palmitate or maleate, constitute a lacquer with the addition of volatile solvents said to be especially efficacious as a priming composition[1]. Coumarone resin with tetrachlorethane[2], gamboge[3], dammar resin[4], benzoin[5], shellac[6], anhydroformaldehyde-aniline[7], amber[8], beeswax[9], and balsams[10] have all been proposed, and details of manipulation are contained in the respective patents cited.

Benzene-, toluene- and xylene-sulfonamide-formaldehyde resin[11] with cellulose ethers, especially in the company of glycol ether or derivatives, have been brought forth by British Celanese, Ltd. Artificial resins from alkylene oxides upon abietic acid as glycol abietate[12], the use of dimethylol urea[13], urea and thiourea condensation products[14], acrolein-urea condensates[15], or *pp'*-diaminodiphenylurea and 4.4'-di-

1. I. G. Farbenind., E. P. 330895; abst. Brit. Plastics, 1930, **2**, #18, 129.
2. F. Lehmann and J. Stocker, U. S. P. 1191801; abst. C. A. 1916, **10**, 2299; J. S. C. I. 1916, **35**, 924. F. P. 469925; abst. J. S. C. I. 1915, **34**, 25.
3. J. Fichtmueller, U. S. P. 984805; abst. C. A. 1911, **5**, 1527. See U. S. P. 976994. Can. P. 131434.
4. J. McClelland, U. S. P. 366231; abst. J. A. C. S. 1887, **9**, 158.
5. O. Egner, U. S. P. 1202495; abst. C. A. 1917, **11**, 216.
6. W. Dux, D. R. P. 551093; abst. C. A. 1932, **26**, 4487. E. P. 350764; abst. C. A. 1932, **26**, 3124.
7. U. S. P. 1168626, Re-14087, 1188439, 1216265, 1216266, 1217115, 1228428.
8. U. S. P. 1199798, 1245476, 1263284, 1396075.
9. L. Lilienfeld, U. S. P. 1217027. K. Weber, U. S. P. 1442917.
10. L. Lilienfeld, U. S. P. 1188376, 1505043, 1505044.
11. E. P. 342144; abst. J. S. C. I. 1931, **50**, 357-B.
12. I. G. Farbenind., E. P. 328190; abst. C. A. 1930, **24**, 5518. F. P. 662603; abst. C. A. 1930, **24**, 516.
13. Pollopas, Ltd., E. C. Baly and E. J. Baly, E. P. 299487. M. Luther and C. Heuck, U. S. P. 1699245; abst. Plastics, 1929, **5**, 513.
14. I. G. Farbenind., E. P. 290192, Addn. to E. P. 278390; abst. J. S. C. I. 1929, **48**, 709-B. British Cyanides, Ltd., and E. Rossiter, E. P. 266028; abst. C. A. 1928, **22**, 505. F. Pollak, Can. P. 276324. F. Lauter, U. S. P. 1633337; abst. J. S. C. I. 1917, **46**, 788-B.
15. A. Gams and G. Widmer, U. S. P. 1654215; abst. Plastics, 1928, **4**, 194.

amino-3.3′-dimethyldiphenylurea[1], indicate the more recent attempts to combine artificial resinous bodies with the cellulose ethers and esters. It is necessary for best results that the urea used should be of high purity[2].

The B. Gaisenband and C. Piestrak[3] process for lacquer manufacture with a cellulose ether base involves the use of tetrahydro-toluene, -xylene, -cymene- and -cumene, hexahydro-toluene, -xylene, -cumene and -cymene, hexyl hydride, amyl hydride with resin oil or condensates. British gum (water-soluble) has been used with ethylcellulose as a thickener in textile applications[4], and combinations with casein[5], dextrin[6], maltodextrin with borax[7] and starch[8] have been described. They are obviously indicated only in preparations with a limited range of usefulness.

T. Bradley[9] has given the densities and refractive indices of some of the more common natural and synthetic resins which have been proposed for combination with the cellulose ethers and esters, his results being as follows: glyceryl phthalate, density 1.389, refractive index, 1.575; ethyleneglycol phthalate, 1.352, 1.57; pentaerythritol phthalate 1.39, 1.584; rezyl II 1.21, 1.573; vinyl acetate polymer 1.15, 1.473; cyclohexanol-formaldehyde resin 1.21, 1.67; rosin grade M 1.069, 1.525; rosin ester 1.095, 1.496; congo

1. I. G. Farbenindustrie, E. P. 254667; abst. C. A. 1927, **21**, 2478.
2. L. Bub, U. S. P. 1659190; abst. C. A. 1928, **22**, 1365. J. Breslauer and C. Goudet, U. S. P. 1630050; abst. C. A. 1927, **21**, 2274. I. G. Farbenindustrie, E. P. 266378; abst. C. A. 1928, **22**, 597. H. v. Euler and E. Brunius, Biochem. Zts. 1927, **183**, 1; abst. C. A. 1927, **21**, 2280. W. Naunton, J. S. C. I. 1926, **45**, 376-T. L. Guglialmelli, A. Novelli, C. Ruiz and C. Anaslasi, Anales asoc. quim. Argentina, 1927, **15**, 337; abst. C. A. 1928, **22**, 3407.
3. F. P. 483316; abst. C. A. 1922, **16**, 4063.
4. L. Lilienfeld, U. S. P. 1505043; abst. C. A. 1924, **18**, 3272.
5. H. Ensminger, E. P. 3045, 1903; abst. J. S. C. I. 1904, **23**, 202.
6. Rheinische Gummi und Zelluloidfabrik, D. R. P. 168497.
7. Soc. Indust. de Celluloid, D. R. P. 221081.
8. *Ibid.* F. P. 319542, 407846. D. R. P. 141310; abst. Wag. Jahr. 1903, **49**, II, 569. D. R. P. 221081; abst. C. A. 1910, **3**, 2732.
9. Ind. Eng. Chem. Anal. Ed. 1931, **3**, 304; abst. C. A. 1931, **25**, 4722; Brit. Plastics, 1931, **3**, #29, 67.

hard amber 1.059, 1.545; manilla hard 1.072, 1.544; manilla ester 1.09, 1.506; congo ester 1.076, 1.506; sandarac 1.078, 1.545; mastic 1.07, 1.536; pontianac 1.068, 1.545; East India gum 1.087, 1.537; kauri grade 303 1.043, 1.565; shellac orange 1.152, 1.516; shellac bleached 1.11, 1.534; polyvinyl acetate 1.19 density.

Esterified Oils. Nitrated and acetated vegetable oils have been used to a quite limited extent in conjunction with cellulose compounds as solvents and gelatinants. Acetylated castor oil[1], nitrated soy bean, cottonseed, olive, linseed, sperm, corn and castor oils with nitrocellulose form the essence of the B. Goldsmith process[2], while W. Reid and E. Earle[3] specify nitrolinolein and nitroricinolein for the same purpose. This formed the basis of the coating material known as Velvril[4]. Nitrated castor oil with nitrocellulose amalgamated with pyroxylin by the interposition of low boiling solvents[5], constitutes the coating mixture of E. Kingscote and P. Square.

Proteids. Compositions of albumen with the cellulose ethers have been described[6], and albumen has been used in celluloid substitutes[7] and as a cellulose dispersing and colloiding agent[8]. The proteid from beans has been incorporated with nitrocellulose for thermoplastic compositions[9], and formylated albumen[10] has been used for imitation celluloids, but lacks the thermoplasticity so important in celluloid combinations. Maizin, a proteid from corn, is recommended for the partial replacement of camphor in nitrocellulose plastics[11].

1. Imperial Chemical Industries, Ltd., E. P. 357670; abst. J. S. C. I. 1931, **50**, 1106-B; Chem. Zentr. 1931, II, 3684.
2. U. S. P. 1152625.
3. D. R. P. 96365.
4. Velvril Co., Ltd., D. R. P. 103726.
5. D. R. P. 113566.
6. L. Lilienfeld, U. S. P. 1217028, 1505043, 1505044.
7. E. Krause, U. S. P. 1319666. H. Bassett, U. S. P. 1360356.
8. H. Plauson, U. S. P. 1458542. Cf. F. P. 404028.
9. S. Satow, U. S. P. 1245975, 1245976, 1245983, 1245984.
10. Societe anonyme l'Oyonnaxienne, F. P. 331819; abst. J. S. C. I. 1903, **22**, 1206; Mon. Sci. 1904, **60**, 69.
11. L. Desvaux and H. Allaire, D. R. P. 207869; abst. Chem. Zentr. 1909, I, 1293. See D. R. P. 144217, 185240, 185241.

Casein made plastic by borax[1], or borax and glycerol[2], and ammonia[3] dissolved in glacial acetic acid[4], have been put forward as desirable adjuncts to camphor in association with pyroxylin to diminish the cost of plastics carrying a high percentage of camphor. Casein hardened with formaldehyde[5], or in combination with boric acid and a small amount of free alkali[6], or the replacement of casein by alkali metal or alkaline earth caseinates, as potassium, sodium, ammonium or calcium caseinates, have also been sanctioned in attempts to minimize plastic production costs by partial elimination of camphor[7].

Agar agar has been patented for use in cellulose ether compositions[8], in explosives[9], and as a leather substitute[10]. N. Hornstein[11] uses agar agar partially indurated by formaldehyde.

Amyloid has been suggested as the initial material for ethyl- and benzyl-cellulose production[12], and has been used in conjunction with nitrocellulose for solid compositions.

By means of the mutual solvent acetic acid, pyroxylin and gelatin have been combined[13], the gelatin being afterwards hardened by the use of formaldehyde[14]. Such compounds have not the resiliency that is imparted to nitro-

1. H. Franquet, D. R. P. 138783; abst. Chem. Zentr. 1903, I, 485.
2. H. Proveux, F. P. 339081; abst. J. S. C. I. 1904, **23**, 1234.
3. Societe Industrielle de Cellulose, F. P. 319926; abst. J. S. C. I. 1902, **21**, 1550.
4. Casein Co. of America, E. P. 23752, 1903.
5. H. Ensminger, E. P. 3045, 1903; abst. J. S. C. I. 1904, **23**, 202. See F. P. 326576.
6. A. Spitaler, D. R. P. 115681; abst. Wag. Jahr. 1900, **46**, II, 567.
7. H. Franquet, D. R. P. 139905; abst. Chem. Zentr. 1903, I, 800. D. R. P. 138783.
8. L. Lilienfeld, U. S. P. 1217028; abst. J. S. C. I. 1917, **36**, 383.
9. J. Bronstein, U. S. P. 1398931.
10. B. Kepner, U. S. P. 1174734. L. Heilbronner, U. S. P. 1387004.
11. F. P. 429166.
12. U. S. P. 1217028, 1473178, 1483738, 1505043.
13. F. Kohl, D. R. P. 114278; abst. Chem. Zentr. 1900, II, 1002.
14. Societe anonyme L'Oyonnaxienne, F. P. 320133; abst. J. S. C. I. 1903, **22**, 104.

cellulose when camphor alone is used. The E. Mestrallet-Petry[1] process combines nitrocellulose with gelatin.

Polysaccharides. Sugars. In the formulation of celluloid masses, especially in those instances where a slight hygroscopicity is desirable or not contra-indicated, the sugars have been employed to a limited extent. The main drawback is their water-solubility, combined with a tendency to absorb moisture. The Rheinische Gummi- u. Celluloidfabrik[2] heat glucose, levulose and lactose under strong pressure with nitrocellulose to partially substitute camphor. Bondet combines glucose with gelatin in plastic aggregates fabrication[3], and pentaerythrite and nitropentaerythrite[3] form the basis of another plastic process. For data on glucose, see pp. 330, 657, 1162, 1178, 1320, 1368; on glucose acetate, see pp. 311, 462; levulose acetate, p. 320.

Saccharose acetate, tetracetate, heptacetate and octoacetate[5] have also been described as plastic inducing bodies in combination with esterized cellulose.

Inflammability Reduction. Several classes of compounds have been introduced into cellulose ester and ether compositions with the primary object of reducing the speed of burning, some of which, although mainly of inorganic composition, exert solvent powers.

Methyl, ethyl, propyl, butyl and amyl silicates[6], sodium tungstate, tin tetrachloride or antimony trichloride[7], borax[8], boric acid[9], strontium lactate[10], fish glue and acacia[11], hy-

1. F. P. 372018; abst. J. S. C. I. 1907, **26**, 430.
2. D. R. P. 140855; abst. J. S. C. I. 1903, **22**, 569; Jahr. Chem. 1903, **56**, 1019; Chem. Zentr. 1903, I, 941. D. R. P. 168497.
3. L. Bondet, F. P. 372599; abst. J. S. C. I. 1907, **26**, 634.
4. Rheinisch-Westfälische Sprengstoff-Aktien-Gesellschaft, D. R. P. 81664.
5. L. Collardon, U. S. P. 830493. Rheinische Gummi u. Celluloidfabrik, D. R. P. 140263.
6. W. Campbell, U. S. P. 794851. E. P. 14293, 1910.
7. Farben. vorm. F. Bayer & Co., D. R. P. 268627, Addn. to D. R. P. 256922; abst. C. A. 1914, **8**, 2060.
8. D. Young and J. Minuto, F. P. 436900.
9. F. Seaton-Snowdon and D. Young, E. P. 28848, 1910; abst. C. A. 1912, **6**, 1526. E. P. 16133, 1912; abst. J. S. C. I. 1912, **31**, 15. F. P. 437411; abst. J. S. C. I. 1912, **31**, 549. F. P. 437473; abst.

pophosphorus acid or barium hypophosphite[1], ethyl sulfate[2] and magnesium chloride and ammonium borate or phosphate or magnesium ammonium phosphate[3] are indicative of the lines in which work has been done. See p. 1372.

Antimony trichloride dissolved in ethyl acetate[4], alcoholic solutions of magnesium chloride or sodium ethyl sulfate dissolved in ethyl ether[5], sodium tungstate with methylated spirit[6], and magnesium chloride with tetrachlorethane[7] are examples of fluid combinations. Barium hydroxide[8], oxychloride[9], or sulfate[10]; ammonium hydroxide[11], chloride[12], bromide[13], carbonate[14], sulfate[15] or phosphate[16]; zinc or calcium chlorides[17], methyl and ethyl chlorides with methyl bromide[18], and calcium sulfate[19] are some of the products tried. Those insoluble in volatile solvents are usable, of course, only in translucent and opaque products.

Cinnamic acid dibromide (cinnamyl dibromide) has recently been described as a useful addition to organic cel-

J. S. C. I. 1912, **31**, 255. Belg. P. 241975. Ital. P. 122890; abst. Chem. Ztg. 1913, **37**, 32.

10. B. Buchstab, D. R. P. 214398; abst. J. S. C. I. 1909, **28**, 1221.
11. G. Woodward, E. P. 9277, 1904. See U. S. P. 1388824.
1. S. Assadas, F. P. 387537; abst. J. S. C. I. 1908, **27**, 873.
2. M. Blancato, U. S. P. 1709056; abst. C. A. 1929, **23**, 2793; Brit. Plastics, 1929, **1**, #2, 72.
3. Titanine, Ltd., T. Ward and J. Fletcher, E. P. 203847; abst. C. A. 1924, **18**, 759. See U. S. P. 1329386, 1393355, 1427941.
4. A. Arent, U. S. P. 1451313; abst. C. A. 1923, **17**, 2050.
5. P. Marino, Belg. P. 215187.
6. C. King and R. Jellicoe, E. P. 24695, 1893.
7. Compagnie Francaise du Celluloid, F. P. 440955; abst. Kunst. 1912, **2**, 460.
8. C. Ellis, U. S. P. 1502945.
9. W. Freeman, U. S. P. 1175425.
10. G. Mowbray, U. S. P. 294661. F. Tone, U. S. P. 1259806.
11. U. S. P. 1245818, 1245976, 1245983, 1245984, 1275324, 1280862, 1427645.
12. H. Judson, U. S. P. 1235037.
13. A. Arent and R. Kuever, U. S. P. 1318523, 1318524.
14. B. von Ehrenthal, U. S. P. 1509273.
15. G. Blenio, U. S. P. 1427941. C. Schwartz, U. S. P. 1398804.
16. U. S. P. 1321708, 1325363, 1329386, 1393355, 1440178.
17. S. Groves and T. Ward, E. P. 128659; abst. C. A. 1919, **13**, 3028; J. S. C. I. 1919, **38**, 518-A.
18. A. Henning, U. S. P. 1393124.
19. U. S. P. 1183201, 1365882, 1493207, 1493209.

lulose derivatives to reduce their inflammability and increase the plasticity.

Flash Points of Solvents. The following are flash points of the 107 more common solvents and diluents used in the cellulose ether and ester industries, taken from a compilation, with modifications, as made by E. v. Mühlendahl[2]:

Acetic acid[3], +44°. Acetone[8], —18°. Allyl alcohol[4], +22°. *i*-Amyl acetate[12], +25°. *i*-Amyl alcohol[8], +44°. *ter*-Amyl alcohol[4], +20°. Amyl salicylate[16], +132°. Aniline[7], +72°. Benzaldehyde[5], +62°. Benzoic acid[5], +121°. Benzol benzene[8], —12°. Benzylacetate[16], +102°. Benzyl alcohol[16], +100°. Benzyl benzoate[15], +148°. Brombenzene[14], +65°. *i*-Butyl acetate[15], +18°. *n*-Butyl acetate[12], +24°. *i*-Butyl alcohol[9],+28°. *n*-Butyl alcohol[8], +38°. *sec*-Butylbenzene[14], +52°. *n*-Butyl formate[9], +18°. Chlorbenzene[5], +29°. Chlorethyl acetate[14], +67°. *m*-Cresol[9], +86°. *o*-Cresol[5], +81°. *p*-Cresol[9], +86°. Cresyl *p*-toluenesulfonate[15], +184°. Cumene[9], +52°. Cyclohexane (Hexahydrobenzene[8], —17°. Cyclohexanol[14], +68°. Cyclohexanone[12], +64°. Δ^2-Cyclohexen-1-on[15], +34°. Cyclohexyl acetate[12], +64°. *di*-Cyclohexyl adipate[15], +196°. Decahydronaphthalene[14], +58°. Dianisidin[5], +206°. Dibenzyl ether[15], +135°. Di-*i*-butyl phthalate[15], +161°. Di-*n*-butyl phthalate[15], +160°. *o*-Dichlorbenzene[14],+77°. *p*-Dichlorbenzene[5], +67°. Dichlorethylene[14], +17°. Diethyl carbonate[16], +25°. Diethyldiphenyl urea[15], +150°. Diethylether[8], —41°. Diethylglycol phthalate[16], +173°. Diethyl phthalate[15], +140°. Dimethylaniline[5], +61°. Dimethyl ether[14], —41°. Dimethylglycol phthalate[16], +187°. Dimethyl phthalate[15], +132°. *m*-Dinitrobenzene[5], +150°. Dinitrochlorbenzene[5], +187°. Diphenylamine[5], +153°. Diphenylmethane[16], +130°. Diphenyloxide[16], +115°. Ethylacetanilid[15], +108°. Ethylacetate[9], —5°. Ethyl alcohol[8], +11°. Ethylbenzene[9], +16°. Ethyl-*n*-butylcarbon-

1. C. Dreyfus and J. Scheidegger, U. S. P. 1884619.
2. Chem. Ztg. 1931, **55**, 557; abst. C. A. 1931, **25**, 5303. Cf. C. A. 1930, **24**, 1526; 1931, **25**, 1106.

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3. F. Gannter, Chem. Techn. Report, 1887, 65.
4. P. Raikow, Chem. Ztg. 1902, **26**, 436.
5. W. Ormandy and E. Craven, Journ. Inst. Petroleum Techn. 1922, **8**, 145.
6. F. Seeligmann and E. Zieke, Handbuch der Lack-und Firnis-Industrie, 3 Ed. 1923, 800.
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CHAPTER XIII

COMMERCIAL APPLICATION OF CELLULOSE ETHERS ARTIFICIAL FILAMENTS AND TEXTILES

The indicated technical uses of the cellulose ethers in the dry or previously undissolved condition are very few, in this respect being similar to the *organic* cellulose esters (acetylcellulose), in contradistinction to the inorganic esters typified by the cellulose nitrates, which have commercial uses in the explosives industry by virtue of their inflammability and propulsive power upon vaporization. Therefore the practical fields proposed for the cellulose ethers are all in connection with the peaceful arts, and as solutions or colloidal masses, both of which have passed through the dissolution or intumescence stage, usually by the use of a proportion of volatile solvents, which are afterwards dissipated. The dependence upon solvents for technical usefulness is the reason that Solvents as a general classification has preceded an enumeration of the application of the cellulose ethers in this work.

This Chapter and the one succeeding aim at chronicling the multitudinous avenues of exploitation which have been proposed, made the basis of patent application and issuance, or expanded from laboratory experimentation to factory production, in those fields where water-solubility coupled with high viscosity, or water-insolubility and solvency in a wide selection of liquids and solid bodies gives rise to transparent bodies—usually pellicles, films of mass aggregates—of great tensile strength and resistance to wear and abrasion, and where an inherent thermoplasticity in conjunction with a plasticity which may be augmented by the addition of certain bodies or coupling agents, gives rise to products desirable in the photographic, plastic, textile, pharmaceutical and other fields. And of these indicated uses, those which have to do with the fabrication of

individual filaments and their combination into aggregates by textile operations form the subject matter of this Chapter.

For the production of artificial filaments, it will be realized from their properties that they may be considered almost ideal raw material, more particularly as they possess to a high degree, those properties which heretofore have been lacking in all artificial silks so far manufactured, such as resistance to water, either hot or cold, and also to alkalis and acids, even at high temperatures. While it is true that these properties taken by themselves are not conclusive as to the suitability of the cellulose ethers for filament formation on a large scale, they yet are dependent also upon such physical properties as luster, softness, feel and whether in dyeing alone or in mixed filaments unsurmountable difficulties arise, and particularly whether the cost of production is too high when prepared on a manufacturing basis. While manufacture of the cellulose ethers may be said to have been firmly established, the formation of artificial filaments therefrom has not as yet become a seasoned industry.

When it is remembered the years that Chardonnet fought for success, and the over twenty years continuous experimentation with acetylcellulose for its emergence to the present comparative state of perfection, the present outlook for the successful exploitation of "ether silk" appears very favorable by virtue of the fact that it possesses properties not attained by any other synthetic filament process. The final thread, of course, is a cellulose ether just as that from cellulose acetate is a cellulose ester, and in sharp contradistinction to the filaments prepared by the viscose, copper-ammonia and nitrocellulose methods, in all of which products the cellulose ethers excel in respect to electric and heat conductivity, permeability to ultra-violet rays, and fastness to light in the dyed fabric.

The subject matter of this Chapter has been roughly divided into ten sections as follows:

Section One. The steps involved in transformation of a cellulose ether solution into finished filament, in 21 numbered topics as follows: Artificial Filaments (page 2066), Preparation of the Spinning Solution (2072), Clarifying the Spinning Solution (2073), Removal of Dissolved Gases (2073), Spinning Operation (2074), Filament Formation by Wet Spinning (2074), Coagulation Baths (2085), Filament Formation by Dry Spinning (2087), Filament Formation by Either Wet or Dry Spinning (2102), Spinning Cellulose Derivatives with Resins (2104), Box Spinning (2106), Cap Spinning (2107), Spinning Nozzles (2108), Regulating Pressure and Flow (2110), Spinning Cells (2111), Stretching and Twisting (2116), Washing and Bleaching Filaments (2119), Lubricating Filaments (2121), Drying Filaments (2122), Winding (2123), Spools (2125), Solvent Recovery (2125).

Section Two. Treatments applied to the formed filaments, or aggregates of filaments in the woven or unwoven stage. Processing (2129), Strengthening Artificial Filaments (2130), Sizing (2136), Conditioning (2143), Loading, Weighting, Mordanting (2144), Waterproofing (2157), Coating (2160), Increasing Heat Resistance (2162), Modifying Luster (2166), Increasing Luster (2168), Preserving Luster (2170), Delustring (2173), Relustring (2198), Mildewproofing (2201), Imparting Scroop (2202), Carbonizing (2203), Wetting (2206), Solubilizing Agents (2210), Swelling and Softening Cellulose Ether Fibers (2214).

Section Three. Operations involved in the dyeing of filaments, filament aggregates (yarns) or textiles and fabrics produced therefrom, or containing a proportion of cellulose ethers. Increasing Affinity for Dyestuffs (2221), Dyeing of Cellulose Ethers (2223), Identification Tints (2230), Direct Dyes (2232), Fastness to Washing (2234), Basic Dyestuffs (2234), Dyeing with Volatile Solvents (2236), Dyeing with Volatile Colors (2238), Dyeing Cellulose Ethers with Lakes (2238), Dyeing and Printing with Vat Colors (2239).

Section Four. Classes of Dyestuffs for Cellulose Ethers according to their chemical constitution and classification. Dyestuffs for Cellulose Ethers and Esters (2245), Azo Colors (2259), Anthrarufins (2281), Dianisidine Group (2282), Indophenols (2282), Naphthalic Acid Types (2283), Phenylamine Dyes (2284), Pyrazolones (2285), Quinones (2285), Thiazoles (2286), Urea Colors (2286), Urethanes (2287), Xanthenes (2287).

Section Five. Dyestuffs used for coloring cellulose ethers and esters by commercial classification of trade names. Altex Dyes (2288), Azonines (2288), Cibacet (2289), Ionamine Colors (2289), Cellit (2290), Duranol (2291), Celatene (2291), Nacellan (2292), Setacyl (2292), S. R. A. Dyes (2293).

Section Six. Dyestuffs applicable to the cellulose ethers producing stated shades upon dyeing. Yellow (2293), Green (2296), Red (2296), Rose (2297), Violet (2297), Blue (2297).

Section Seven. Specific Dyeing Operations and treatment of cellulose ethers preparatory to or after the dyeing operation. Dyeing with Logwood Colors (2298), Black Dyeings on Cellulose Ethers and Esters (2298), Dyeing Processes Involving Saponification (2306), Package Dyeing (2307), Dyeing Composite Fabrics (2308), Immunizing (2313), Producing Resists (2314), Discharge Effects (2316), Stripping Dyestuffs (2319).

Section Eight. Operations upon cellulose ether textiles involving printing, stencilling or similar operations. Printing on Cellulose Dedivatives (2320), Reserve Printing (2326), Color Printing (2327), Warp Printing (2327), Printing Inks (2329), Resist Effects (2330), Effect Threads (2331).

Section Nine. Operations applied to fabrics of or containing cellulose ethers in order to produce specific effects. Producing Woolly Effects (2331), Crepe Effects (2332), Damask Effects (2340), Moire Effects (2341), Pattern Effects on Textiles (2342), Ornamental Effects (2352),

Embossing (2355), Creasing (2357), Weaving (2358), Sealing Edges of Thermoplastic Fabrics (2359), Metallization of Textiles (2361).

Section Ten. Preparation of various textile products from cellulose ether and ester filaments as a finished textile operation. Hollow Filaments (2363), Staple Fiber (2371), Artificial Bristles, Straw, Ribbons (2373), Pile Fabrics, (2378), Milanese Cloth (2380), Preparation of Lace (2381), Elastic Fabric (2382), Hosiery (2382), Electrical Discharge (2383).

Artificial Filaments. Synthetic Silk. Of all the natural fibers, silks are the simplest in structure, the most beautiful and hence most sought after, which undoubtedly accounts for the fact that the output of the natural silk industry has seldom met the demand. The silk worm quietly and without ostentation proceeds to spin out its period of existence, and it is a biological tragedy that having exercised so high a degree of intuitive ingenuity so cunningly and to the best of its ability it perishes in the effort, and the crypt formed becomes the product of its life work and last resting place, if left alone.

You know, there is a certain intriguing and impelling fascination about the subject of *silk*. Its rustle seems to stir up dormant memories of bye-gone but not forgotten days. The social and economic supremacy of one old principality over another in the pre-Christian era was not always measured by man-power, intellectual superiority or artistic attainment, but by the stocks of silks which the country possessed, for then as now, war was possible only when money was forthcoming, and silk was the highest and most desirable form of money in those long past days.

Purple and silk were symbolical of royalty, the insignia of regal splendor and opulence and mundane power. For many centuries the bewitching damsels and aristocratic dames were—if we are to believe recorded history—never so bewitching nor appeared so aristocratic as when arrayed in garments made of silk. And so, down through the pages

of ancient and medieval history have trickled innumerable stories of the swaying of the ruler, and through him the people, by stocks of silk in the warehouse or in the adornment of femininity. And the austere Roman patrician was never so awe-inspiring to the multitude (and probably never so complacent with himself) as when bedecked in those long-flowing robes of *silk.*

Therefore it appears obvious that the artificial silk industry of which the cellulose ethers comprise the youngest member, having the heritage of thousands of years of acquaintance and knowledge as a background with natural silk, should so fire the imagination and offer such alluring potentialities, both from an aesthetic, esoteric and practical viewpoint. And many a story in fact and fiction has been woven with a silken thread therein—some stories mental phantasies, probably most of them based on fact.

It is quite natural that man's mind should turn upon the question of attempts to outwit the silk worm as an artificer of filaments by attempts to produce a substitute synthetically and without the aid of the life-process. It was reasoned that inasmuch as natural silk was round and entirely structureless, being apparently a homogeneous material, it would only be necessary to draw out some other homogeneous liquid into a filament and let it harden in the air to simulate natural silk. Reaumur in 1734 approached the subject first by a minute study of the anatomy of the silk worm extruding glands in an attempt to apply practically the lessons taught by Nature. He demonstrated that silk was the product of a liquid secretion normally located in certain glands on the under side of the body of the silk worm, but was never able to solve why it was that the secretion solidified almost instantly on contact with the air into a filament of such high tenacity. And today we are not much nearer the solution of this particular point than was Reaumur. He sold himself the idea that it was only necessary to impinge into the atmosphere a semi-solid structureless mass preferably containing nitrogen in some

form, and let the atmosphere act upon it to form a merchantable filament, and experimented with various combinations of pitch in endeavors to simulate the fibroin of the silk worm.

Then in 1855, when savants were first aroused as to the possibilities of nitrocellulose by virtue of its success in pharmacy and medicine as an "ether glue" and "liquid cuticle," George Audemars conceived the idea that if he selected the food of the silk worm as initial material for nitration he would produce a collodion, structureless, and probably identical in properties with that elaborated in the silk worm organism, and so he patented a method for manufacturing nitrocellulose by the nitration of mulberry leaves. Theory and fact in this instance did not coincide, the reason being, as we now know it, because he used too volatile solvents, ether and ethyl alcohol. The subject quiesced for over thirty years when, in 1884, Count Hilaire de Chardonnet deposited a private communication with the French Academy of Sciences, which, when opened on November 7, 1887, bore the title "On an Artificial Textile Material Resembling Silk." His first patent issued Nov. 17, 1884[1], and contained a description of a process for preparing nitrocellulose and squirting an ether-alcohol solution thereof through minute orifices into the air, and laid down basic generalizations which in their entirety may be said to constitute the basis of the artificial filament industry of today, insofar as dry-spinning operations are concerned. The industry remained in a more or less adolescent and somnolent condition, until spasmodically improved by advances in solvents or refinements in mechanical appliances—these two factors being primarily responsible for advancement rather than improvements in the basic cellulose material in the ester form. The cellulose acetate filament industry was builded upon nitrocellulose filament information, and its bid for technical supremacy was and is based upon the fundamental fact that in its merchantable form it is still an

1. F. P. 165349.

ester, and not subject to the disadvantages arising from the use of a form of regenerated cellulose as the final filament form, made necessary with nitrocellulose by its inherent inflammability.

And in a manner analagous to the building of the acetylcellulose filament upon the accumulated knowledge of attenuated cellulose nitrate threads, both having first been dissolved in volatile solvent combinations and extruded through microscopic orifices into an evaporative or coagulating medium, now comes the cellulose ethers, having nearly all the desirable characteristics of the organic cellulose esters, and in addition possessing the desirable characteristics in a heightened degree over all spinnable cellulose derivatives both inorganic and organic, of high stability towards heat and chemical reagents, being unaffected by strong alkalis and concentrated acids; of having an inherent thermoplasticity, and of being soluble in a much wider range of organic solvents, solvent combinations and colloiding and plasticizing bodies, than the nitrocelluloses and acetylcelluloses combined. And it is believed, once the tremendous economic significance of these desirable properties is realized, and adjustments made in methods of manipulation and mechanical technic to favor their peculiarities, that, if the raw materials can be produced on a competitive basis with those used in the nitro- and acetyl-cellulose artificial filament art, the industry of filament formation involving the use of cellulose ethers in a very few years will transcend that of all filaments synthetically fabricated in which regeneration to a reconstituted cellulose is not the final product.

At the present moment, however, the art of synthetic filament formation in which information concerning the manipulation of a solution of a cellulose ether into filament form is so new, comparatively speaking, and in contradistinction to the relatively older but analogous cellulose acetate silk industry, that in many of the processes herein described which relate to the manipulation of both cellulose

organic esters and ethers taken as a class, the individual examples embodying illustrations of carrying the process into effect read usually upon an acetylcellulose, but it is to be remembered that both acetyl- and ether-cellulose dissolve in the same general line of organic solvents, and that the formation of these filaments comprises merely projecting the cellulose derivative in the dissolved condition through orifices of predetermined diameter into a medium which will cause the colloid stream to solidify, whether that medium be air or a solution, and it is apparent that basically, processes for synthation of acetylcellulose filaments in their broad conception, are applicable to those of cellulose ethers.

In endeavors to establish every new branch of industry, complex problems arise inherent in the idiosyncrasies of the particular products operated upon, and the industry of cellulose ether filaments and aggregates of those filaments is no exception. Unforeseen defects in the manufactured product result in temporary setbacks; as the culmination of much labor, many stagnations and as yet unexplained anomalies, the basic principles of the various etherized cellulose as applied to filament formation and textile fabrication are rapidly becoming understood, and it is the purpose of this Chapter to indicate the various details of the many manipulative steps which have been advocated in the transformation of dissolved organic cellulose derivatives into acceptable textiles.

The industrial application of the cellulose ethers to the production of filaments is due to L. Lilienfeld who in 1913 disclosed his process for "artificial textile material" manufacture by preparing the cellulose ethers and the production "of threads and filaments" therefrom by means of suitable solvents of which he names a large number (see p. 19, last par.). He dissolved ethylcellulose in a mixture of alcohol and benzene, ethylene trichloride or acetylene dichloride and alcohol, or a mixture of alcohol and ether, "and then spun in the usual manner through fine nozzles or capillary orifices, with or without the admixture of an-

other cellulose derivative as nitrocellulose, acetylcellulose, formylcellulose or the like, or of softening agents as oils, fats or phosphoric esters of the phenols." "The filaments issuing from the nozzles may either be dried immediately or be led through suitable precipitating baths in which the cellulose ethers are insoluble"[1]. This original process was subject to many variations, it having been found that the solubility, viscosity and other properties varied greatly with the degree of etherification and the particular cellulose ethers produced, which in turn were modified by the nature of the alkalicellulose employed and the method of procedure in transforming the alkalicellulose into the particular etherized cellulose required.

In 1924, A. Eichengrün[2] described a non-inflammable homogeneous spinning solution which may be prepared in the cold, obtained by dissolving acetone-soluble cellulose acetate of any degree of acetylation, in a compound solvent comprising methylene chloride in admixture with alcohol or a higher alcohol than ethyl, the solvent mixture components of which may or may not singly be acetylcellulose solvents. Mixtures containing about 30% alcohol or 20% of acetone represent the safe limit for inflammability. Suitable spinning solutions are obtained by dissolving 10 parts cellulose acetate in methylene chloride-alcohol (10:65) with 25 parts alcohol, or a mixture of 65 parts methylene chloride, 7.5 of alcohol and 7.5 of benzene.

In 1922, L. Lilienfeld supplemented his earlier work in the cellulose ether filament field by the employment of an ether insoluble in water at 16°, but which swells or dissolves in water at lower temperatures[3], and which in the water-swollen condition dyes readily with substantive, acid, vat, mordant or basic dyestuffs. For the preparation of the spinning solution the ether is dissolved in an organic

1. L. Lilienfeld, U. S. P. 1217028; abst. C. A. 1917, **11**, 1545; J. S. C. I. 1917, **36**, 383.
2. E. P. 243350; abst. C. A. 1926, **20**, 2823; J. S. C. I. 1927, **46**, 579-B.
3. E. P. 181394; abst. C. A. 1922, **16**, 3759. Can. P. 249776. F. P. 556781. Dan. P. 30791. Norw. P. 37354.

solvent of which a wide range is specified, the filaments after extrusion, being precipitated either by water to which may be incorporated salts, acids, sugar, glycols or glycerol. Instead of water, gasolene, ligroin or petroleum ether is specified. During spinning and precipitation the threads are preferably maintained in a stretched condition, and to render them more resistant to water, treatment with tanning agents is advocated.

The general steps in filament formation comprise dissolving the cellulose ether or ester in a suitable solvent combination, usually pure acetone for facility of solvent recovery, clarification by repeated filtration of the solution, application of a vacuum to the solution in order to remove air bubbles and dissolved air therein, extrusion of the solution at a pre-determined temperature through orifices (usually circular) into a medium which will precipitate or coagulate the liquid stream into a coherent filament, either heated air or a liquid precipitant, and finally after removal of solvent, washing, bleaching and perhaps softening, and finally winding the filament into the form of package desired.

In more detail, a schematic process involves the following distinct steps:

1. *Preparation of the Spinning Solution.* The first requisite is the selection of a cellulose ether of etherification represented by 2.5-2.8 substituted groups in cellulose as represented by three replaceable hydroxyls and which is not only insoluble in water, but as little affected by water as possible, both hot and cold. From the viewpoint of solvent recovery, either from atmosphere laden with recuperated solvent, or that obtained from a coagulating bath, it is essential to spin as concentrated a solution as possible, and likewise one in which the viscosity has been reduced to the lowest point compatible with the spinning of a filament of the requisite tensile strength and other desirable physical characteristics. For purposes of solvent recovery by refrigeration, it is also advisable to have a unitary solvent rather than a solvent mixture.

2. *Clarifying the Spinning Solution.* Once the cellulose ether has been brought into solution it is unnecessary that the solution be kept for any proscribed length of time before use as in the ageing and ripening of a viscose or copper-ammonia solution, but it has been found that if the solution is allowed to stand at rest for several days after being prepared, there appears to be an agglomeration or coalescence of fine particles or haze which not only facilitates filtration, but also insures of the more nearly absolute removal of the "haze," particles on the border line between individual entities and colloidal suspensions.

Plate filtration through segments lined with canton flannel and having pledgets of absorbent material between has proven quite satisfactory, it being practice to submit the solution to two filtrations, the last just before spinning. The efficiency of the spinning operations is dependent upon the number of plates in the press, the relative porosity of the clarifying layers and the speed of propulsion of solution through the filtration medium. Cold filtration in general, is preferable to filtering a hot solution, it having been observed that an apparently perfectly clarified hot solution upon standing will often develop a haziness or opalescence, not noticeable when the solution has been plate-filtered at room temperature. The addition of coalescing agents as barium sulfate, magnesium oxide, fuller's earth, cotton flock or asbestos finely dispersed is not used in practice. There is considerable loss from entanglement of solution in the solid media added for clarification purposes, and its recovery by re-solution and extraction has not proven profitable.

3. *Removal of Dissolved Gases.* In the preparaiton of acetate silk the usual concentration of solution is 25% ester and the acetic acid percentage in combination with the cellulose close to 54%. The solvent used is 98% acetone, water being intentionally added towards the close of the dissolving period so that the spinning solution contains about 12%, the object of the addition being so that the

cellulose compound will coagulate or set more quickly. The total solids and viscosity are brought to a definite standard, either at 15° or at the temperature of spinning.

After clarification the solution is pumped into storage tanks, glass-lined being especially suitable, and subjected to a partial vacuum for 12-24 hrs. immediately before spining for the removal of entrained and dissolved air, this being necessary in order to insure absence of minute bubbles in the individual filaments after coagulation or evaporation to the solid state.

4. *Spinning Operation.* This may be carried on either by so-called "Wet Spinning" which was the earlier method employed, or by "Dry Spinning" by the evaporative method which appears the preferable and which is carried on almost exclusively at the present time. There are, in addition, processes apparently applicable to either the wet or dry method of filament formation. This operation, therefore, is indicated herein under those three headings as follows:

5. *Filament Formation by Wet Spinning.* According to F. Ohl[1], although a major portion of artificial filaments from organic cellulose derivatives is prepared by the dry spinning process at the present time, a filament of considerably higher quality and tensile strength may be obtained by the wet spinning method, with the latter a wet strength of 3 gms. per denier being not unusual. In viscose rayon it would be marvelous. The practical difficulty of the wet spinning method apparently lies in the spinning bath which must be so adjusted as to allow maximum stretching of the filaments without affecting their coagulability; the coagulation must not involve a shriveling of the filaments; the components of the setting bath must exert an appreciable swelling action on the filament and must be readily removed from the filaments upon washing. Only

1. Kunstseide, 1929, **11**, 434; abst. C. A. 1930, **24**, 1973. Jentgen's Rayon Review, 1930, II, #2, 72; abst. C. A. 1930, **24**, 5483. Rayon Record, 1931, **5**, 443, 445; abst. C. A. 1931, **25**, 5285. Textilber. 1931, **12**, 200.

neutral or weakly acid baths are recommended. The extensibility of the wet filament is to a large degree (90%) elastic, whereas with dry spun filaments it seldom exceeds 5% elastic, this condition being modifiable by the addition of such softening agents as cyclohexanone and cyclohexanol. Ohl recommends acetone as the solvent for the cellulose compound.

The wet spinning of cellulose ether and ester filaments may be classified as to general processes under the following subdivisions:

(a). *Celanese and Dreyfus Methods.* In 1921 it was disclosed that ammonium, sodium, potassium or calcium thiocyanate owing to their latent solvent power and ability of exerting a swelling and coagulation-controlling action on the coagulated filaments and tendency to preservation of continuity of structure[1], were a useful addition to the coagulating bath or for incorporation in the cellulose derivative solution prior to extrusion into filament form. The amount of thiocyanate should be used in such limited amount as not to interfere with coagulation of the filaments, yet be sufficient to exert the required modifying influence on the shrinkage action of the water in the coagulating bath. If the thiocyanate is in the setting bath a strength of 11.5-12% is recommended.

As examples of other swelling and controlling agents may be mentioned acetone, diacetone alcohol, formic or acetic acids or zinc chloride, which like the thiocyanates, have a latent solvent power[2]. If a 16% solution of cellulose acetate is being spun, then the setting bath should contain 10-50 parts acetone or 100 parts alcohol, or 5 parts diacetone alcohol or acetic acid, per 100 parts water. It is recommended to extrude solutions of cellulose derivatives through orifices of compact or squat shape[3], having indentations in

1. C. Palmer and W. Dickie, U. S. P. 1465994; abst. C. A. 1923, **17**, 3919. Can. P. 317110.
2. *Ibid.* U. S. P. 1467493; abst. C. A. 1923, **17**, 3789. E. P. 179234. Can. P. 314449.
3. W. Whitehead and C. Dreyfus, E. P. 318631; abst. C. A. 1930, **24**, 2293; J. S. C. I. 1930, **49**, 985-B; Silk J. 1930, **6**, #68, 66.

the form of re-entrant angles, into a precipitating medium or evaporative atmosphere, or through a cluster of holes which are so close together that the filaments after extrusion coalesce to form a single filament, useful for artificial horsehair or imitation bristles. A method has been patented whereby acetylcellulose filaments immediately after extrusion into 50-55% aqueous diacetone alcohol[1], are immediately passed into a 2.5% NaOH solution to induce superficial saponification.

It is claimed that if a 30% solution of cellulose acetate in acetone is spun through an aperture 17 mm. by 0.07 mm. into water at a winding speed of 1.5 meters per min.[2], the length of immersion being 3 ft., and the product from the bath being led around a steam-heated roller and then directly wound on a bobbin, a clear product of high transverse strength is obtained, the augmentation as regards

1. British Celanese, Ltd., W. Dickie and P. Sowter, E. P. 330950; abst. C. A. 1930, **24**, 6015; J. S. C. I. 1930, **49**, 813-B. See E. P. 165519, 177868, 179234, 198023, 312203. H. Dreyfus, W. Dickie and P. Sowter, Can. P. 321722.

2. British Celanese, Ltd., R. Roberts and L. Gregory, E. P. 338936; abst. C. A. 1931, **25**, 2567; J. S. C. I. 1931, **50**, 153-B. R. Roberts, R. Dean and L. Gregory, Can. P. 321720. C. Dreyfus, F. P. 697814; abst. C. A. 1931, **25**, 3168. In one of the H. Dreyfus processes (F. P. 703114), artificial threads are made by extruding a solution through several groups of spinning nozzles, receiving the extruded filaments into a coagulating or evaporative agent, and winding the filaments on a series of bobbins. British Celanese, Ltd., and W. Taylor (E. P. 326461) direct a fluid stream on to a number of artificial filaments extruded from spinning orifices into a medium rich in the solvent employed, so that they converge together while in a tacky condition and unite to form one filament of large cross-section. A solvent or latent solvent (dichlorethylene, methylene chloride, methylphenyl ketone, triacetin) for the cellulose derivative at high temperature which is not readily soluble in the spinning bath is added to the spinning solution, and the filaments subsequently heated to 90-125°. Alternatively, ordinary spinning solutions may be used, the length of travel or time of contact of the filaments being so regulated that the filaments retain a proportion of solvent. J. Huebner and J. Gaebel (E. P. 309204) prevent separation of filaments from the main bulk during spinning by causing the moving liquids which flow from the filaments due to their high speed, to flow or converge toward the filaments, which can be effected by arranging in the bath a baffle or rod, or by raising the bottom of the bath in proximity to the filaments. See I. G. Farbenindustrie, E. P. 356427. A. Lehner, C. Landolt and O. Kohorn & Co., D. R. P. 543146.

tensile strength and improved clarity being due to the heat treatment.

In the formation of filaments from methyl-, ethyl- or benzyl-cellulose by the wet coagulation process[1], there is employed a coagulation bath containing a relatively high proportion of solvent for the cellulose ether, so that the filaments on emergence from the bath will be in so plastic a state that if brought together they will coalesce. Water, methyl or ethyl alcohol, benzene, toluene, gasolene and kerosene are specified as components for the coagulating bath, organic solvents less volatile than the non-solvent media being preferably employed. If water or alcohol or mixtures of them be used as the non-solvent portion, diacetone alcohol, diethyl tartrate, ethyl lactate or mono- or di-acetin, or mixtures of solvents of low volatility are preferred. The concentration of the solvent depends upon spinning conditions and the type of product desired, the concentration being higher according as the denier number of the filaments is lower.

Before collecting the products, excess solvent should be washed out or otherwise removed to prevent coalescence of the filaments, as by washing with water or salt solutions. During coagulation a stretch may be applied so as to produce individual filaments of one denier or less, even with the use of relatively large spinning jet orifices. The filaments obtained are said to be distinctive in that although wet spun, their luster is reduced by moist steam and hot or boiling aqueous media, and in that ironing or treatment with solvents does not increase the luster of the non-lustrous products. Alternatively[2], coagulating baths may be used directly and the filaments then stretched or the filaments dried immediately upon extrusion by means of drying cells

1. British Celanese, Ltd., W. Dickie and P. Sowter, E. P. 340324; abst. J. S. C. I. 1931, **50**, 1043-B; Silk J. 1931, **7**, #83, 52; Chem. Zentr. 1931, I, 1858. See E. P. 311790.

2. *Ibid.* E. P. 340325; abst. C. A. 1931, **25**, 4708; Silk J. 1931, **7**, #83, 52; J. S. C. I. 1931, **50**, 1043-B.

or chambers[1]. There may be incorporated in the spinning solution, wholly or in part for the solvent of the coagulation bath, solvents which are less volatile than the non-solvent portion of the precipitating bath[2]. Also, the filaments may first be coagulated[3], and immediately thereafter brought into a plastic state by passage through a secondary bath concentration containing a solvent for the cellulose ether of relatively high concentration.

According to one process[4], it is advisable to maintain the spinning solution at a temperature above that of the setting bath, the cellulose ether being dissolved either in acetone, acetone-water, acetone-methanol, acetone-ethanol, acetone-methylene dichloride or a mixture of methylene and ethylene dichlorides with methyl or ethyl alcohols. Coagulation is effected in a suitable non-solvent liquid at least partially miscible with the solvent or with a constituent of the solvent mixture, and hydrocarbon oils and castor oil. If it is desired to include a stretching operation in order to reduce the denier of the filaments[5], the filament may be softened by being brought in contact with a solvent in liquid or vapor form, being afterwards coagulated.

When manufacturing filaments from methylated, ethylated or benzylated cellulose solutions[6], there is employed as a coagulation bath a relatively high sōlvent for the cellulose derivative and also salts, sugars or other substances capable of exerting an osmotic pressure or reducing the

1. British Celanese, Ltd., W. Dickie and P. Sowter, E. P. 340326; abst. Jour. Text. Inst. 1931, **22**, 287-A. F. P. 654062. See E. P. 203092, 340324, 340325, 340436, 340437.

2. *Ibid.* E. P. 340436, Addn. to E. P. 340324; abst. C. A. 1931, **25**, 4707; Silk J. 1931, **7**, #83, 52; Chem. Zentr. 1931, I, 1858; J. S. C. I. 1931, **50**, 1043-B.

3. *Ibid.* E. P. 340437, Addn. to E. P. 340324, 340325; abst. C. A. 1931, **25**, 4707; Silk J. 1931, **7**, #83, 52; Chem. Zentr. 1931, I, 1858; J. S. C. I. 1931, **50**, 1043-B.

4. British Celanese, Ltd., E. P. 341148; abst. C. A. 1931, **25**, 5029; J. S. C. I. 1931, **50**, 342-B; Silk J. 1931, **7**, #84, 53. C. Dreyfus, F. P. 684144; abst. C. A. 1930, **24**, 5496.

5. British Celanese, Ltd., H. Dreyfus and W. Taylor, E. P. 342651; abst. J. S. C. I. 1931, **50**, 481-B.

6. British Celanese, Ltd., W. Dickie and P. Sowter, E. P. 343062; abst. C. A. 1931, **25**, 5557. See E. P. 178868, 179234, 246879, 259265, 259266, 336217, 340324, 340325, 340436, 340437.

solubility of the solvent in the non-solvent medium. In order to obtain unusually fine deniers, the cellulose ether may be projected into a setting liquid of such high solvent capacity that the filaments emerge therefrom in a substantially plastic condition, when they are subjected to a drawing or stretching treatment and then immersed in another bath where the non-solvent is very high, being there coagulated after completion of the attenuating operation[1]. If the solution of cellulose ether is spun into an aqueous coagulating bath containing thiocyanates or zinc chloride while the contents of the bath are caused to move so that a stretch is applied to the filament, then the original denier may be materially reduced[2].

If the extrusion of the cellulose derivative is made into a precipitating bath under such conditions that the formed filaments contain a substance that has at least a latent solvent power for the cellulose compound[3], subsequent subjection of the filament to an elevated temperature is said to increase the luster.

(b). *The I. G. Farbenindustrie Methods.* Cellulose ethers are rendered capable of stretch spinning by including in the solvent an ingredient which is extractable only with difficulty in the precipitating bath[4], such as carbon tetrachloride, pyridine, benzene, aniline, phenol, benzyl alcohol, ethyl acetate or propyl acetate. For example, a solution of 25 parts by weight of ethylcellulose in 68 parts of denatured alcohol and 7 parts carbon tetrachloride is spun

1. H. Dreyfus, E. P. 359976; abst. Silk J. 1932, **8**, #97, 55. F. P. 683463; abst. C. A. 1930, **24**, 4632. F. P. 37857, Addn. to F. P. 683463; abst. C. A. 1931, **25**, 4707. F. P. 38175, Addn. to F. P. 683463; abst. C. A. 1931, **25**, 5559. F. P. 687471; abst. C. A. 1931, **25**, 815. See E. P. 177868, 309201, 334838, 334853, 351718, 359971, 359975. F. P. 694048, 694119. Ital. P. 268699. Belg. P. 314568, 351182, 351295, 351556, 351776, 357100, 357297, 364509, 364627.

2. British Celanese, Ltd., E. P. 356343; abst. Textile Mfr. 1932, **51**, #686, 80. H. Dreyfus, E. P. 371343; abst. J. S. C. I. 1932, **51**, 675-B.

3. C. Dreyfus and W. Whitehead, Can. P. 314312; abst. C. A. 1931, **25**, 5289. See Can. P. 312668.

4. O. Leuchs and E. Hubert, D. R. P. 487024; abst. C. A. 1930, **24**, 2292.

through an orifice 0.7 mm. wide into a solution containing 30-35% calcium chloride at 50-55°. This is said to be preferable to the spinning of ethyl alcohol solutions of ethylcellulose into a calcium chloride bath[1], on account of the water-insoluble adjuncts to the cellulose ether solvent.

In a variant of the above[2], in order to render the cellulose derivative solutions capable of stretch spinning, there is added to the spinning solution a compound which is extracted by the bath more slowly than the solvent. Thus, to the acetone solution which is to be spun into a bath of concentrated calcium chloride solution there may be added ethyl acetate, aniline, pyridine, benzene or chlorbenzene. In order to increase the ability of the filaments to be drawn[3], the filament is treated with swelling agents immediately upon leaving the precipitating bath, and during winding is treated with hardening agents. Sulfuric acid or sulfates are also claimed as useful components of the coagulating bath in order to harden the filaments[4].

To the spinning bath of cellulose derivative in acetone[5] may be added a true sulfonic acid or its alkali salt for the purpose of obtaining softened filaments, bodies such as sodium oleosulfonate, sodium oleate, butyl oleate, sodium palmitosulfonate or ammonium sulforicinoleate being specified as applicable. Precipitating baths of high viscosity are stated to be preferable[6], such as containing large amounts of sugar, glycerol, glycol or urea, with or without the addition of such swelling agents as ammonium thiocyanate, ammonium nitrate or calcium chloride.

1. E. Hubert, D. R. P. 352192, Addn. to D. R. P. 352191; abst. Chem. Zentr. 1922, IV, 599.
2. E. Hubert, O. Leuchs and L. Lock, D. R. P. 479003; abst. C. A. 1929, **23**, 4819. See D. R. P. 477066; abst. C. A. 1929, **23**, 4070.
3. I. G. Farbenindustrie, A.-G., E. P. 318646; abst. C. A. 1930, **24**, 2293; J. S. C. I. 1931, **50**, 242-B; Silk J. 1929, **6**, #67, 72. See E. P. 309558. F. P. 681301, 682084; abst. C. A. 1930, **24**, 4391.
4. K. Weisbrod, D. R. P. 542814; abst. Chem. Zentr. 1932, I, 2258.
5. I. G. Farbenindustrie, A.-G., E. P. 336250; abst. Silk J. 1931, **7**, #80, 54. See E. P. 26928, 1910; 288612, 303917, 306052, 326815.
6. *Ibid.* F. P. 682912; abst. C. A. 1930, **24**, 4632.

(c). *Farbenfabriken vorm. F. Bayer & Co. Procedure.* The E. Thiele process[1], in which a cuprammonium cellulose solution is squirted into a precipitating bath consisting of a layer of relatively cold water in which the thread is drawn out, superimposed on a layer of hot water in which the thread is hardened, may be modified to permit of being used for the production of cellulose ether filaments[2], by reversing the above outlined procedure so that the layer is drawn out in a hot layer of liquid, the temperature, depth and nature of which depend on the character of the solution it is desired to spin. The filament is then hardened in an underlying cooler layer of liquid arranged to circulate in the direction of travel of the filament. Thus, a cellulose ether soluble in acetone is dissolved in dry pyridine bases to give a 20-25% solution, which after filtration, is spun into a known form of apparatus[3], and provided with apertures 0.6 mm. in diameter. Water at 60° is introduced at the rate of 30-50 cc. per min. at the top of the spinning chamber which should previously be filled with cold water, and forms a layer 3-5 cm. deep having a temperature of 45-55°. Cold water is introduced into the funnel and, providing that the length of the funnel together with the tube leading to it is 25-30 cm., the introduction of 300-400 cc. of water per min. suffices for a spinning speed of 40 m. per min. During their passage through the hot layer, the threads are drawn out by the combined action of their weight, the flow of water through the funnel, and the winding mechanism. In order to enhance the spinning properties, 10-30% of acetylene tetrachloride based on the weight of cellulose derivative, is added to the spinning solution to increase the density.

It is claimed that good luster and high tenacity can be obtained by injection of a cellulose ether solution into

1. E. P. 8083, 1902; abst. J. S. C. I. 1903, **22**, 550. U. S. P. 710819; abst. J. S. C. I. 1902, **21**, 1393.
2. Farbenfabr. vorm. F. Bayer u. Co., E. P. 194666; abst. J. S. C. I. 1924, **43**, 51-B. U. S. P. 1517627; abst. C. A. 1925, **19**, 404.
3. Soc. Générale de la Soie Artificelle Linkmeyer, E. P. 14655, 1907; abst. J. S. C. I. 1908, **27**, 278.

an aqueous salt solution, sodium or calcium chloride, ammonium chloride or nitrate or calcium chloride, the spinning temperature being raised almost to the boiling point of the cellulose ether solvent used. For instance:

1. 10 parts ethylcellulose are dissolved in 40 parts denatured alcohol and the solution carefully filtered. The solution is then sprayed by means of a spinning nozzle of 0.1-0.2 mm. diameter into calcium chloride solution at 60-70° (sp. gr. 1.3 at 15°), the fibers rinsed, then washed free from salts[1].

2. Ethylcellulose 10 is dissolved in denatured alcohol 30, water 10 and Brilliant Green 0.1, and treated as in Ex. 1. Instead of calcium chloride solution of 1.3 sp. gr., crystallized $CaCl_2.6H_2O$ in the melted condition may be used at 70°.

3. 20 parts ethylcellulose are dissolved in 110 parts acetone and worked up as in Ex. 1, zinc chloride solution (sp. gr. 1.85) being used as precipitating bath at 40°.

4. In a modification of the above[2], 10 parts ethylcellulose are dissolved in 40 parts denatured alcohol, filtered, and sprayed through a nozzle of 0.1-0.2 mm. diameter orifices into a 75% urea solution maintained at 60-70°.

(d). *Rhodiaseta Process.* The cellulose ether or ester is dissolved in thiocyanates as ammonium, sodium, potassium or zinc, or the doublt salts, ammonium zinc thiocyanate or calcium zinc thiocyanate[3], it being claimed that the use of thiocyanates possesses considerable advantage over the more expensive use of volatile solvents, in that it renders possible the coagulation in an aqueous medium, and thereby admits of complete recovery of solvent. The

1. Farbenfabr. vorm. F. Bayer & Co., E. P. 219333; abst. C. A. 1925, **19**, 580; J. S. C. I. 1925, **44**, 843-B. D. R. P. 274260, 352191.

2. E. Hubert, D. R. P. 352192, Addn. to D. R. P. 352191; abst. Chem. Zentr. 1922, IV, 599.

3. H. Chavassieu, U. S. P. 1622368; abst. C. A. 1927, **21**, 1713; J. S. C. I. 1927, **46**, 438-B; Chem. Zentr. 1927, I, 2957. Soc. Pour la Fabrication de la Soie Rhodiaseta, E. P. 246430; abst. C. A. 1927, **21**, 496; Silk J. 1927, **4**, #42, 60; Chem. Zentr. 1926, II, 1216. See F. P. 677263, 689800.

process is claimed as especially applicable to the spinning of methyl- and ethyl-cellulose filaments. The aqueous solution of the cellulose ether, sometimes alcoholized, properly filtered, is treated in the usual cellulose acetate spinning unit, the precipitating bath being periodically renewed and rejuvenated.

(e). *Ruth-Aldo Methods,* consist in forcing a cellulose ether solution through a nozzle into a coagulating liquid[1], or by distributing the solution over the filaments by means of a flat surface or endless band, or on a drum with a dull or polished surface which is sprayed with or immersed in the coagulating liquid. The latter consists of an aqueous solution of ammonium, potassium or sodium oleate, palmitate, ricinoleate, sulfopalmitate or sulforicinate or other similar suitable emulsifying agent. The tenacity and luster may also be improved, it is asserted, by the addition of other compounds to mix with or emulsify the bath, such as butyl alcohol, glycol, glycerol, cyclohexanol, decane, tridecane, hexadecane, toluene, xylols, tetrahydronaphthalene, terpenes, sesquiterpenes, polyprenes and mineral oils.

(f). *Aceta Disclosures.* In the manufacture of synthetic filaments according to this firm from cellulose ether solutions[2], the aqueous precipitating bath is covered with a layer of liquid which is immiscible or only partially miscible with the bath, but dissolves the solvent used in dissolving the cellulose ether. Accumulation of solvent in the bath is thus avoided, and solvent recovery facilitated. Fatty oils or higher fatty acids are suitable covering liquids. The covering liquid is continually replaced and regenerated by supplying it in finely divided form at the bottom of the precipitating bath, and collecting it from an overflow. So-

1. H. Barthelemy, U. S. P. 1826718; abst. C.A. 1932, **26**, 597. E.P. 282790; abst. C.A. 1928, **22**, 3989; Silk J. 1928, **4**, #47, 70; J.S.C.I. 1929, **48**, 714-B; Brit. Plastics, 1929, **1**, #5, 191; Chem. Zentr. 1928, I, 1824. F. P. 638899; abst. C. A. 1929, **23**, 514. D. R. P. 505222; abst. C. A. 1930, **24**, 6015; Chem. Zentr. 1930, II, 2334. Ital. P. 258937. See E. P. 282788, 282791, 282793, 282794.

2. Aceta, G. m. b. H., D.R.P. 505332; abst. C. A. 1930, **24**, 6015. See U. S. P. 1599230, 1634980.

lutions of keratin or glutin may also be used, alone or in conjunction with ammonium thiocyanate[1].

(g). *Tubize Procedure.* A solution of cellulose acetate in a solvent as alcohol and acetone[2] is employed for filament formation and the latter then treated with a solution of sulfuric acid, niter cake, calcium chloride or other inorganic substance in which the cellulose acetate solvent is soluble, but in which the ester is not.

In another process[3] designed primarily for the spinning of acetylcellulose solutions, the spinning bath of water or dilute acetic acid is kept at 10°[4]. Where precipitation of a cellulose ether filament is made in a chemically inert bath[5], the filament may be attenuated by stretching in the presence of a chemically inert vapor, or the threads may be disposed at an angle, acute or obtuse, to the direction of the flow of the precipitating fluid instead of being perpendicular or parallel to it[6], the threads being supported on an inclined carrier which may be perforated or provided with drainage grooves, or formed as a grating.

According to R. Herzog and Röhm & Haas[7], acetylcellulose is spun in association with one or more partly polymerized products of unsaturated organic acids, as methyl acrylate, ethyl acrylate, polyvinyl acetate or styrol, polymerization of the organic compounds being afterwards completed if desired.

1. Aceta, G. m. b. H., Swiss P. 142406.
2. E. Bindschedler and G. Juer, U. S. P. 1551791; abst. C. A. 1925, **19**, 3379; J. S. C. I. 1925, **44**, 844-B; Caout. et Gutta. 1926, **23**, 13315. Tubize Artificial Silk Co. of America, E. P. 211889; abst. C. A. 1924, **18**, 2255; J. S. C. I. 1925, **44**, 126-B.
3. N. V. "Fluida," Maatschappij Tot Exploitatie van Kunstzijdefabrieken, Holl. P. 20680; abst. C. A. 1930, **24**, 4633; Chem. Zentr. 1931, I, 2142. N. V. Fabriek van Chemische Producten, Holl. P. 20725; abst. C. A. 1930, **24**, 4633; Chem. Zentr. 1931, I, 2291.
4. N. V. "Fluida," Maatschappij Tot Exploitatie van Kunstzijdefabrieken, Holl. P. 21752; abst. C. A. 1930, **24**, 4633; Chem. Zentr. 1931, I, 2141. Swiss P. 139513; abst. Chem. Zentr. 1931, II, 937.
5. K. Weissenberg and B. Rabinowitsch, Can. P. 320915.
6. Sondermann & Co., E. P. 314402; abst. J. S. C. I. 1930, **49**, 610-B.
7. E. P. 311784; abst. C. A. 1930, **24**, 962; J. S. C. I. 1930, **49**, 985-B; Silk J. 1929, **6**, #64, 64. F. P. 681156; abst. C. A. 1930, **24**, 4391. See E. P. 308284.

A laboratory method for the production of fine filaments by the stretch-spinning process has been described by M. Friedmann[1], the cellulose derivatives being dissolved in acetone, freed from air and forced through spinneretts into a precipitating bath in a vertical cylinder. The precipitating liquid flows in at the bottom and out at the top, carrying with it the acetone which may be recovered so that the bath may be re-used. The filaments, which are still weak, are drawn onwards through an S-shaped guide which also serves to remove any drops of the precipitant into an aldehyde strengthening bath. From here it is carried over a godet wheel to a spinning frame, where it is well washed with water, and finally to the spinning box. By this process it is claimed yarns up to 120 denier with 120 filaments can be produced. The nature of the solutions is such that brightening and bleaching materials are not required, and by varying the composition of the precipitating bath, all stages between matt and full luster are obtainable without subsequent treatment.

6. *Coagulation Baths.* Among the various components of the setting bath suitable for cellulose ethers which have been advocated may be mentioned the following:

(a). Animal or vegetable oils as castor or linseed oil[2].

(b). Hydrocarbon boiling above 80° as toluene, the three xylols, liquid dimethylnaphthalenes, decane, tridecane, hexadecane, terpenes, cyclohexane, methylcyclohexane, and tetra- and deca-hydronaphthalene[3].

(c). Ammonium thiocyanate or zinc chloride asso-

1. Kunstseide, 1931, **13**, 173; abst. C. A. 1931, **25**, 4400; Rayon Record, 1931, 421.

2. W. Glover, U. S. P. 1599230; abst. C. A. 1926, **20**, 3579; J. S. C. I. 1926, **45**, 1010-B; Rev. gen. mat. Plast. 1927, #1, 49. Courtaulds, Ltd., L. Clement and C. Riviere, E. P. 224404; abst. J. S. C. I. 1925, **44**, 38-B. E. P. 224405; abst. C. A. 1925, **19**, 1352; J. S. C. I. 1925, **44**, 38-B; Chem. Zentr. 1925, I, 1472; Ann. Rep. S. C. I. 1925, **10**, 154. Can. P. 261967; abst. C. A. 1926, **20**, 3578. Ital. P. 235232. Holl. P. 15344.

3. H. Barthelemy, U. S. P. 1826718. E. P. 308271; abst. C. A. 1930, **24**, 240; J. S. C. I. 1929, **48**, 513-B; Silk J. 1929, **6**, #62, 70. F. P. 638896; abst. C. A. 1929, **23**, 514. Can. P. 315965, 315966. E. P. 282787.

ciated with molasses, sulfite lyes, albumin, soluble starch or soluble synthetic resin[1].

(d). Halogenated hydrocarbon as di- or tri-chlorethylene, pentachlorethane, monochlorbenzene, monochlortoluenes, *a*-bromnaphthalene, 1.2.3-trichlorbenzene, benzyl chloride, *o*-, *m*-, and *p*-toluonitriles, xylonitriles, nitrobenzene, nitrotoluene[2].

(e). Sodium chloride, calcium or ammonium nitrate, ammonium sulfate, sodium acetate, in conjunction with alcohol, ether, acetone, carbon tetrachloride, methylethyl ketone[3]. For example, a dilute solution of methylcellulose and acetylcellulose in methylethyl ketone is first passed into a mixture of acetone and water and then into a mixture of calcium or ammonium nitrate containing methylethyl ketone, and then into the pure salt solution free from ketone.

(f). Solvent absorbents as the methyl, ethyl, propyl and amyl stearates, oleates and palmitates[4].

(g). Ammonium sulfo-oleic acid amide, ammonium ricinsulfonate (sulforicinate), sodium sulfopalmitate (palmitosulfonate)[5].

(h). Sulfuric acid of 30-50% concentration or acid esters[6].

(i). Concentrated aqueous solutions of ammonium, calcium, strontium or magnesium nitrates[7], the solvent for the cellulose ether being so selected as to be miscible with an aqueous solution of the salt employed.

1. Aceta G. m. b. H., E. P. 310842; abst. C. A. 1930, **24**, 724; J. S. C. I. 1930, **49**, 943-B; Chem. Zentr. 1929, II, 2743; Silk J. 1929, **6**, #63, 68. F. P. 672962; abst. C. A. 1930, **24**, 2293; Cellulose, 1930, **1**, 246. D. R. P. 513375; abst. C. A. 1931, **25**, 1380. Swiss P. 142406.
2. H. Barthelemy, E. P. 308273; abst. J. S. C. I. 1929, **48**, 513-B.
3. E. Berl, U. S. P. 1679850; abst. C. A. 1928, **22**, 3777; J. S. C. I. 1928, **47**, 744-B. E. P. 230813; abst. J. S. C. I. 1925, **44**, 877-B; Ann. Rep. S. C. I. 1925, **10**, 154; Chem. Zentr. 1925, II, 369. Belg. P. 306174.
4. H. Barthelemy, E. P. 308272; abst. J. S. C. I. 1929, **48**, 513-B; Silk J. 1929, **6**, #62, 70.
5. I. G. Farbenindustrie, E. P. 336250; abst. Silk J. 1931, **7**, #80, 54. See E. P. 26928, 1910; 288612, 303917, 306052, 326815.
6. H. Dreyfus, F. P. 690772; abst. C. A. 1931, **25**, 1350. See F. P. 36751, Addn. to F. P. 531816; abst. C. A. 1931, **25**, 1084.
7. L. Clement and C. Riviere, F. P. 711668; abst. C. A. 1932, **26**, 2055.

(j). Mixture of sulfuric acid and methyl alcohol[1].

(k). Calcium chloride solution of 1.3 sp. gr. at 15° for ethylcellulose dissolved in denatured alcohol[2].

(l). Urea in 75% aqueous solution at 60-70°[3].

(m). Water at a low temperature, at least 20° for a first bath, followed by a second bath of water at 40° to which alkalis or salts may be added[4].

(n). Aqueous or organic solutions of urea, thiourea, guanidine or their alkyl or other simple derivatives[5].

(o). Sugars or other polyhydric alcohols which lower the solubility of the cellulose ether solvent in the water of the precipitating bath[6].

(p). A mixture of water containing acetone and methyl alcohol[7].

7. *Filament Formation by Dry Spinning,* also known as the evaporative method, involves the use always of a volatile solvent or solvent combination, the solvent portion of which is recaptured by means of spinning into the air, and the solvent laden air either passed through a solution for the recuperation of solvent contained therein, or the solvent precipitated as the result of refrigeration, or distilled after absorption in a body as charcoal.

The representative processes of filament formation of this general classification are as follows:

1. Wolff & Co. Komm. Ges. auf Akt. and R. Weingand, E. P. 360688; abst. J. S. C. I. 1932, **51**, 141-B.
2. Farbenfabriken vorm. F. Bayer & Co., D. R. P. 352191; abst. J. S. C. I. 1922, **41**, 807-A; Chem. Ztg. 1922, **46**, 240; Faser. 1922, **4**, 66; Chim. et Ind. 1923, **10**, 543; Chem. Zentr. 1922, IV, 599; Textilber. 1922, **3**, 374.
3. *Ibid.* D. R. P. 352192, Addn. to D. R. P. 352191; abst. J. S. C. I. 1922, **41**, 807-A; Chem. Zentr. 1922, IV, 599; Chem. Ztg. 1922, **46**, 240; Chim. et Ind. 1923, **10**, 543; Textilber. 1922, **3**, 374.
4. Bemberg, A.-G., E. P. 244492; abst. Chem. Zentr. 1926, II, 2266.
5. H. Dreyfus, F. P. 657764; abst. C. A. 1929, **23**, 4572.
6. *Ibid.* F. P. 39211, Addn. to F. P. 683462; abst. C. A. 1932, **26**, 2317. See F. P. 713847.
7. C. Dreyfus and W. Whitehead, Can. P. 309131; abst. C. A. 1931, **25**, 1994.

(a). *Dreyfus and Celanese Processes.* H. Dreyfus[1] reports that by incorporating in the spinning solution a solvent of higher boiling point, it is possible to dry the extruded filaments to very fine deniers, on account of the longer time the filaments remain in the plastic or semi-plastic condition. The higher boiling solvents recommended for this purpose include acetylcarbinol (b. pt. 147°), acetylacetone (137°), cyclopentanone (130°), diacetone alcohol (163-165°), and cyclobutanone (99°). These solidification retarders are employed with the more volatile solvents acetone and methyl acetate in proportions varying with the degree or extent of filament stretch desired. By the use of lower boiling solvents as formaldehyde or acetaldehyde[2], lower boiling non-solvents as benzene or ethyl alcohol may be employed.

In order to cause the air or other evaporative medium to flow in close proximity to the spinning nozzle[3], collector devices are fitted at the top of the spinning chamber. In this way it is claimed possible to utilize practically the whole of the evaporative capacity of the air, and at the same time to exercise a stricter control on the cross-section of the filaments. In order to increase regularity in physical characteristics, H. Dreyfus[4] spins solutions of cellulose derivatives into an evaporative chamber in which they traverse a path of 3-6 yards, loss of solvent outside the cham-

1. U. S. P. 1566384; abst. C. A. 1926, **20**, 511; J. S. C. I. 1926, **45**, 122-B. E. P. 182166; abst. C. A. 1922, **16**, 4356; J. S. C. I. 1922, **41**, 627-A; Chim. et Ind. 1923, **9**, 1197; Chem. Zentr. 1922, IV, 907. Can. P. 281189, 299013. Belg. P. 373801.

2. H. Dreyfus, U. S. P. 1616789; abst. J. S. C. I. 1927, **46**, 295-B. U. S. P. 1669158; abst. J. S. C. I. 1928, **47**, 445-B. E. P. 209125; abst. C. A. 1924, **18**, 1576; J. S. C. I. 1924, **43**, 213-B; Chem. Zentr. 1925, I, 1471; Faser. 1924, **6**, 46. See F. P. 593102. D. R. P. 450900. Can. P. 279892. Belg. P. 354874.

3. British Celanese, Ltd., E. Kinsella, J. Bower, W. Taylor and H. Dreyfus, E. P. 300998; abst. J. S. C. I. 1929, **48**, 203-B. E. P. 304674, Addn. to E. P. 300998; abst. J. S. C. I. 1929, **48**, 353-B. H. Dreyfus, F. P. 654062; abst. C. A. 1929, **23**, 3808. F. P. 39394, Addn. to F. P. 654062; abst. C. A. 1932, **26**, 2318.

4. E. P. 315729, Addn. to E. P. 165519; abst. J. S. C. I. 1929, **48**, 810-B. F. P. 36751, Addn. to F. P. 531816; abst. C. A. 1931, **25**, 1084. Belg. P. 310428.

ber being prevented. In the C. Palmer cellulose ether spinning apparatus[1], the fibers are dry spun in a metier casing and directly withdrawn therefrom, feeding the threads of other fibers into intimate association with these filaments as the latter leave the casing, continuously twisting and winding the traveling associated threads to form a compound yarn.

By employing methyl-, ethyl- or benzyl-cellulose solutions of 25-30% concentration[2], it is alleged filaments of greater mechanical strength and rounder section result, and show less tendency to crinkle or turn woolly in appearance when brought in contact with hot liquids. In spinning these concentrated solutions[3], better results are alleged to be obtained by incorporating in the solution before extrusion, di- or tri-acetin, mono oil or methyl(or ethyl)-toluenesulfonamide in amounts of 0.5-5% on the weight of the cellulose derivative. If it is desired to reduce the viscosity of the spinning solution in order to enable finer filaments to be drawn out, the addition of methyl alcohol is recommended[4].

Cellulose ether fibers of maximum stretchability are said to result when the solvent portion contains a low-boiling solvent (formaldehyde, acetaldehyde, methyl formate or acetate, ethyl formate), a higher boiling non-solvent (water, benzene, propyl alcohol, ethyl alcohol, methyl alcohol) and a still higher boiling solvent (diacetone alcohol, acetyl carbinol, acetyl acetone, cyclopentanone and

1. U. S. P. 1672083; abst. C. A. 1928, **22**, 2669; Rayon, 1928, **7**, #1, 17.

2. H. Dreyfus, U. S. P. 1688531; abst. C. A. 1929, **23**, 278; J. S. C. I. 1929, **48**, 14-B. E. P. 210108; abst. C. A. 1924, **18**, 1757; J. S. C. I. 1924, **43**, 251-B; Ann. Rep. S. C. I. 1924, **9**, 153; Chem. Zentr. 1924, I, 2760; Faserstoffe, 1924, **6**, 67. F. P. 566385.

3. *Ibid.* U. S. P. 1688532; abst. J. S. C. I. 1929, **48**, 513-B. See U. S. P. 1278885, 1280975. E. P. 6463, 14101, 1915; 207562. F. P. 631344.

4. British Celanese, Ltd., E. P. 310046; abst. J. S. C. I. 1930, **49**, 943-B; Silk J. 1929, **6**, #63, 68. See C. Dreyfus and W. Whitehead, Can. P. 318521. J. Briggs and R. Roberts, Can. P. 311592.

glycol ethers)[1]. If variation in denier is desired[2], the filaments may be drawn at varying linear speeds by passing them round a roller the peripheral speed of which is varied, whereby a more or less frequent and systematic variation in denier is imparted.

Cellulose ether filaments may be stretched continuously while in the set elastic condition during their travel from one point to another, and in order to increase the stretch to the maximum, are simultaneously or previously treated with solvents or swelling agents or are wetted with water or inorganic acids[3]. If the spinning solution is extruded into a chamber through which an evaporative medium flows in countercurrent to the filaments while an additional evaporative medium is introduced inside or outside the bundle of filaments in the vicinity of the jet[4], a more uniform filament is claimed to result and a maximum of solvent recuperation possible. In order to reduce the viscosity of the spinning solution[5], it is advocated to add 10-12% of water, which facilitates production of filaments of fine denier, and also renders coagulation more easily accomplished by reducing the solvent avidity of the solution. Acetone is the preferred solvent, either alone or with a relatively small proportion of diacetone alcohol or ethyl alcohol.

If it is desired to control to the maximum the stretch

1. H. Dreyfus, E. P. 312203; abst. C. A. 1930, **24**, 963; J. S. C. I. 1929, **48**, 594-B; Silk J. 1929, **6**, #64, 66. F. P. 38124, Addn. to F. P. 666867; abst. C. A. 1931, **25**, 5559. F. P. 676728; abst. C. A. 1930, **24**, 3113. F. P. 713847; abst. C. A. 1932, **26**, 1785. Can. P. 252227, 252228. See E. P. 165519, 203092.

2. British Celanese, Ltd., H. Dreyfus, W. Dickie and W. Taylor, E. P. 321762; abst. J. S. C. I. 1930, **49**, 98-B.

3. H. Dreyfus, E. P. 323790; abst. C. A. 1930, **24**, 3369; J. S. C. I. 1930, **49**, 319-B. Can. P. 297694. Ital. P. 275773. See E. P. 277089.

4. British Celanese, Ltd., J. Briggs and R. Roberts, E. P. 325233; abst. C. A. 1930, **24**, 4156. E. P. 341075, Addn. to E. P. 325233; abst. J. S. C. I. 1931, **50**, 342-B. See E. P. 203092, 300998, 304674.

5. H. Dreyfus, E. P. 328636; abst. C. A. 1930, **24**, 5496; J. S. C. I. 1930, **49**, 656-B. F. P. 672306; abst. C. A. 1930, **24**, 2293. F. P. 683076; abst. C. A. 1930, **24**, 4632. Can. P. 322386. See E. P. 320363; abst. C. A. 1930, **24**, 2600. F. P. 671921.

and insure its maximum uniformity[1], the extruded filaments are caused to traverse a counter-current of evaporative medium in the spinning cell, the stretching being applied to the filaments while they still contain 20-40% residual solvent. For cellulose ether filaments of very fine count[2], it is recommended to wind and twist them in a centrifugal box of relatively small diameter and at the high speed of 10000-20000 r.p.m. Resistance of yarn of ethyl- or benzyl-cellulose to hot or boiling aqueous liquids is increased by stretching the fully set and finished filaments beyond their elastic limit[3], the stretching being assisted by pre-treatment with swelling agents as acetone, alcohol, formaldehyde or glycerol. A stretch of 15-25% is recommended. The threads treated as above are said not to become curly or wool-like in boiling water. In a variant of this method[4] the threads are extruded in the usual manner into an evaporative atmosphere, and after a peripheral skin has been formed by solvent evaporation, but while the filaments contain 25-50% of liquid solvent, they are then stretched to the extent or degree desired, and the balance of the solvent then removed.

The upward dry spinning of solutions of organic cellulose derivatives in volatile solvents[5] is initiated by the use of a liquid coagulating bath containing water, methyl alcohol, ethyl alcohol, benzene and carbon tetrachloride or kerosene with soap, which is afterwards withdrawn. Not

1. British Celanese, Ltd., H. Dreyfus and W. Taylor, E. P. 331229; abst. C. A. 1931, **25**, 204; J. S. C. I. 1930, **49**, 813-B. H. Dreyfus, F. P. 685977, 685978, 685979, 685980; abst. C. A. 1930, **24**, 6015. See E. P. 165519, 198023. F. P. 661810, 681317, 681529, 681759.

2. *Ibid.* E. P. 340471; abst. Chem. Zentr. 1931, I, 2290; Silk J. 1931, **7**, #83, 52. F. P. 697725; abst. C. A. 1931, **25**, 3168. See E. P. 165519, 198023, 340504, 340505. F. P. 531816, 561588.

3. Timbersbrook, Ltd., and A. Hall, E. P. 277089. British Celanese, Ltd., E. P. 340929. H. Dreyfus, F. P. 697427; abst. C. A. 1931, **25**, 3167. See E. P. 165519, 198023, 203092, 277089, 323790. F. P. 566385, 651588, 654062, 678314, 679618.

4. British Celanese, Ltd., H. Dreyfus and W. Taylor, E. P. 342712; abst. C. A. 1931, **25**, 5559; J. S. C. I. 1931, **50**, 480-B. See E. P. 340929, 340930.

5. British Celanese, Ltd., E. P. 351718; abst. J. S. C. I. 1931, **50**, 836-B; Silk J. 1932, **8**, #92, 54.

dependent upon the evaporation of a volatile solvent is the following cellulose ether or ester dry spinning method[1], the cellulose derivative being dissolved in a substance or mixture which is a solvent at comparatively high temperatures, but substantially non-solvent at lower, glycerol or some of the glycols being examples. With cellulose acetate, for instance, it is completely dispersed (where a 20-25% solution is to be spun) at 170-180° with glycol or 180-210° with glycerol. If the cellulose compound is allowed to soak in the glycol or glycerol at room temperatures for some hours, dispersion and solution will take place at considerably lower temperatures (around 140°), being, while still hot, forced into a candle and spinning jet maintained at 140° and into a dry spinning metier at 100°, adjustments being made so as to obtain 10 denier filaments at a winding speed of 50 m. per min.[2].

If it is desired to obtain artificial yarns of an irregular character not depending on variation in denier[3], two filaments may be extruded simultaneously, feeding them together irregularly with respect to the other, and doubling them on a twisting and winding device whereby the faster-fed forms slub on the other. If more than two filaments are extruded, at least one must be fed irregularly. Where fine denier filaments are to be produced[4], the filaments are extruded into an evaporative atmosphere contained in a cell, the nozzle of which is surrounded by a shield in the form of a cup-shaped device adapted to seclude the filaments in the early stages of their formation.

In forming methyl-, ethyl- or benzyl-cellulose filaments, the minimum of viscosity of the ester and hence minimum

1. H. Dreyfus, U. S. P. 1865358; abst. C. A. 1932, **26**, 4471. British Celanese, Ltd., W. Dickie and P. Sowter, E. P. 355298. Cites E. P. 320632, 338490, 340324, 340325, 341897, 343062. C. Dreyfus and W. Whitehead, Can. P. 319735.

2. H. Dreyfus, E. P. 358500; abst. J. S. C. I. 1932, **51**, 17-B; Silk J. 1932, **8**, #96, 49. See E. P. 312203, 333926, 342712.

3. British Celanese, Ltd., and W. Taylor, E. P. 360010; abst. Textile Mfr. 1932, **58**, #688, 164.

4. British Celanese, Ltd., H. Dreyfus and W. Taylor, E. P. 364654; abst. Silk J. 1932, **9**, #98, 46; Textile Mfr. 1932, **58**, #691, 287.

of solvent employed, results when the viscosity is reduced by the addition to the spinning solution up to 4% on the weight of the cellulose compound[1], of metallic salts as aluminum chloride, sulfate or resinate, barium chloride, copper, magnesium or zinc oleate, potassium ricinoleate or triethanolamine. If it is desired to increase the rate of aggregation[2], filaments dry spun from organic cellulose derivatives are passed on their way to collection round a friction-driven feed roller, which is slowed down during initial operation and gradually speeded up during spinning[3].

Uniformity in filament denier is possible by heating the cellulose ether spinning solution and maintaining this temperature until after the solution has been projected through the issuing orifices[4]. By varying the conditions under which the spinning solution is extruded[5], as change in temperature and volume of the air immediately surrounding the filament upon issuance from the jet, filaments of varying cross-section are obtainable. To facilitate the starting up of spinning jets in the manufacture of etherized cellulose filaments[6], a vacuum is first applied to the jet and continued until uninterrupted extrusion is obtained. Indentations may be produced in the filament after spinning[7], by extrusion into an atmosphere which fluctuates as to temperature and varies as to bulk of air in contact with the extruded filament. Where the filaments are allowed to

1. British Celanese, Ltd., E. P. 366110; abst. J. S. C. I. 1932, **51**, 336-B.
2. British Celanese, Ltd., W. Taylor, R. Parkinson and R. Roberts, E. P. 368341; abst. J. S. C. I. 1932, **51**, 500-B.
3. H. Dreyfus, F. P. 561588. See F. P. 678400.
4. *Ibid.* F. P. 677461; abst. C. A. 1930, **24**, 3113. Can. P. 292894.
5. *Ibid.* F. P. 702979; abst. C. A. 1931, **25**, 4402.
6. *Ibid.* Can. P. 253168; abst. Chem. Zentr. 1926, I, 3516. H. Dreyfus, E. Kinsella, J. Bower and W. Taylor, Can. P. 285981. H. Dreyfus and W. Taylor, Can. P. 298722. See F. P. 39394, Addn. to F. P. 654062; abst. C. A. 1932, **26**, 2318. F. P. 713184; abst. C. A. 1932, **26**, 1785. F. P. 722631; abst. C. A. 1932, **26**, 4174.
7. C. Dreyfus, Can. P. 304450.

set under greatly reduced pressure[1], their porosity is increased and their power of imbibing fluids augmented.

Another method for increasing the stretch and reducing the denier is to extrude the filament into a gaseous or other fluid stream in such a manner that the filaments are propelled by the stream at a speed greater than that of the extrusion—i.e., they are drawn[2]. If a wetting agent is a component of the cellulose ether solution, after the formed filament has set, it may be immediately dyed heavy shades, due to the increased receptivity of the fiber by virtue of the wetting agent therein[3]. The alkali metal salt of a higher fatty acid as sodium oleate, palmitate or stearate dissolved in the spinning solution acts analogously[4].

(b). *I. G. Farbenindustrie Methods.* Cellulose ether silk which will withstand boiling is prepared by dry spinning ethers which are insoluble in ice cold water or 10-30% alcohol, for instance[5], by dissolving 1 kilo ethylcellulose (47% ethoxyl) which at room temperature is not more than 5% soluble in 50% alcohol, in a mixture of 4 kilos benzene and 250 gms. alcohol, filtered and dry spun in the usual manner. Or[6], the solution for spinning is made from a cellulose ether entirely insoluble in water and entirely free from components of low viscosity and which swell in water, or the cellulose ether may be treated with 30-50% aqueous alcohol and whatever dissolves therein discarded insofar as filament formation is concerned. Thus, 1 kilo cellulose ether of relative viscosity 13, is dissolved in 4 kilos benzene and 0.25 kilo ethyl alcohol, filtered and dry spun at a spinning speed of 6 m. per min., at a nozzle temperature of 95°,

1. H. Dreyfus, Can. P. 311409.
2. W. Taylor, Can. P. 315537.
3. *Ibid.* Can. P. 317109.
4. C. Dreyfus and W. Whitehead, Can. P. 319736. H. Dreyfus, Can. P. 321532. W. Whitehead, Can. P. 323575, 323576.
5. I. G. Farbenindustrie, A.-G., and H. Henecka, D. R. P. 525860; abst. C. A. 1931, **25**, 4707; Nitrocellulose, 1931, **2**, #5, 104. See D. R. P. 511019.
6. I. G. Farbenindustrie, A.-G., E. P. 322730; abst. C. A. 1930, **24**, 2882; J. S. C. I. 1930, **49**, 319-B; Silk J. 1930, **6**, #70, 62. See E. P. 321651.

using nozzles whose individual orifice diameter is 0.075 mm. There is thus obtained a silk whose luster is said to be completely stable to a one hour's treatment with boiling water, and which displays unusual fastness to ironing.

Taking advantage of Roentgen ray investigations wherein it has been demonstrated that under otherwise identical conditions as regards initial materials and cross-section, the strength of the artificial threads is greater when the particles have a better orientation therein (see p. 232)[1], it has been found that the orientation may be brought about by producing a difference in the speed of the single particles in relation to each other within the cross section of the threads during their formation and while still plastic, the particles thereby arranging themselves with their longitudinal axes in the direction of flow. This is accomplished in practice by the use of very long spinning nozzles, or by passing the threads after leaving the nozzles through a layer of liquid having only a slight or no coagulating action. The longer the nozzle, the more marked is the orientation, and accordingly by the use of a nozzle 0.5-5 mm. much stronger silk is obtained on account of the filaments being much better in this respect. The process reads upon the use of solutions of cellulose ethers.

It is claimed that particularly valuable cellulose ether silk is obtainable by replacing the solvent which is contained in the threads leaving the nozzles[2], by a swelling agent so that threads of a jelly-like character are produced, then subjecting them to a stretching action, and subsequently removing the swelling agent. For instance, a cellulose ether in acetone is first spun into a dish of ethyl alcohol whereby the acetone is displaced by the alcohol, so that gelatinous threads are obtained, the alcohol being incapable of dissolving the cellulose ether, only swelling it. Since the threads are to be stretched, a speed in drawing must be chosen higher than the speed at which the

1. I.G.Farbenindustrie, A.-G., E.P. 325857; abst. C.A. 1930, **24**, 4156; J.S.C.I. 1930, **49**, 504-B. F.P. 674268; abst. C.A. 1930, **24**, 2601.
2. *Ibid.* E. P. 327420; abst. Cellulose, 1930, **1**, #10, 270.

solution leaves the nozzle in order to obtain an extrusion. After passage through the alcohol bath, the thread is passed through a current of warm air where it solidifies upon evaporation of the alcohol.

It is recommended where cellulose ether spinning solutions contain benzene and alcohol in addition to the usual solvents[1], to heat the solution before spinning to near the boiling point at which they begin to boil within the nozzle, being then extruded into a chamber where the threads meet a countercurrent of air containing the vaporized solvent, if desired, at a lower temperature. In dry spinning cellulose ethers[2], a product of especially high tensile strength is obtained by use of nozzles of glass, quartz glass or other suitable vitreous material, the length of the bore of which is at least 5 times (and preferably at least 10 times) the diameter, and by stretching the filaments immediately after extrusion to at least 5 times their original length.

Likewise very fine deniers are obtainable with cellulose ether filaments[3], by causing the liquid threads after leaving the spinning nozzle, to enter a chamber which has been freed from air and filled with the vapor of a swelling agent for the purpose of causing exchange of solvent in the threads for swelling agent, so that there is formed a gelatinous thread, which is stretched and afterwards dried. The filaments may also be swollen by impregnating the filaments with aqueous formic, acetic or propionic acids at 15-30°, and then stretching the swollen filaments 50-400% of their original length before drying[4].

(c). *Ruth-Aldo Procedure.* Filaments formed by extrusion of a cellulose ether solution are coagulated by the use of a liquid medium of such composition in respect to

1. I. G. Farbenindustrie, A.-G., E. P. 327423; abst. C. A. 1930, **24**, 5158; J. S. C. I. 1930, **49**, 655-B. See E. P. 278814.
2. *Ibid.* E. P. 327737, Addn. to E. P. 327671; abst. C. A. 1930, **24**, 5168; J. S. C. I. 1930, **49**, 609-B. F. P. 674269; abst. C. A. 1930, **24**, 2601.
3. *Ibid.* E. P. 340570; abst. Silk J. 1931, **7**, #83, 52. See E. P. 327420.
4. *Ibid.* Can. P. 305459.

its solvent absorption rate from the filaments, as to give the latter the desired properties. Among the materials which may be used are toluene, xylene, dimethylnaphthalene, decane, tridecane, hexadecane, terpenes, polyterpenes, cyclohexane, methylcyclohexane, tetra- and deca-hydronaphthalene, ethyl, butyl or propyl alcohol, glycol, glycerol, cyclohexanol, methylcyclohexanol, cyclohexylcarbinol, tetrahydro-*b*-naphthol, oleic or ricinoleic acids, methyl, ethyl, propyl, butyl or amyl oleate, palmitate, stearate or margarate, monochlor-benzene or -toluene, *a*-bromnaphthalene, 1.2.3-trichlorbenzene, benzyl chloride, and nitrites as "benzonitrite, toluononitrites or xylonitrites"[1].

R. Thenoz[2] has described a drawing device used in the spinning of cellulose ether threads which is provided with a pair of drawing-rollers rotating in opposite directions and at the same or different speeds, and adapted to be adjusted in position in such a manner that they control the extent of the drawing action, and also the length of travel of the filaments in the spinning chamber.

(d). *Aceta Advancement.* Filaments may be spun from cellulose ether or organic ester solutions in a mixture of solvents composed principally of methylene chloride and an aliphatic alcohol boiling below 100°, containing also swelling agents the b. pt. of which is above that of methylene chloride[3]. The minimum water content of the spin-

1. H. Barthelemy, E. P. 282787; abst. C. A. 1928, **22**, 3989; J. S. C. I. 1929, **48**, 595-B; Silk J. 1928, **4**, #47, 70; Chem. Zentr. 1928, I, 1823. See U. S. P. 1107222. The Ruth-Aldo Co. (E. P. 308564) apparatus includes one or more cells for spinning cellulose esters dissolved in volatile solvents, a circulating system enabling independent regulation of the air admitted to each cell, its temperature and the proportion of vaporized solvent present in the atmosphere of each cell, and this enables the bulk of the solvent employed to be recovered.

2. E. P. 283139; abst. C. A. 1928, **22**, 3990; Silk J. 1928, **4**, #48, 64.

3. Aceta G. m. b. H., F. P. 719569; abst. C. A. 1932, **26**, 3920. For the purpose of controlling the cross-section of the filaments (E. P. 248696, 308350. D. R. P. 542890. U. S. P. 1861912) there is provided at the spinning dies so as to affect the solution to be spun, an amount of heat in such manner as to maintain at the dies and their immediate neighborhood a temperature determined by the desired cross-section, and which is adjusted according to the conditions maintain-

ning solution is 2.5%. For spinning cellulose acetate, a solution of 65% methylene chloride, 30% alcohol, 5% methylethyl ketone and 1% water is recommended. Threads having jagged sections are made by dry spinning a solution of a cellulose derivative in a mixture of solvents having two components[1], the component of higher b. pt. not being a direct solvent. A gaseous drying current is directed on to the threads immediately as they leave the spinning nozzles. A mixture of methylene chloride 7 and alcohol 3 is a suitable solvent combination for the cellulose ethers.

Especially appropriate for the filtration of ethyl-, benzyl- and ethylbenzyl-cellulose solutions for filament formation[2] is a method said to be both economical and satisfactory, for the extraction of material from filter cloths, liquid sulfur dioxide being employed as the solvent. The process is carried out by charging a pressure extractor with a suitable amount of used filter cloths with the spinning solution residue adhering thereto, and exhaustively extracted with liquid SO_2. After the extraction, the major portion of the SO_2 is distilled under pressure, and the cellulose derivative then precipitated by running in hot water with continuous thorough agitation. The balance of the SO_2 present is recovered by condensation.

A machine for dry spinning cellulose derivative fibers has been evolved[3], comprising a tubular spinning cell provided at the top with means to supply the spinning solution in form of threads, and at the bottom with an opening for the discharge of the threads formed, the cell being further provided with symmetrically arranged holes at the lower part and an outlet tube at the upper. A heating jacket surrounds the spinning cell and a casing external to the heating jacket is in communication with the holes at the

ing the temperature being independent of that maintaining in the body of the individual spinning cell. See E. P. 233383, 236393. S. Wild, E. P. 348168.

1. Aceta, G. m. b. H., F. P. 708761; abst. C. A. 1932, **26**, 1440.
2. *Ibid.* D. R. P. 536890; abst. C. A. 1932, **26**, 1119.
3. A. Friederich and P. Schlack, U. S. P. 1861912. D. R. P. 543701; abst. C. A. 1932, **26**, 3378.

lower part of the cell, and insulated against loss of external heat. The casing is open at the top.

(e). *Rhodiaseta Methods.* The temperature in the vicinity of the extruding dies in the formation of filaments from volatile solvent solutions[1] is rendered independent of the temperature of the drying atmosphere which has penetrated by the opposite end of the cell, by abstracting the evaporating medium at an intermediate region of the cell. It is recommended to produce the threads in controlled section by introducing into the cell a gaseous evaporating medium as air or an inert gas, richly laden with a requisite proportion of vapors of the solvent used, insufficient to effect saturation at the temperature in the cell[2].

It is alleged that stable filaments showing no scintillating effects may be spun at speeds of 400 m. per min.[3] with a filament denier of one or even less, by heating the spinning solution before it reaches the jet and introducing a cold, drying atmosphere, as the spinning room temperature at 20°, into the spinning cell in the vicinity of the dies. The lower portion of the cell is heated to remove last traces of solvent.

(f). *Results of A. Eichengrün.* Cellulose ether or ester filaments of less than 3-4 deniers are made by the dry spinning methods while using spinning apertures of normal dimensions, by employing cellulose ether solutions containing a direct or latent solvent and a coagulant having a b. pt. higher than that of the solvent[4], the latter being used in such proportions as permits the use of winding speeds in excess of the normal. According as the propor-

1. Societe Chimique des Usines du Rhone, E. P. 236393. See E. P. 218913; abst. C. A. 1925, **19**, 580.

2. Societe pour la Fabrication de la Soie Rhodiaseta, E. P. 248696; abst. J. S. C. I. 1926, **45**, 945-B. J. Lahousse, U. S. P. 1583475; abst. C. A. 1926, **20**, 2079. F. P. 598081.

3. *Ibid.* E. P. 300672; abst. C. A. 1929, **23**, 4072; J. S. C. I. 1929, **48**, 50-B. D. R. P. 428745; abst. Chem. Zentr. 1926, II, 517. D. R. P. 487242; abst. C. A. 1930, **24**, 2292.

4. A. Eichengrün, E. P. 317408; abst. C. A. 1930, **24**, 2294; J. S. C. I. 1929, **48**, 848-B; Silk J. 1929, **6**, #67, 70. F. P. 669309; abst. C. A. 1930, **24**, 1740; Cellulose, 1930, **1**, #5, 150. See E. P. 1441, 18076,1910; 243350.

tion of coagulant is greater, so may winding speeds be increased, the filament becoming of increased fineness. As suitable solvents designated are methylene chloride-alcohol, alcohol-benzene-acetone, ethylene chloride-alcohol, ethyl acetate-alcohol, ethyl formate-alcohol acetone-alcohol and acetone-alcohol-benzene-water. The process is specified as applicable to the production of ethyl- and benzyl-cellulose filaments. In effectuating this process an apparatus has been devised, designed especially for producing continuous film bands[1], being a combination of supply means for the cellulose derivative solution, a traveling band repellent to the film when solidified, and means for removing the film when it has assumed the solid state, the traveling band being arranged in the form of loops or festoons individually driven, and supported by the borders only.

(g). *Advances by Courtaulds.* Their basic patent[2] involves producing synthetic silk from a solution of cellulose ether in a volatile solvent by forcing through a jet or drawplate into a space containing warm air, thereby volatilizing the solvent and leaving the cellulose derivative in the filamentous form, which is then led into a rapidly rotating spinning box. It is recommended to maintain the air in the spinning chamber at the same temperature as that of the spinning solution being extruded, by subjecting the solution and the whole of the air in the spinning chamber to the action of the same supply of heat[3].

Uniformity of filament is said to be assured by providing the spinning cells with heating elements of substantially identical construction, communicating in parallel with supply and discharge mains of such capacity that the

1. A. Eichengrün, U. S. P. 1824337. Can. P. 320555.

2. W. Glover and C. Topham, U. S. P. 1665958; abst. J. S. C. I. 1928, **47**, 364-B. E. P. 268455; abst. C. A. 1928, **22**, 1474; J. S. C. I. 1927, **46**, 472-B; Chem. Zentr. 1927, II, 654. D. R. P. 481945; abst. C. A. 1930, **24**, 500.

3. Courtaulds, Ltd., and F. Lewis, E. P. 278814; abst. C. A. 1928, **22**, 2840; J. S. C. I. 1927, **46**, 934-B; Chem. Zentr. 1928, I, 770. F. P. 633957; abst. C. A. 1928, **22**, 3990. D. R. P. 498418; abst. C. A. 1930, **24**, 3902. Can. P. 282326; abst. C. A. 1928, **22**, 3529. E. P. 273506; abst. Chem. Zentr. 1927, II, 2025.

flow of water is sufficiently plentiful and rapid to limit the temperature drop through the heating elements within 0.1-0.2°. Furthermore, the spinning cells are all in communication with a common aspirating system sufficiently large to maintain a constant rate of flow of air through the cells, by means of interchangeable, but not individually adjustable, outlets of the same size[1].

In spinning by the downward dry spinning process[2], the whole of the evaporative atmosphere is introduced into the spinning cell in the neighborhood and on one side of the extrusion nozzle, and is then withdrawn from the cell on the opposite side of the nozzle wholly at the nozzle level, the whole of the evaporative atmosphere being thus drawn across the extrusive nozzle.

(h). *Other Processes.* G. Bouffe[3] spins a cellulose acetate solution in a closed apparatus (which he illustrates) through which gas or inert fluids traverse, the apparatus being electrically heated. Provision is made for union of the individual filaments into a larger thread. H. Wade[4] has described a procedure for high speed spinning in which filaments are produced of the order of 600 ft. per min. by heating the air in the spinning cell to 140°, using acetone as solvent for the cellulose ester. In the H. Suter process[5], the cellulose derivative filaments are drawn under adequate tension in the presence of swelling agents and other organic compounds which diminish the solvent power. Methylene chloride, trichlorethane and tetrachlorethane are used as swelling agents and carbon tetrachloride, benzene,

1. Courtaulds, Ltd., F. Wood and E. Turney, E. P. 281058; abst. J. S. C. I. 1928, **47**, 154-B; Chem. Zentr. 1928, I, 1244. Courtaulds, Ltd., C. Topham, E. Hazeley and E. Morton, E. P. 365365, Addn. to E. P. 290833; abst. J. S. C. I. 1932, **51**, 336-B.

2. Courtaulds, Ltd., and C. Diamond, E. P. 353597; abst. J. S. C. I. 1931, **50**, 921-B.

3. F. P. 523590; abst. Chim. et Ind. 1922, **8**, 653; Caout. et Gutta. 1922, **19**, 11195. See E. P. 160859; abst. Chem. Met. Eng. 1921, **25**, 33.

4. E. P. 323031; abst. Rayon Record, 1930, **4**, #6, 338.

5. F. P. 696306; abst. C. A. 1931, **25**, 2849; Chem. Zentr. 1931, I, 1699.

toluene and xylene as substances to reduce the solvent action[1].

In dry spinning cellulose ethers by the G. Tocco method[2], the filaments are formed in a closed chamber under reduced pressure, the filaments obtained after evaporation of the solvent being continuously evacuated from the chamber through a tight joint, preferably a hydraulic joint. A more nearly complete solvent recovery is alleged to result where recovered by a gas in a closed cycle and directed at right angles to the thread[3], the gas being caused to circulate by passing it through a heated zone.

8. *Filament Formation by Either Wet or Dry Spinning.* Several methods have been proposed and processes patented for the production of filaments from cellulose derivatives, in which the claim is made that the method is operative with equal efficiency irrespective of whether the emerging filaments are coagulated by immersion in a precipitating bath, or whether spun from a volatile solvent into an evaporative atmosphere. As representative of these methods may be mentioned the following:

The British Celanese, Ltd.[4], spin filaments of methyl-ethyl- or benzyl-cellulose, incorporating in the solution a non-solvent or precipitant of the cellulose ether, being extruded either into a precipitating bath or into a dry atmosphere. The cellulose ether is first dissolved in acetone methyl or ethyl alcohols, chloroform, ethylene dichloride or methylene chloride with either methyl or ethyl alcohols and glycerides of fatty acids as olein, stearin, palmitin, or benzene, toluene, xylene, petroleum jelly (vaseline) or paraffin wax added. After clarification of the composition by filtration, it is squirted either into the air whereby the filament hardens by dissipation of the volatile solvent portion, or into a liquid which is a solvent of cellulose ether

1. E. Prince, U. S. P. 1856401; abst. C. A. 1932, **26**, 3668
2. F. P. 719146; abst. C. A. 1932, **26**, 3378.
3. Chatillon (Soc. Anon. Italiana per la Seta Artificiale), F. P 712143; abst. C. A. 1932, **26**, 2054.
4. E. P. 348625; abst. Silk J. 1931, **8**, #89, 56. E. P. 359910 Addn. to E. P. 348625.

dissolvant but a non-solvent of the cellulose ether. Direct solvents for the cellulose ether of relatively high boiling point may be used in the spinning solution[1], as ethylene, diethylene, propylene and trimethylene glycols, glycerol and glyceryl mono-ethers.

On leaving the spinning nozzles[2], liquid threads consisting of a cellulose derivative in a volatile solvent, with or without a swelling agent, are treated for a short time with a volatile liquid or vapor capable of swelling the cellulose compound without completely coagulating it while being stretched, the filaments being then solidified by evaporation of the volatile material, with or without continued stretching. L. Clement and C. Riviere[3] have disclosed a method for the direct production of colored artificial fibers having a basis of cellulose ethers, there being employed for the spinning solution a cellulose ether which previously has been colored by intimate contact with a mineral pigment reduced to powder in the presence of a liquid capable of being absorbed by the etherized cellulose to an extent insufficient to produce any material change in the latter.

O. v. Kohorn and H. Schupp[4] claim to produce a spinning solution which may be readily spun without fear of the thread tearing and which enables the production of a uniform, fine thread, by adding to the solution a dispersively acting substance in such quantity that a solution of uniform and minimum particle size is obtained, and this stage is considered to have been reached when a solution having the minimum viscosity is obtained for the concentration chosen, and which viscosity remains constant for at least

1. H. Dreyfus, F. P. 713847; abst. C. A. 1932, **26**, 1784.
2. I. G .Farbenindustrie, A.-G., E. P. 327420; abst. C. A. 1930, **24**, 5158; J. S. C. I. 1930, **49**, 656-B. F. P. 677663; abst. C. A. 1930, **24**, 3369; Cellulose, 1930, **1**, 198. See E. P. 318646. F. P. 672301; abst. C. A. 1930, **24**, 2293.
3. E. P. 350894; abst. Textile Mfr. 1931, **57**, 422; Silk J. 1931, **8**, #91, 56. F. P. 710345; abst. Chem. Zentr. 1931, II, 3061.
4. E. P. 318151; abst. C. A. 1930, **24**, 2293; J. S. C. I. 1931, **50**, 388-B; Silk J. 1929, **6**, #67, 72. F. P. 680173; abst. C. A. 1930, **24**, 3902.

24 hours. It has been pointed out[1] that when the two heterogeneous systems of material, the spinning solution and the precipitating bath are made to act upon each other, surface tension is produced which exerts an unfavorable influence upon the formation of the threads. These difficulties may be overcome with certainty, it is said, if provision is made to reduce the surface tension on the bounding surfaces of the two systems by the addition of substances, *iso*propylnaphthalenedisulfonic acid or other di- or tri-sulfonic acids being employed. 0.1% of sodium propyl-*b*-naphthalenesulfonate or sodium *b-iso*propylnaphthalenedisulfonate is said to be sufficient.

Where acetylcellulose filaments are to be produced, L. Levy[2] recommends increasing the spinning solution to 25-30% cellulose ester, on the grounds that less solvent is required and the filaments obtained are stronger. G. v. Frank, H. Krüger and W. Wolff[3] have described suitable apparatus and technique for the dry and wet spinning of cellulose acetate solutions on a laboratory scale.

9. *Spinning Cellulose Derivatives with Resins, Etc.* British Celanese, Ltd.[4], have described a process of filament formation in which organic cellulose derivatives as cellulose ethers are combined with 1-25% of their weight of synthetic resins obtained by the condensation of aldehydic or ketonic substances with phenol, or of sulfonamides with aldehydes. They form filaments by dissolving natural silk in an acid, and precipitating by means of one or more alcohols, low temperatures being used to prevent deterioration[5]. The filaments so obtained are associated with yarns

1. R. Sajitz and F. Pospiech, U. S. P. 1689894; abst. C. A. 1929, **23**, 279. E. P. 280608; abst. J. S. C. I. 1928, **47**, 85-B. Chem. Fabr. Pott & Co., F. P. 617600; abst. J. S. C. I. 1927, **46**, 963-B.

2. E. P. 217003; abst. C. A. 1925, **19**, 398; J. S. C. I. 1924, **43**, 706-B. See E. P. 194666, 210108.

3. Zts. ang. Chem. 1931, **44**, 342; abst. C. A. 1931, **25**, 5984; J. S. C. I. 1931, **50**, 625-B.

4. E. P. 317457; abst. J. S. C. I. 1931, **50**, 128-B; Brit. Plastics, 1931, **2**, #23, 529.

5. British Celanese, Ltd., E. P. 349220; abst. Silk J. 1931, **8**, #90, 51; Textile Mfr. 1931, **57**, #682, 381.

of organic cellulose derivatives to form textiles of differential dyeing properties[1].

Cellulose acetobutyrate filaments stable to boiling, soaping and alkali (?) are claimed to result by using a mixed ester containing 2.2-2.4 mols. acetic acid and 0.5 mol. butyric acid in combination[2]. The combination of synthetic polymerization products of diolefines with cellulose derivatives has been described as leading to filaments of enhanced technical usefulness[3], while Courtaults, Ltd., and C. Diamond[4] add melted wax or paraffin or spermaceti in the homogenized state to cellulose organic ester solutions, the product being dry spun at a temperature above the m. pt. of the added material until after it has passed the spinning jet.

In the W. Beatty process for filament formation[5], a mixture of cellulose acetate and dioxydiphenyldimethylmethane in alcohol, ether, acetone or tetrachlorethane is spun in the usual manner, the proportion of dioxydiphenyldimethylmethane being 25% on the weight of the cellulose ester. The filaments formed, which are insoluble in water, are said to be very resistant to moisture and to burn with difficulty. C. Shrager and R. Lance[6] have described a compound filament obtainable by adding to the cellulose derivative a metallic resinate of high fusing point as zinc or magnesium resinate, which is said to markedly increase resistance to water[7].

H. Schuhmann and F. Streuber[8] have discovered that synthetic resins of the polyhydric alcohol-polybasic acid

1. British Celanese, Ltd., E. P. 356170; abst. J. S. C. I. 1931, **50**, 1044-B; Textile Mfr. 1932, **58**, #686, 79.
2. I. G. Farbenindustrie, A.-G., F. P. 687627; abst. C. A. 1931, **25**, 813; Chem. Zentr. 1931, I, 2289. Can. P. 300573.
3. *Ibid.* E. P. 327164; J. S. C. I. 1930, **49**, 609-B. F. P. 676658; abst. Chem. Zentr. 1930, I, 2976.
4. E. P. 360626; abst. J. S. C. I. 1932, **51**, 142-B.
5. U. S. P. 1156969; abst. Kunst. 1916, **6**, 98.
6. Swiss P. 64683.
7. E. Hubert, A. Röst-Grande and K. Weisbrod, D. R. P. 521598; abst. C. A. 1931, **25**, 3482. W. Dickie and P. Sowter, Can. P. 316198.
8. U. S. P. 1884289.

type known as alkyd resins, in association with triphenyl or tricresyl phosphates and in the presence of suitable volatile solvents, result in the formation of highly elastic and strong fibers when extruded under high pressure. The artificial resins of glycerol and phthalic acid are the type recommended.

10. *Box Spinning.* In the W. Glover and C. Topham method of box spinning of cellulose ether and ester solution in a volatile solvent as acetone[1], the solution is passed through a jet or draw-plate into space containing warm air or other heated gas to effect volatilization of the solvent, the filaments produced being led in association from the warm space, and collected in a rapidly rotating spinning box. In the spinning of artificial filaments by the centrifugal box method as outlined by the I. G. Farbenindustrie[2], the impurities such as salts or acids are removed in a counter-current of washing-liquor which is preferably caused to enter the guide-funnel at the lower part and leave at the upper, the escape of liquor through the thread outlet being prevented or minimized by an injector effect of the flowing liquor or by injection of compressed air, or by the narrow dimensions of the thread outlet.

According to the H. Dreyfus and W. Taylor process[3], in spinning by the centrifugal box method the filaments are introduced into and through the guide or funnel by means of an ejector device operating in conjunction with the guide, or forming a part of it. The ejector comprises a double conical member fitted to the guide or funnel, a blast of compressed air or other fluid being supplied to the annular space so that a filament dropped in the cone is sucked through the apex and blown through the guide into the spinning-box. By means of a guide device in the form of a spiral[4], the threads may be thrown to the outer

1. U. S. P. 1665958; abst. C. A. 1928, **22**, 1854.
2. E. P. 337610; abst. J. S. C. I. 1931, **50**, 109-B.
3. E. P. 340504; abst. J. S. C. I. 1931, **50**, 342-B.
4. British Celanese, Ltd., H. Dreyfus and W. Taylor, E. P. 340505; abst. J. S. C. I. 1931, **50**, 342-B.

:urn of the spiral and are then carried by the rotation of :he box to the center of the spiral which constitutes a tube-ike guide.

An artificial filament spinning-box has been described[1], nade of material not attacked by chemical agents, being flanged with metal.

11. *Cap Spinning.* In the production of filaments from methyl-, ethyl- and benzyl-cellulose[2], the filaments formed by extrusion of the solution into an evaporative atmosphere are simultaneously spun and wound by cap spinning devices, the filaments being lubricated by passage over a pad or roller impregnated with oil, and damped either by humidified air or by coming in contact with a damp roller. It is claimed that the twisting and winding capacity of a plant for artificial filament manufacture[3] is increased by providing two rows of cap spinning devices on the same side of the plant and at substantially the same level, together with guards for preventing interference between the threads. This is accomplished by providing the spinning cell with a slot partly covered by a hinged flap, and having notches through which the threads pass. The threads pass round a feed-roller to guides which are alternately short and long so as to lay over the two rows of cap spinning devices.

In cap spinning operations, particularly for the winding and twisting of yarns and threads continuously with their production, and especially when produced by the evaporative method[4], crossing layers are formed in the yarn package by providing the cap with an edge which does not lie wholly in a plane at an angle to the axis of the spindle. To maintain a uniform balloon, the guide is displaced. Cap

1. Soc. de Constructions Mecaniques de Stains, F. P. 702431; abst. C. A. 1931, **25**, 4402.
2. British Celanese, Ltd., C. Palmer and W. Whitehead, E. P. 198023; abst. J. S. C. I. 1923, **42**, 765-A. Can. P. 252227, 252228.
3. British Celanese, Ltd., W. Crosse and W. Taylor, E. P. 343965.
4. British Celanese, Ltd., and A. Tidmus, E. P. 346366.

spindles for spinning filaments by the acetate process[1] may be provided with ball bearings having oblique reaction, and mounted on a sleeve secured in the lifting rail, and a flywheel secured to the upper part of the wharl[2].

12. *Spinning Nozzles.* In one form[3], the spinning jet is provided with an annular depression on the side to which the spinning solution is supplied, and on the other side with a central circular depression into which a reinforcing member engages to support the centre of the jet and prevent its distortion. In multiple jet spinning[4], artificial threads are produced by extruding the spinning solution through a jet having a plurality of groups of spinning orifices, the filaments from each group of orifices being collected as a separate thread.

In the extrusion orifices as devised by W. Whitehead and C. Dreyfus[5], and intended primarily for artificial horse hair and bristles manufacture, instead of being a circular cross-section, they are compact or squat-shape having indentations in the form of re-entrant angles. It is claimed that by the use of such orifices more uniform filaments are obtainable, substantially similar effects being secured by the use of a cluster of small circular orifices arranged so close together that the filaments after extrusion coalesce to form a unitary filament. The process is designed for cellulose ether or ester filament formation. In apparatus for making filaments, ribbons and straw[6], particularly by the dry process, two spinning jets are arranged in series and in proximity to each other on a single supply pipe in such a way that the second jet may be removed or replaced

1. Fabrique de Soie Artificielle de Tubize Soc. Anon., E. P. 219674; abst. C. A. 1925, **19**, 737.
2. N. V. Philips' Gloeilampenfabr., E. P. 361842; abst. J. S. C. I. 1932, **51**, 225-B.
3. H. Taylor, U. S. P. 1883423. Celanese Corp., E. P. 355720; abst. J. S. C. I. 1931, **50**, 1045-B; Silk J. 1932, **8**, #94, 54. Can. P. 308936.
4. British Celanese, Ltd., and W. Taylor, E. P. 344851; abst. J. S. C. I. 1931, **50**, 533-B.
5. E. P. 318631; abst. J. S. C. I. 1930, **49**, 985-B.
6. British Celanese, Ltd., A. Tidmus, F. Reeson and R. Riley, E. P. 339670.

without interfering with the first jet. When the second jet is removed, spinning proceeds through the first jet which also serves as a pressure retaining member. The first jet is formed with one or more holes of sufficient total area to enable the second jet to receive an adequate supply of spinning solution.

It is said that by providing a matt finish to the exterior surfaces of metallic spinning jets[1], or at least the parts adjacent to the spinning orifices, increased stability of spinning is assured and greater drawing down of the filaments is possible. The matt surface may be formed before or after perforation of the spinning orifices, and may be produced by etching or sand-blasting. R. Thenoz[2] has described a rotary device for spinning artificial threads from cellulose ether and ester solutions, combining a rotatably mounted carrier, from which nozzles lead, being inclined with respect to the axis of rotation of the carrier, and a protective casing for the threads issuing from the nozzles[3]. A nozzle has been described manufactured from condensation products of glycerol and phthalic anhydride[4]. If it is desired to coat the spinning nozzle with a hard glaze[5], a rare earth as beryllium or zirconium is mixed with an ordinary porcelain mass comprising aluminum silicates. The mixture is molded and fired in the usual way.

In the C. Ruzicka multiple spinning nozzle[6], each spinning element is secured into a plate from the exterior, and is provided with a tapered passage, the entrant end of which is larger in diameter than the exit end[7].

1. British Celanese, Ltd., R. Parkinson and F. Reeson, E. P. 327454.
2. E. P. 283140; abst. C. A. 1928, **22**, 3990.
3. R. Thenoz and H. Barthelemy, E. P. 293416; abst. C. A. 1929, **23**, 175; Silk J. 1928, **5**, #54, 88.
4. Bakelite G. m. b. H., D. R. P. 536666; abst. C. A. 1932, **26**, 1121. L. Levy, India P. 12573.
5. E. Brill, D. R. P. 543006; abst. C. A. 1932, **26**, 2594.
6. E. P. 318464.
7. S. Wild, D. R. P. 536574; abst. C. A. 1932, **26**, 1121. Swiss P. 145408; abst. C. A. 1932, **26**, 307.

In the cleaning of spinning heads and nozzles[1], especially machines for the dry spinning of cellulose ethers and organic cellulose esters, pins carrying soap or oil are used. By rubbing over with such pins any stopped-up holes in the nozzle, it is claimed the impurity is rendered slippery and is ejected by the spinning solution. In dry spinning by the J. Nelson method[2], a spinning head is employed having an annular liquid space which is closed at the bottom by a detachable annular sheet-metal jet perforated with a ring of holes. The liquid is forced through the annular jet, and air is supplied to or drawn off from the spaces inside and outside the jet.

13. *Regulating Pressure and Flow.* One method for assuring constancy of pressure at the spinning jets[3] is to interpose between the main supply pipe for the spinning solution and the separate spinning machine, a pressure-reducing valve such as will reduce the pressure to a degree slightly above atmospheric pressure. For the storage of the solution suitable for spinning[4], the Societe Industrielle de Moy has described a system comprising the use of endless conduits. Thus, a series of tanks, mixers, presses, etc., is supplied by a conduit forming a closed circuit, and receiving the solution so that whichever tank is being fed, the solution flows in opposite direction thereto and no dead spaces occur in the conduit. The supply to each tank is controlled by a "distributor."

In the dry spinning method[5], a temporary increase in pressure at the jets to assist in starting the spinning is obtained by cutting off the solution from the jets and supplying it to a pressure chamber into which it is pumped until the desired pressure is obtained, after which the pres-

1. O. v. Kohorn and H. Schupp, E. P. 334109; abst. C. A. 1931, **25**, 816.
2. E. P. 338881; abst. J. S. C. I. 1931, **50**, 153-B.
3. M. Holken Ges., E. P. 352761; abst. Silk J. 1932, **8**, #93, 54.
4. Soc. Industrielle De Moy, E. P. 356182; abst. Silk J. 1932, **8**, #94, 54.
5. Cellulose Acetate Silk Co., Ltd., and H. Curtis, E. P. 344591; abst. C. A. 1932, **26**, 306.

sure chamber is connected with the jets. The E. Mossgraber device is similar[1].

To avoid waste of spinning solution when a jet or nozzle is changed[2], there is associated with each spinning jet or nozzle, a valve adapted to close when the nozzle is removed and to open when the nozzle is fitted or replaced. Preferably the valve in its closed position is arranged to pass a small quantity of spinning solution, a quantity as is normally passed by the nozzle, for which purpose the valve or the seating may be slotted or grooved. The control device of J. Rast, F. Kummer and F. Pauli[3] works on an analogous principle. The Soie de Clairoix[4] have also described means for regulating the flow of spinning solution to the nozzle in making acetate silk.

14. *Spinning Cell.* In the process of British Celanese, Ltd.[5], of spinning of artificial filaments from solutions of organic cellulose derivatives, the filaments are extruded into a current of evaporative medium which for the major part of its flow passes through an area substantially greater than that occupied by the filaments in the neighborhood of the spinning orifices, constricting the passage of the evaporative medium so that a definite proportion of it is constrained to pass through the immediate vicinity of the spinning orifices. After passage through the cells[6], the threads are wound up on cap- or ring-spinning machines. In a

1. D. R. P. 517932; abst. C. A. 1931, **25**, 2849.
2. British Celanese, Ltd., and J. Bower, E. P. 299405; abst. J. S. C. I. 1929, **48**, 14-B.
3. Swiss P. 134401.
4. F. P. 710778; abst. C. A. 1932, **26**, 1783.
5. British Celanese, Ltd., E. Kinsella, J. Bower and W. Taylor, E. P. 300998; abst. C. A. 1929, **23**, 4072; J. S. C. I. 1929, **48**, 203-B; Chem. Zentr. 1929, I, 1635. H. Dreyfus, E. Kinsella, J. Bower and W. Taylor, U. S. P. 1814468; abst. C. A. 1931, **25**, 5289. F. P. 566385; abst. Chem. Zentr. 1924, I, 2760; Faserstoffe, 1924, **6**, 67. H. Dreyfus, F. P. 661810; abst. C. A. 1930, **24**, 500. See U. S. P. 1541104, 1602125. E. P. 165519, 203092.
6. British Celanese, Ltd., E. P. 340326; abst. Silk J. 1931, **7**, #83, 52. H. Dreyfus, F. P. 39238, Addn. to F. P. 679618; abst. C. A. 1932, **26**, 2317. F. P. 722631. Aceta G. m. b. H., F. P. 725421. C. Dreyfus, F. P. 725385. H. Dreyfus, Can. P. 285981. British Cell. & Chem. Mfr. Co., C. Palmer and W. Whitehead, Ital. P. 217761.

variant of the above method[1], the filaments from each group of orifices are collected as a separate thread, and on separate winding or twisting devices.

In order to produce filaments from cellulose ether solutions[2], a separate cell is used wherein each single cell is equipped with a waste gas duct which leads the air bearing the vapors to a collecting duct. These waste gas ducts are furnished with an arrangement which shows the volume of air flowing out of each cell. A valve is further provided by means of which the escaping stream of air can be regulated or limited.

In the M. Klein apparatus for spinning solutions of cellulose ethers[3], each cell is subdivided by one or more diaphragms into an upper zone containing the spinning nozzle and lower heating zone where aspiration is effected, and which are successively traversed by the spun thread. The diaphragms, which consist of a fixed portion and a central hinged part (the latter containing a triangular notch which may be partially closed so as to leave only sufficient space for the passage of the thread) serve to prevent hot air passing into the upper zone. Or[4], the cellulose ether solution may be spun downward in a closed chamber, fresh air entering at the top around the spinning

H. Dreyfus, Ital. P. 227065. Belg. P. 323360, 330789, 343916, 345567, 347479, 350136, 352234, 352642, 353304, 356527, 359431, 362731, 363571, 363674. H. Dreyfus and E. Kinsella, Belg. P. 357749. H. Dreyfus and W. Taylor, Belg. P. 363462, 363568, 363570, 363812. H. Dreyfus, W. Dickie and F. Hale, Belg. P. 365773.

1. British Celanese, Ltd., W. Crosse and W. Taylor, E. P. 343965; abst. C. A. 1932, **26**, 307. British Celanese, Ltd., W. Taylor and H. Dreyfus, E. P. 343936; abst. C. A. 1932, **26**, 307. British Celanese, Ltd., and W. Taylor, E. P. 344351; abst. C. A. 1932, **26**, 307; Silk J. 1931, **8**, #86, 53. See E. P. 324061.

2. British Celanese, Ltd., E. Kinsella, J. Bower, J. Briggs and R. Roberts, E. P. 341075. H. Dreyfus, F. P. 566385; abst. Chem. Zentr. 1924, I, 2760; Faserstoffe, 1924, **6**, 67. Can. P. 308433. Belg. P. 376997.

3. U. S. P. 1767216; abst. J. S. C. I. 1930, **49**, 761-B. E. P. 292561; abst. J. S. C. I. 1929, **48**, 595-B; Chem. Zentr. 1928, II, 1407. F. P. 658826; abst. C. A. 1929, **23**, 5317.

4. M. Klein, U. S. P. 1716781; abst. C. A. 1929, **23**, 3808; J. S. C. I. 1929, **48**, 773-B. E. P. 292608; abst. J. S. C. I. 1929, **48**, 774-B; Chem. Zentr. 1928, II, 1407. F. P. 648397; abst. C. A. 1929, **23**, 3099.

nozzles, the chamber being divided into two compartments, separated by a diaphragm. The air is admitted to an upper zone about the spinning nozzle, hot air and solvent vapors being withdrawn from a lower zone[1].

The air circulation arrangement above was later modified[2], each zone of the cell having its own inlet and outlet so that the circulation of the evaporative medium in one zone is independent of that in the other. The evaporative medium issuing from one zone may, optionally after passing through heating, cooling or other devices, be circulated in the other zone. The orifice through which the thread issues, in the dry spinning of cellulose ether solutions[3], is situated in the bottom of the cell, and preferably in a direct vertical line below the spinning nozzle, so that the thread passes directly from the spinning nozzle to the winding bobbin with as few changes in direction as possible. The thread may pass round rollers in the spinning cell[4], the cell being provided with diaphragms.

In the construction of the dry spinning cell[5], there is a section enclosing a nozzle in which the atmosphere is stagnant and contains a high concentration of solvent vapor, a middle section traversed by a current of air in a direction opposite to the traveling of the filaments, and a section in which the atmosphere is stagnant and contains a low concentration of solvent vapor. The cell is associated with a circulatory system so that the admission of air to each cell and the temperature and solvent vapor content of the admitted air are all regulable[6], while the bulk of the solvent is recovered.

1. M. Klein, U. S. P. 1767215; abst. C. A. 1930, **24**, 4390.
2. *Ibid.* E. P. 300166; abst. C. A. 1929, **23**, 3574; J. S. C. I. 1929, **48**, 893-B; Silk J. 1929, **5**, #57, 74; Chem. Zentr. 1929, I, 1169. F. P. 686027; abst. C. A. 1930, **24**, 6015. See E. P. 292561, 292608.
3. *Ibid.* E. P. 303056; abst. Silk J. 1929, **5**, #59, 74.
4. *Ibid.* E. P. 283139.
5. Ruth-Aldo Co., Inc., E. P. 308563.
6. M. Klein, U. S. P. 1767215; abst. C. A. 1930, **24**, 4390. E. P. 308564. F. P. 660365; abst. C. A. 1930, **24**, 239. Ruth-Aldo Co., Inc., D. R. P. 487552; abst. C. A. 1930, **24**, 1980. Belg. P. 352198. Aust. P. 117706. Cites D. R. P. 428745.

P. Schlack[1] has described a cell for the production of threads by the dry spinning process, in which the drying is effected by an ascending current of a gaseous medium in counter-current to the filaments, comprising a constriction of the drying cell at a medium level of the cell forming two compartments within, with means provided for withdrawing one part of the drying medium at the upper end of the lower compartment, and means for withdrawing another portion of the medium ring from the upper compartment, in proximity to the point of issue of the filaments from the nozzle.

To ensure uniform temperature conditions through a range of cells for the dry-spinning of threads[2], each cell is provided at its upper and lower parts with separate heating elements, the individual members of the two sets being connected together in series, each in two groups, and the heating liquid circulated through the elements in opposite directions. The upper and lower parts of the spinning cells are also each provided with a water-jacket[3], the upper ones being connected to one another and likewise the lower ones, while the heating medium circulates through each lower jacket in a direction opposite to that through the corresponding upper jacket.

In another process[4], the cell is divided longitudinally into a heating chamber which may occupy a portion only of the length of the cell, and a spinning chamber. The gaseous atmosphere passes upwards through the heating chamber and downwards through the spinning chamber in the same direction as the filaments to a smaller chamber, and thence, through a main artery to all the cells and on to the solvent-recovery plant.

1. U. S. P. 1834806; abst. C. A. 1932, **26**, 1121. Aceta Ges, E. P. 311763, 317368. F. P. 708652; abst. Chemical Abstracts 1932, **26**, 1441.
2. Aceta, Ges., E. P. 313165.
3. A. Friederich, U. S. P. 1804530; abst. J. S. C. I. 1932, **51**, 142-B.
4. Cellulose Acetate Silk Co., Ltd., and P. Chaumeton, E. P. 351091; abst. J. S. C. I. 1931, **50**, 799-B; Textile Mfr. 1931, **57**, #683, 422; Silk J. 1932, **8**, #92, 53.

The N. Grillet method passes the extruded filaments into a heated gaseous current passing through a cell[1], the volume of gaseous current being regulable in a group comprising a large number of cells by acting upon the temperature of the gaseous current by means of a double series of temperature controlling elements. The filament may be spun into an atmosphere already partially saturated with solvent vapor[2], whereby an economy in solvent recuperation is possible. In producing "non-scintillating" filaments[3], in the region of the spinning jets is provided an atmosphere laden with solvent, this being withdrawn by a heating device from the lower part of the spinning cell and delivered to the region of the spinning jets[4].

E. Prince[5] extrudes the viscous liquid from the spinning die into an evaporative atmosphere in a closed cell individual to the spinning die, admitting a cooled gaseous medium in the vicinity of the die to lower the temperature, and then withdrawing the gas laden with the solvent to recuperating columns for recovery and re-use[6]. The C. Ruzicka spinning cell is arranged for downward spinning[7], and is provided with a casing or jacket having at the upper part a connection through which heated air is supplied, while at the lower part are openings which communicate with the spinning cell so that the heated air passes down-

1. N. Grillet, U. S. P. 1571474. E. P. 238842. D. R. P. 428745.
2. *Ibid.* U. S. P. 1695094. Soc. pour la Fabrication de La Soie Rhodiaseta, E. P. 238842; abst. J. S. C. I. 1926, **45**, 627-B. E. P. 269377; abst. C. A. 1928, **22**, 1474; J. S. C. I. 1927, **46**, 472-B. D. R. P. 443414; abst. Rayon, 1927, **5**, #1, 24. Aust. P. 112857; abst. Chem. Zentr. 1929, I, 3055. Belg. P. 351420. See U. S. P. 1583475; abst. J. S. C. I. 1926, **45**, 580-B.
3. Chatillon Societa Anon. Italiana per la Seta Artificiale and E. Orioli, E. P. 344385; abst. C. A. 1932, **26**, 306. F. P. 702628; abst. C. A. 1931, **25**, 4402. D. R. P. 542811, 542812; abst. C. A. 1932, **26**, 3111. Aust. P. 126572; abst. C. A. 1932, **26**, 2594.
4. F. Shedden, A. Delph and N. Baguley, U. S. P. 1790599; abst. C. A. 1931, **25**, 1381. F. Lewis, U. S. P. 1835956; abst. C. A. 1932, **26**, 1121. E. P. 353597; abst. Textile Mfr. 1932, **58**, #685, 36.
5. U. S. P. 1856401.
6. E. Prince, U. S. P. 1572955; abst. C. A. 1926, **20**, 1328.
7. E. P. 317108.

wardly through the jacket, and upwardly through the spinning cell.

In the Scientifil apparatus[1], filaments prepared from acetone solutions of organic cellulose derivatives by the dry spinning method, are guided from the spinning nozzle to the winding bobbin by a current of gas, with the result that spinning can be carried on continuously and the winding of the filaments on bobbins started at normal spinning speed. To obviate disturbances during spinning due to the entry of air at the outlet orifice of the extrusion cabinet used in the dry spinning process[2], the thread is led out of the cabinet through a liquid seal. The guide under which the thread passes may constitute the lower edge of a sliding door by means of which access is gained to the interior of the cabinet. Or in the dry spinning operation[3], the solution is extruded downwardly into a slowly ascending gaseous medium, the temperature of which gradually increases in an upward direction. The spinning chamber comprises a tube open at the lower end and provided with a heating jacket, the heating fluid being supplied to the upper part of the jacket and exhausted at the lower part. The rate of flow of the evaporating medium is controlled by means of an outlet at the upper part of the chamber.

15. *Stretching and Twisting.* A process applicable to the formation of methyl-, ethyl- and benzyl-cellulose filaments has been disclosed by British Celanese, Ltd., H. Dreyfus and W. Taylor[4], by extruding a spinning solution into an evaporative atmosphere followed by passing the filaments, after formation of a skin-layer on them, into an atmosphere of solvent vapor to soften the outer layer, and then stretching the softened filaments. Very low deniers

1. E. P. 295354; abst. C. A. 1929, **23**, 2294.
2. L. Levy, E. P. 250683; abst. C. A. 1927, **21**, 1355. O. Silberrad, E. P. 289233; abst. C. A. 1929, **23**, 706. H. Barthelemy, F. P. 711536; abst. C. A. 1932, **26**, 2054. See E. P. 168986, 213138, 219106.
3. N. V. Nederlandsche Kunstzijdefabriek, A.-G., E. P. 282326; abst. Rayon, 1928, **6**, #10, 26.
4. E. P. 340929; abst. C. A. 1931, **25**, 5028; Silk J. 1931, **7**, #84, 53.

as 0.5-1.5 or lower are said to be obtained. To facilitate stretching, plastifiers or high boiling point solvents may be added to the spinning solution. Tension is applied to stretch the filaments[1], the tension being wholly or partially confined to that portion of the filaments which has been submitted to the softening influence of the vapor. Or[2], the partly coagulated filaments after leaving the coagulating bath in the wet spinning method, are stretched by passage through a narrow tube through which flows a current, either direct or counter-current, thereby offering a resistance to the forward movement of the filaments, which are drawn forward by independent means such as a roller.

According to the W. Harrison plan[3], the filaments are first treated to remove non-resistant celluloses (which should have been removed prior to the filament-forming stage), and then treated with a swelling or plasticizing agent and stretched, the plasticizer being afterwards removed. In filament manufacture of cellulose ether solutions in volatile solvents[4], the filaments are supported in their travel through the evaporative atmosphere so as to prevent the entire weight of the filament from bearing upon the stream of solution flowing from the spinning orifice, this method being particularly applicable to the manufacture of heavy filaments as bristles, horsehair and straw. The filaments may be drawn out while drying by passing them over rollers rotating at successively greater peripheral speeds, and are thereby attenuated to a finer denier.

Systematic variation in denier may be produced by drawing the filaments or threads at varying linear speeds by means of a roller driven at controllable speeds, thereby imparting a regular or systematic variation in denier to

1. British Celanese, Ltd., H. Dreyfus and W. Taylor, E. P. 340930; abst. C. A. 1931, **25**, 5028; Silk J. 1931, **7**, #84, 53.
2. Comptoir des Textiles Artificiels, E. P. 335613; abst. J. S. C. I. 1930, **49**, 1146-B.
3. E. P. 344873; abst. C. A. 1932, **26**, 306.
4. W. Whitehead and C. Dreyfus, E. P. 318630. K. Burgemeister, D. R. P. 523300; abst. C. A. 1931, **25**, 3502.

the filaments[1]. The F. Gahlert method of stretching[2] involves unwinding the filaments from bobbins or reels and passing from delivery rollers through a treatment bath, from which they are taken up and wound upon a spool rotated by means of a friction winding drum, the peripheral speed of which causes stretching of the threads. In order to obtain in the dry spinning process[3] a rapid replacement by swelling agent of the solvent carried by the threads, the latter are extruded into a chamber which has been freed from air and is filled with the vapor of a swelling agent. The jelly-like threads so obtained are in a condition such that, on stretching, the desired orientation of the micelle is obtained. In the wet spinning and stretching[4], some of the stretching devices are recommended to be heated, and if desired, rinsed.

Another proposed method of stretching (and hence obtaining finer denier filaments)[5], involves applying a fluid stream to the filaments in the course of their production in such a manner that they are propelled by the stream at a speed greater than that at which they are extruded, so that they are stretched and their denier reduced.

H. Dreyfus and S. Welch[6] have devised a method of twisting and winding threads continuously with their production by means of a ring or flyer, by threading the ring-traveler flyer or similar device, while the thread is being

1. British Celanese, Ltd., H. Dreyfus and W. Taylor, E. P. 329620; abst. C. A. 1930, **24**, 6015. British Celanese, Ltd., H. Dreyfus, W. Dickie and W. Taylor, E. P. 346354; abst. C. A. 1932, **26**, 2054. H. Dreyfus, F. P. 664064; abst. C. A. 1930, **24**, 963. F. P. 667209; abst. C. A. 1930, **24**, 1217. F. P. 681038; abst. C. A. 1930, **24**, 4157. F. P. 681317; abst. C. A. 1930, **24**, 4392. F. P. 39410, Addn. to F. P. 681317; abst. C. A. 1932, **26**, 2318. H. Dreyfus, W. Dickie and W. Taylor, Can. P. 324226.

2. E. P. 349232; abst. Textile Mfr. 1931, **57**, #682, 381.

3. I. G. Farbenindustrie, A.-G., E. P. 340570. See E. P. 327420, 341021.

4. H. Meyer and H. Pfannenstiel, D. R. P. 526264; abst. C. A. 1931, **25**, 4402.

5. British Celanese, Ltd., and W. Taylor, E. P. 322557; abst. C. A. 1930, **24**, 2883; Silk J. 1930, **6**, #70, 62. See E. P. 165519, 198023, 277089.

6. Can. P. 301530.

delivered, to a continuous winder for collecting the thread as fast as produced. In the production of highly twisted or creped threads[1], the yarns are drawn off from a rotating yarn package and are led to a point above and in alignment with the axis of the yarn package, causing the yarn to coil round a rotating member co-axial with and extending through the yarn package, and to pass in a balloon-shaped path.

To facilitate the starting operations in twisting artificial silk[2], by means of box, ring or traveler, the ends of a double auxiliary thread are attached to the twisting device so that the ends are twisted and form a loop, through which a loop of the filament running from the spinning device to the lap roller is drawn. In the J. Brandwood method of delivering filaments during twisting[3], the threads wound on a large spool, are led to a twisting device without being passed over the end of the spool which is vertically mounted on a turntable having a friction surface. Another method of facilitating the starting operation in twisting filaments, the end issuing from the spinning chamber or tube is collected in a tube or bottle connected with a vacuum tank and then threaded through the traveler and attached to the bobbin, whereupon it is broken and normal twisting and winding proceeds[4], the filaments being guided before or after the threading of the traveler.

16. *Washing and Bleaching Filaments.* One method of washing as disclosed by the I. G. Farbenindustrie is to collect the filaments into bundles of around 300 fibers[5],

1. W. Dickie and R. Martin, Can. P. 297857.
2. H. Deile, U. S. P. 1822018. Aceta Ges., E. P. 343791, 343792, 343817.
3. U. S. P. 1846627; abst. C. A. 1932, **26**, 2593. E. P. 348161; abst. Silk J. 1931, **8**, #89, 56.
4. Cellulose Acetate Silk Co., Ltd., and H. Curtis, E. P. 356473; abst. Textile Mfr. 1932, **51**, #686, 80. E. P. 359627; abst. Textile Mfr. 1932, **58**, #688, 163.
5. E. P. 356975; abst. J. S. C. I. 1931, **50**, 1136-B. The I. G. Farbenindustrie (E. P. 311399) for the washing and bleaching of a large number of filaments and of high total titre (say 60000-90000 deniers), place the material on a band which is passed with little or no tension through a succession of baths between each of which are

these being then passed, in a parallel position and with avoidance of stretching or other mechanical stress, through washing and treating baths to the receiving device of a speed greater than 50 m. per min., by means of adjusted rotating guides. According to T. Banigan[1], the filaments are washed with water as long as the economic removal of acids or salts warrants, and then with a solution of a volatile compound which reacts with an acid to form water-soluble salts, as 0.015% aqua ammonia.

A two-phase process for washing artificial silk has been proposed which comprises subjecting the filaments wound on spools to a relatively short preliminary washing with water forcibly applied by mechanical means[2], followed by immersing the spools for a relatively long treatment in a body of water which is renewed until the washing is completed.

In the bleaching of artificial filaments of whatever nature, an important point is to see that the rinsing is thorough and complete, a further safety measure being to use a small amount of sodium bisulfite or hydrosulfite as an "antichlor," which will destroy the last traces of bleaching solution. Peroxides or hydrogen dioxide bleach artificial filaments without injury, and its absolute removal is not necessary. Decoloration may be effected by successively treating the filaments with cold potassium permanganate solution, then washing and treating with sodium bisulfite solution made slightly acid with HCl until the brown color disappears[3].

arranged pressure rollers, the drives of the several rollers being so arranged that the speed may be varied. The band is held beneath the surface of the liquid by glass rods, or by passing round a reel. By applying slight tension to the band, the filaments composing it are maintained in an opened-out condition.

1. T. Banigan, U. S. P. 1802935; abst. J. S. C. I. 1931, **50**, 1136-B.

2. H. Lummerzheim, U. S. P. 1553252; abst. C. A. 1925, **19**, 3599. See J. Brandwood, E. P. 311803. Compare also E. P. 311391, 312034, 328013, 332003, 337590, 348644, 359860. U. S. P. 1829678. D. R. P. 540351, 552290. F. P. 713346. Can. P. 317658.

3. Gillet et Fils, F. P. 570264; abst. J. S. C. I. 1930, **49**, 280-B; Rayon J. 1926, **1**, #1, 55.

Aqueous oxalic acid is the basis of another patented process[1], being afterwards removed by washing to strict neutrality. In the bleaching of filaments of cellulose acetate[2], decolorization is effected by treating the material with 10-20 times its weight of 1-20% acetic acid solution or 0.5-2% NaOH solution to induce a slight swelling, and then treating with hypochlorite or free (electrolytic) chlorine.

According to W. Harrison who has patented a process for so doing[3], filaments spun from cellulose derivatives are first treated with a swelling agent whereby impurities contained therein may more readily be removed, which agent is removed after the step of purification by washing, the purifying step being applied at any stage during or after filament formation, but before final stretching.

17. *Lubricating Filaments.* In the British Celanese, Ltd., method of lubricating and softening cellulose derivative filaments[4], there is added to the spinning solution up to 4% of a material which raises the electric conductivity of the solvent and which remains in the filament after washing—at least to a substantial degree—organic bases such as triethanolamine being especially useful. Turkey-red oil has been used for the same purpose[5], as has diethylene glycol[6].

In the application of treating liquids to filaments which are being produced at high speed[7], the filament is placed in contact with the edge of a disc dipping into the treating liquor and rotating in a plane substantially at right angles

1. W. Moss, Can. P. 319149.
2. K. Roos, E. P. 326471; abst. C. A. 1930, **24**, 4931; J. S. C. I. 1930, **49**, 457-B; Chem. Zentr. 1930, II, 989.
3. E. P. 344873; abst. J. S. C. I. 1931, **50**, 533-B.
4. E. P. 366110; abst. Chem. Zentr. 1932, I, 2791. See Parcofil A. G., Swiss P. 147115. A. Friederich and Aceta Ges., E. P. 348407. D. R. P. 533060. British Celanese, Ltd., and W. Taylor, E. P. 337433. Can. P. 316197. H. Gill, E. P. 357971. F. Gahlert, U. S. P. 1847827. Sondermann & Co., E. P. 297778, 318211.
5. H. Dreyfus, F. P. 688625; abst. C. A. 1931, **25**, 1084.
6. British Celanese, Ltd., E. P. 313885; abst. J. S. C. I. 1930, **49**, 1146-B. W. Whitehead, Can. P. 317116; abst. C. A. 1932, **26**, 1454.
7. *Ibid.* E. P. 359477; abst. J. S. C. I. 1932, **51**, 225-B.

to the direction of travel of the filament. In the spinning of organic cellulose derivative filaments by one process[1], 1.5% (calculated on the filament weight) of olive and cocoanut oil, olein, butter fat, beef suet, bone oil or lard is added to the spinning solution for purposes of lubrication. Oleic acid, castor oil, paraffin oil or solution of alkali oleates are supplied as a dressing to the thread by means of a pad or roller impregnated with the dressing[2], being applied to the thread just before it is wound into hank, cone or spool farm.

18. *Drying Filaments.* The threads may be dried loosely in the air as in hank form, or afterwinding on spools. In the latter method[3], the filaments are wound on a resilient bobbin or spool, for example, a gapped cylinder or a cylinder made in the form of a spiral, to prevent development of undue stresses during drying, and at the same time to provide means whereby the initial tension of winding is automatically increased slowly and continuously as the drying proceeds. A liquid (water, paraffin, glycerol, olive oil) is applied to the filaments during an early stage of drying and while they still contain a relatively large proportion of solvent, to impart improved extensibility, tenacity, type and regularity of cross-section and levelness of dyeing[4].

In the drying in hank form, the bundles or hanks are usually wrapped in soft cheese cloth, centrifuged to a moisture content of 75-85%, removed from the protecting cloth, and hung on a movable arm drier of the Philadelphia Dryer type, where the arms are slowly rotatable in order

1. N. V. Nederlandsche Kunstzijdefabriek, F. P. 661992; abst. C. A. 1930, **24**, 500.

2. British Cellulose & Chemical Mfr. Co., Ltd., C. Ryley, C. Palmer and S. Welch, E. P. 215417; abst. C. A. 1924, **18**, 2967; Faser. 1924, **6**, 130; Chem. Zentr. 1924, II, 1534.

3. J. Zdanowich, E. P. 260642; abst. J. S. C. I. 1927, **46**, 103-B. U. S. P. 1630285; abst. C. A. 1927, **21**, 2385; J. S. C. I. 1927, **46**, 519-B. Can. P. 258764. See E. P. 139232, 190732, 196641, 200186, 203599, 227134, 244148.

4. British Celanese, Ltd., and W. Taylor, E. P. 355652; abst. J. S. C. I. 1931, **50**, 1044-B; Textile Mfr. 1932, **51**, #686, 78. E. P. 327740; abst. C. A. 1930, **24**, 5169.

not to allow stretching from the weight of the hank to be applied to one portion of the skein for an unduly long period. Air heated at about 65° is introduced into the drying chamber from the bottom, and removed by fans from the sides. About one hour is required to reduce the moisture content to about 8%, which is considered technically dry. If the filaments have dried to a point materially below this standard, they are afterwards allowed to remain in a moisture-controlled room with humidifying apparatus until the moisture regain has reached about the point of 9%.

19. *Winding.* In machines for spinning artificial silk wherein the winding-spindles are mounted in pairs on a rotatable carrier which is rotated so as to disconnect the spindle carrying a fully wound spool from the driving gear[1], and to connect the spindle carrying an empty spool, the speed of the shaft which drives the spindles is reduced while the frame is being rotated, to disconnect one spindle and connect another. A traverse mechanism has been described for the winding apparatus of artificial silk spinning machines[2], particularly of the type having two traverse cam-drums, comprising a forked level actuating the traverse rail, and an arrangement which is adjustable to vary the traverse while the machine is in action.

The S. Percival process[3] involves winding the filaments into cops (bottle or splicer bobbins) which are preferably at least 3 in. in diameter, the individual layers having an inclination of at least 15°, and consist of superimposed groups of layers, each group being formed by displacing the layers, relatively to each other, first in an upward and then in a downward direction. Courtaulds, Ltd.[4], have described a reciprocating guide for winding filaments onto pirns and tubes, which comprises two spaced and grooved

1. C. Hamel Akt.-Ges. and E. Hamel, E. P. 358045; abst. Textile Mfr. 1932, **58**, #687, 118.
2. *Ibid.* E. P. 341330.
3. S. Percival, E. P. 357606; abst. Textile Mfr. 1932, **58**, #687, 117. Barmer Maschinenfabrik A.-G., E. P. 361696; abst. Silk J. 1932, **8**, #97, 56.
4. E. P. 352962; abst. Silk J. 1932, **8**, #93, 54.

wheels arranged with their axes parallel, and the common plane of the axes at right angles to the axis of the pirn.

In the production of artificial threads by the dry spinning process[1], a tag of soft, flexible metal such as a tuft of fibrous material or a thin strip of chamois leather, is secured to the bobbin below the lowest point of the traverse or to a disc of cardboard, to facilitate starting up. The loop of filaments running onto the waste roller is stretched alongside the bobbin past the tag and is broken, whereupon the tag picks up the broken end and normal winding-on of the filament proceeds. It is claimed that if the fiber is subjected to the action of a moving tensioning pulley as it is unwound off the spool after spinning[2], a fiber is produced more responsive to dyeing. Metallized tubes and bobbins have been described[3].

J. Brandwood[4] advises the winding on foraminous spools of tubular bobbins of threads of artificial silk for subsequent centrifuging and dyeing, the spools while leaving closely set and evenly spaced radial passages of small area extending through the windings, yet leave a free passage for the liquid to ensure uniform treatment[5]. In the Compagnie Scientifil[6] machine for the dry spinning of acetone solutions of organic cellulose derivatives, a winding mechanism is described comprising a driving roller extending longitudinally of the machine, an axially movable rod parallel with the roller, and for each spinning nozzle, a pair of bobbin spindles carried by the rod and axially movable therewith, whereby one bobbin may be shifted below the corresponding nozzle to remove the full bobbin and start the winding.

1. J. Peddler and Courtaulds, Ltd., E. P. 336718.
2. Deutsche Zellstoff-Textilwerke, Ges., D. R. P. 530508; abst. C. A. 1932, **26**, 319.
3. British Celanese, Ltd., W. Dickie and F. Hale, E. P. 334174.
4. E. P. 340201.
5. R. Etzkorn, D. R. P. 544123; abst. C. A. 1932, **26**, 2594.
6. Can. P. 291033. J. Healey, E. P. 317125.

20. *Spools.* In order to ensure a smooth surface and increased wearing[1], it has been proposed to coat bobbins with a composition composed principally of cellulose derivatives of higher fatty acids, as cellulose oleate, palmitate, stearate and laurate. A layer of resin may be applied over the composition.

Pirn tubes, cop tubes, cheese tubes and bobbins and other supports for packages of textile threads[2], which have been metallized, may be given a second metal coating by electrolysis to increase their wearing qualities[3].

21. *Solvent Recovery.* In the recapture of solvent in cellulose ether and ester filament formation by the dry or evaporative method, and to a lesser degree where the solvent used to dissolve the cellulose derivative is entrained in an aqueous solution as in the wet spinning process, the usual solvent is pure acetone, or acetone in combination with another comparatively low boiling liquid. In cellulose acetate filament production, 98% acetone diluted with the intentional addition of a proportion of water constitutes the solvent medium. A comprehensive statement of the details of solvent recovery as practiced in synthetic filament fabrication is too broad for inclusion herein. A synopsis of the three general methods in use is as follows:

(a). *Recovery by Washing with Water.* The air laden vapors are forced or aspirated through a series of chambers containing baffles or other impediments therein acting as scrubbers in which the air containing acetone is brought into intimate contact with the water. When the latter nears the point of saturation with acetone it is distilled in an ethyl alcohol type still with long fractionating

1. I. G. Farbenindustrie, A.-G., E. P. 311287; abst. C. A. 1930, **24**, 976; British Plastics, 1930, **2**, #17, 229. F. P. 673996; abst. C. A. 1930, **24**, 2618. D. R. P. 487011; abst. C. A. 1930, **24**, 1228. Can. P. 290805.

2. British Celanese, Ltd., W. Dickie and F. Hale, E. P. 351074; abst. Silk J. 1931, **8**, #91, 56.

3. Barmer Maschinenfabr. A.-G., E. P. 372395; abst. J. S. C. I. 1932, **51**, 596-B.

column whereby a concentration of 97-99% is obtained in a single distillation slowly conducted. H. Bollmann[1] conveys the gases in a continuous manner along a gradually rising path, alternatively heating and cooling the same during the passage, finally immersing in water. The E. Bindschedler method removes solvent from the mixed vapors by intimate contact with water[2], any ether present being absorbed from the residue by means of concentrated sulfuric acid.

In the solvent process of A. O'Neil[3], material containing the solvent is brought in contact with a current of hot gas, the solvent vapor being forced down a tortuous passage in contact with refrigerated solvent, the gas freed from solvent being re-used. Circulation of gas and vapor is effected solely by the gas-heating and refrigerating operations.

(b). *Recovery by Solvent Extraction.* The J. Bregeat method of acetone recovery, so largely used in the World War in France[4], depends upon being the solvent in either the gaseous condition or in conjunction with water, in intimate association with a phenol or cresol, the acetone afterwards removed from the nearly saturated high-boiler by simple distillation. Cresol, or sodium phenolate or cresylate are the absorbents employed in the

1. U. S. P. 1371546; abst. C. A. 1921, **15**, 1772; J. S. C. I. 1921, **40**, 289-A.

2. U. S. P. 1376069; abst. J. S. C. I. 1921, **40**, 422-A.

3. U. S. P. 1381002; abst. C. A. 1921, **15**, 3351; J. S. C. I. 1921, **40**, 569-A. U. S. P. 1443547; abst. J. S. C. I. 1923, **42**, 254-A.

4. U. S. P. 1315700, 1315701; abst. C. A. 1919, **13**, 2983; J. S. C. I. 1919, **38**, 855-A. See E. P. 128640, 131938; abst. J. S. C. I. 1919, **38**, 621-A, 751-A. In the Syntheta A. G. process (E. P. 265577. D. R. P. 539390; abst. C. A. 1928, **22**, 317; 1932, **26**, 1784) the solvent is recovered in spinning of artificial silk by passing the threads into a chamber heated to a temperature above the boiling point of the solvent, and enclosing a heated atmosphere consisting of the vapors of the solvent evaporated from the threads. The threads are projected from nozzles arranged in the roof of a chamber heated by steam pipes, and collected on spools. The solvent concentration in the chamber is maintained constant by withdrawing vapor from the latter and passing it through a condenser, uncondensed vapor being returned to the chamber.

solvent captation method of W. Runge and H. Curtis[1], while ethyl alcohol constitutes the absorbent in the H. Bassett and S. Sadtler system[2]. E. Bindschedler[3] claims an improvement on the Bregeat set-up, by first passing the vapors through a phenolic tower, and then absorbing last traces by passage through a tower of sulfuric acid, which also holds back any entrained phenolic bodies. Washed flue gas containing phenolic and cresylic derivatives constitutes the solvent recapture medium of W. Lewis and W. Green[4].

(c). *Recuperation by Charcoal or Silica Gel.* Properly activated charcoal is an excellent absorbent for acetone vapors, even of high attenuation, the vapor admixed with air being first led through a brine or calcium chloride refrigerating system for the partial deposition of acetone admixed with water, and then through a horizontal boiler with steam pipes therein containing activated charcoal. Periodically steam is turned on, the acetone driven off where it is condensed by simple refrigeration to a concentration of 97-98%[5]. The H. Lutz apparatus comprises means for retaining carbonaceous material in a thin body and uniformly heating it to a minimum distilling temperature[6]. Passages are provided for the withdrawal of distillate with an area at least as large as the heating surface of the retaining means.

In the G. Coggeshall and T. Rector process[7], the con-

1. U. S. P. 1349128; abst. C. A. 1923, **17**, 841. In the W. Taylor and H. Dreyfus process (Can. P. 321718), the filaments are subjected first to low degree of vacuum with heat until they have attained a desired temperature, and then to a high degree of vacuum.
2. U. S. P. 1395940. S. Sadtler, U. S. P. 1365791; abst. C. A. 1921, **15**, 909; Mon. Sci. 1922, (5), **12**, 8.
3. U. S. P. 1367009, 1368601. In the process of Soie de Chatillon (E. P. 309158) for the recovery of solvent used in the dry spinning of artificial filaments, there is employed a cell containing a pipe for condensing the solvent vapor, located entirely within the cell, and adjacent and substantially parallel to the path of travel of the filaments.
4. U. S. P. 1437980; abst. C. A. 1923, **17**, 841; Chem. Met. Eng. 1923, **28**, 177.
5. G. Burrell, C. Voress and V. Canter, U. S. P. 1382890; abst. C. A. 1921, **15**, 3535; Mon. Sci. 1922, (5), **12**, 44.
6. U. S. P. 1389203; abst. J. S. C. I. 1921, **40**, 763-A.
7. U. S. P. 1418363; abst. C. A. 1922, **16**, 2746.

densable volatile solvents which have been adsorbed on activated charcoal are driven off by subsequent heating in a current of incondensible gas which is cyclicly circulated through the adsorber and a condenser, where the condensable solvent is recovered[1].

1. V. Lebourreau and A. Taylor, U. S. P. 1355402; abst. Caout. et Gutta. 1921, **18**, 11073. P. Gerli and O. Ross; abst. C. A. 1920, **14**, 2534. W. Lewis and W. Green, U. S. P. 1371914. G. Burrell, C. Voress and V. Canter, U. S. P. 1382889; abst. C. A. 1921, **15**, 2534. R. Etter, U. S. P. 1429856; abst. C. A. 1922, **16**, 3989. E. Barbet, U. S. P. 1452778; abst. J. S. C. I. 1923, **42**, 537-A. E. P. 149691. For additional information see: E. Barbet, U. S. P. 1326432. E. P. 101723. F. P. 379039, 432569. T. Baker, U. S. P. 1218616. J. Aurenque, F. P. 349843. A. Barbezat, F. P. 372524. K. Barth, U. S. P. 1264479. E. Barstow and J. Griswold, U. S. P. 1261005. E. Bataille, F. P. 387325. J. Baudot, F. P. 413442. F. Bird, E. P. 25772, 1901. B. Borzykowski, E. P. 4601, 1913. E. Bouchard-Praceiq, U. S. P. 806866. E. P. 6075, 1905. F. P. 341690. Belg. P. 178852. G. Catala, G. Mainsbrecq and J. DeLannoy, Belg. P. 210024. E. Chambers, T. Hammond and G. Jarmain, F. P. 478641. A. Collard, U. S. P. 1003089. E. P. 29879, 1909. F. P. 410555. Belg. P. 212788, 214478, 214711. R. Craig, R. Robertson, J. Masson and A. Drummond, E. P. 129024. W. Cram, Can. P. 188801. C. Crepelle-Fontaine, U. S. P. 951067. E. P. 2400, 1909. F. P. 396664, 401182. Belg. P. 213757. L. Cuntz, F. P. 383412. E. Delhotel, E. P. 9441, 1905. F. P. 344848. Belg. P. 185742. J. Delpech, F. P. 436440, 441551, 475299. M. Denis, U. S. P. 834460. E. P. 4534, 1905. F. P. 341173, 473481. D. R. P. 165331. Swiss P. 33571. M. Denis and S. Barbelenet, D. R. P. 267509. H. Deroy, E. P. 20305, 1909. H. Diamanti and C. Lambert, U. S. P. 919832. E. P. 5019, 5020, 1907. F. P. 372888, 372889. D. R. P. 203916. Swiss P. 39587. Aust. P. 38532. Belg. P. 197958, 197985. D. Dubois, F. P. 384907. L. Donard, F. P. 429827. J. Douge, E. P. 1595, 15372, 1905. F. P. 356835; Addn. F. P. 5160. F. P. 362611. Belg. P. 185342, 197313. C. Downs and R. Bellwood, E. P. 4070, 1915. F. DuPont, U. S. P. 503586, 712406, 1081949, 1209657, 1218616, 1228225, 1236719, 1294066, 1334360. E. P. 17602, 17618, 1910; 10351, 24296, 1914; 123752, 126682, 130962, 131273. F. P. 477343. Can. P. 167714. F. Early, A. Christiansen, The Farrington Works and H. Pontifex & Sons, E. P. 3602, 1911. F. P. 429934. J. Febvre, F. P. 332087. J. Fournaud, F. P. 416064. E. Gathmann, U. S. P. 704628. C. Heinzerling, E. P. 12390, 1892. H. Hirzel, U. S. P. 991205. M. Hopkins and C. Barnett, E. P. 13679, 1909. M. Houdard and J. Vasseur, F. P. 448665. J. Lloyd and J. Wild, E. P. 122685. R. Labruyer, F. P. 391499. A. and E. Lederer, F. P. 464608. F. Leroy, Belg. P. 217148. P. Liedbeck, U. S. P. 718484. E. P. 27397, 1898. D. R. P. 110289. C. M. Libbrecht, F. P. 352298. A. Mallet, F. P. 349997. H. Pooley and G. Scott & Son, E. P. 103682, 127909. T. Parr, E. P. 23150, 1913. P. Persch, E. P. 116590. W. Nikolsky, U. S. P. 904636. E. P. 3661, 1906. F. P. 363519. D. R. P. 198703. Swiss P. 42181. Can. P. 99456. Australian P. 5961. Dan. P. 9102. D. Plumbridge, E. P. 141210. A. Politzer, F. P. 455879. H. Risler, F. P. 444159. W. Schmidt, E. P. 5368, 1913. V. Slavicek, Belg. P. 211270. A. Soly and E. Davier, F. P. 424242, Addn. F. P. 14084.

Processing. On account of the fact that cellulose acetate silk has proven peculiarly and permanently adaptable to certain types of fabrics, its consumption in the last few years has about doubled, and the cellulose ethers, whose desirable properties are beginning to be recognized, appear to have equal or greater potentialities in the textile field. Cellulose acetate has attained its success by the creation of new standards of quality, especially in lining materials, in which one of the desirable characteristics is a tendency to avoid catching or plucking on surfaces such as those of the wearer's hands or other garments. On account of possessing a special softness, smoothness of handle or slipperiness, the cellulose ether or ester textiles are eminently suited for the lining of sleeves, and also on account of ability of withstanding repeated exposure to perspiration, the cellulose ethers exceed the cellulose esters in this respect[1].

The British Celanese, Ltd.[2], reduce fire hazards in the employment of cellulose ethers and organic esters by subjecting the materials to a flameproofing or fireproofing treatment by the use of phosphoric, arsenic or stibnic acids (probably never the latter two on account of their toxicity). The textile is steeped in a 10% solution of the acid for 1 hr. at 40°, after which either cellulose acetate or methyl-, ethyl- or benzyl-cellulose, when held in a flame, melts but does not ignite. Aluminum acetate may also be added to the steeping liquor, in which case insoluble aluminum phosphate is precipitated. In making ether or ester

Belg. P. 234732. Societe l'Air Liquide (Societe Anonyme pour l'Etude et Exploitation des Procedes Georges Claude), U. S. P. 1040886. E. P. 5395, 1909. F. P. 397791, 413571, 425992, 435073. D. R. P. 229001. Belg. P. 214256. Societe Anonyme pour la Fabrikation de la Soie de Chardonnet, F. P. 376785, 387054. Societe pour la Fabrikation en Italie de la Soie Artificielle par le Procede de Chardonnet, F. P. 371544, 371985. C. Tuckfield and W. Garland, E. P. 26360, 1903. A. Zeckendorf and Maschinenbau, A.-G., Golzern Grimma, F. P. 434949. D. R. P. 235300. S. Zipser, E. P. 12321, 1912. Belg. P. 246232.

1. D. Gilmore, Am. Dyestuff Rep. 1931, **20**, 647; abst. C. A. 1932, **26**, 2323; Textile Mfr. 1931, **57**, #683, 412.

2. E. P. 296344; abst. C. A. 1929, **23**, 2569; J. S. C. I. 1929, **48**, 281-B; Chem. Zentr. 1929, I, 169.

cellulose yarns more pliable and amenable to treatment, they are wetted with a solvent or softening agent as ethylene dichloride, when either in the form of hanks, cones, pirns or bobbins, whereby process of winding and otherwise manipulating may be carried on with a minimum breakage of the filaments[1]. By means of the judicious application of a limited amount of solvent to cellulose ether or ester filaments[2], a method has been evolved whereby they may be highly twisted.

E. Bronnert[3] dries artificial silk by causing a strong current of air mechanically arranged so as to ensure intimate contact with the filaments, to pass over them at a predetermined temperature and a definite rate[4].

Strengthening Artificial Filaments was first applied to regenerated cellulose filaments as obtained from the viscose, copperammonia and nitrocellulose processes, on account of its relatively low strength, especially in the wetted condition, and has been expanded to include also cellulose ethers and organic cellulose esters in those processes appearing especially applicable thereto. Formaldehyde has been used to some extent (see p. 1618), but of no interest for treatment of the cellulose ethers (see topic, p. 1378).

C. Snyder[5] passes artificial silk through a hot aqueous solution of but partially saponified olive oil, then over a brush to smooth the fiber, over a steam-heated felt wiper to remove excess solution and thence dried in a steam chest. No stretching of the fibers is involved in the treatment. Dilute sulfuric acid has been claimed by W. Zänker and H. Schreiber[6] as a bath to increase the strength of

1. British Celanese, Ltd., E. P. 295054; abst. J. S. C. I. 1930, **49**, 53-B. Can. P. 295666.
2. British Celanese, Ltd., W. Dickie and R. Martin, E. P. 289321; abst. Silk J. 1928, **5**, #50, 72.
3. U. S. P. 1437491; abst. J. S. C. I. 1923, **42**, 51-A. E. P. 170608. Swiss P. 94410; abst. Chem. Zentr. 1922, IV, 964.
4. British Celanese, Ltd., A. Mellor and R. Mann, E. P. 358942; abst. J. S. C. I. 1931, **50**, 1137-B. Cellulose Acetate Silk Co., Ltd., and H. Curtis, E. P. 359627; abst. J. S. C. I. 1932, **51**, 18-B.
5. U. S. P. 1474560; abst. C. A. 1924, **18**, 593.
6. Textilchem. Col. 1923, 85; abst. C. A. 1923, **17**, 2962.

artificial fibers, the yarn being immersed in a dilute solution of the acid of such concentration that it retains but a trace of acid, but the strength must decrease with moisture absorption and upon standing. H. Dreyfus[1] applies to methyl-, ethyl- or benzyl-cellulose filaments concentrated acids as sulfuric, hydrochloric, nitric and phosphoric; formic, acetic or lactic; or ammonium thiocyanate or zinc chloride, the acid concentration being 30-50%. It is preferred to use the organo-mineral acid as coagulant in the wet spinning of the filaments, which are stretched in the coagulating bath or after emergence therefrom. After the treatment, the filaments are washed with water or dilute alkali until neutral. It is claimed that the qualities of acetate fibers are improved by charging with organic acids as formic or acetic, stretching to about 50%, and removing the acid by stages while under tension[2].

For increasing the tensile strength of artificial fibers, W. Bruckhaus[3] combines condensation products of formaldehyde with insoluble aluminum soap, the filaments being impregnated with alum, lactic acid and formaldehyde, hydro-extracted and then soaped with an olive oil soap. Salt-forming condensation products form the subject matter of the H. Bucherer process[4], who steeps the filaments in an alkali salt solution to form an insoluble calcium or aluminum salt by double decomposition. R. Herzog and H. Selle[5] immerse the fibers in a 1.35 sp. gr. solution of calcium thiocyanate at 18° for 24 hrs. and then wash and dry under tension. NaOH or KOH of sp. gr. not less than 1.5 forms the subject matter of another process[6], the filaments being immersed therein from 1-5 seconds and then immediately washed. Cellulose ether filaments are but lit-

1. E. P. 334853. F. P. 663743; abst. C. A. 1930, **24**, 723.
2. W. Seidel and A. Ernecke, D. R. P. 530803; abst. C. A. 1932, **26**, 318. E. P. 341021; abst. J. S. C. I. 1931, **50**, 342-B. F. P. 672301; abst. Chem. Zentr. 1930, I, 1726.
3. Kunstseide 1926, **8**, 115; abst. C. A. 1927, **21**, 648.
4. D. R. P. 339301; abst. Chem. Zentr. 1921, IV, 712.
5. Kolloid-Zts. 1924, **35**, 199; abst. J. S. C. I. 1925, **44**, 7-B.
6. O. Dubac, E. P. 254695; abst. J. S. C. I. 1927, **46**, 247-B.

tle affected by this treatment. Sodium hypochlorite solution of sp. gr. 1.162 is the basis of another method[1], but there is danger of excessive oxidation unless the procedure is kept under rigid control.

The stretching of filaments beyond the elastic limit in order to impart increased strength thereto may be accomplished in the dry state, especially cellulose ether and acetylcellulose filaments, provided they have been brought to the plastic state by heating at a suitable temperature. For instance, a cellulose acetate thread comprising 13 filaments, which is unwound at a speed of 50 m. per min., is caused to pass through a heating apparatus of about 245° temperature, after which it is rewound at a speed of 100 m. per min. In this particular instance the denier went from 75 to 37.5 deniers, the dry breaking elongation from 28% to 12%, the dry breaking stress from 1.3 gms. to 2 gms. per denier, the moist breaking stress from 9.7 gms. to 1.4 gms. per denier, and the dry elastic stress from 0.7 to 1.3 gms. per denier[2].

By stretching of filaments of cellulose acetate or other organic derivatives of cellulose under certain conditions during their manufacture by the dry or evaporative method, extremely fine denier filaments are obtainable of considerable augmentation in strength, the spinning solution being extruded into an evaporative atmosphere during which such portion of the volatile solvent is dissipated that the filaments comprise an outer hardened integument enclosing or encasing a more plastic, and hence more drawable portion[3]. The filaments having been brought to this condition, are then caused to traverse an atmosphere of solvent which has a softening action upon the peripheral

1. L. Löchner, D. R. P. 433733; abst. J. S. C. I. 1927, **46**, 361-B.
2. Soc. pour la Fabrication de la Soie Rhodiaseta, E. P. 323846; abst. C. A. 1930, **24**, 3384; J. S. C. I. 1930, **49**, 319-B; Rayon Record, 1930, **4**, #6, 338. F. P. 681429; abst. C. A. 1930, **24**, 4391; Chem. Zentr. 1930, II, 1167.
3. British Celanese, Ltd., H. Dreyfus and W. Taylor, E. P. 340929; abst. C. A. 1931, **25**, 5028. E. P. 342712; abst. C. A. 1931, **25**, 5559; J. S. C. I. 1931, **50**, 480-B. See E. P. 165519, 198023, 277089, 323790.

portion in contradistinction to the already plastic core, stretch being now applied drawing the filaments uniformly to a smaller cross-sectional area.

H. Dreyfus[1] submits filaments to the action of sulfonic acids containing at least 6 C-atoms at a concentration of 30-50%, the treatment being said to improve both the tensile strength and elasticity. Other suitable softening and swelling agents as acetic acid, pyridine or ammonium thiocyanate[2] are said to admit of stretching up to 150%, with an increase in tensile strength up to 50%, both in the dry and wet condition. Where the filaments are stretched beyond the elastic limit in the set condition[3], resistance to deterioration by hot aqueous liquids is said to be greatly improved. H. Suter[4] claims that threads of cellulose acetate and other organic cellulose filaments may be stretched 300-900% or more during or after passage through a bath containing a proper swelling agent which has only a slight action upon the cellulose compound, e.g., methylene chloride or chloroform in admixture with carbon tetrachloride, trichlorethylene, tetrachlorethane or hexachlorethane, none of which exercise an appreciable swelling action or are direct solvents for acetylcellulose. They likewise repress the solvent action of the admixed swelling agent. A suitable bath is 70 vol./% methylene chloride and 30% carbon tetrachloride. The stretched threads, the individual filaments of which may be reduced to 0.5-2 deniers, show up to 100% increase in wet and dry strength in gms. per denier, and also reduced extensibility.

A method has been patented for increasing the strength of organic derivatives of cellulose in filament form comprising treating the silk at relatively high temperatures

1. E. P. 338989; abst. Chem. Zentr. 1931, I, 2289; Rayon, 1931, **12**, #3, 54.
2. Soc. Chem. Ind. in Basle, E. P. 363284; abst. J. S. C. I. 1932, **51**, 258-B; Rayon, 1932, **13**, #7, 18. See E. P. 249322, 353978.
3. A. Hall, U. S. P. 1709470; abst. C. A. 1929, **23**, 2838; J. S. C. I. 1929, **48**, 470-B.
4. E. P. 358512; abst. J. S. C. I. 1932, **51**, 17-B; Textile Mfr. 1932, **58**, #687, 119.

with reagents which are inert at room temperature, but which become solvents and plasticizers for cellulose ethers at higher temperatures[1], such as glycerol, glycols or other polyhydric alcohols, alone or in association with inert diluents as water or benzene, or with substances which are solvents or plasticizers at room temperature such as acetic or lactic acids, methyl glycol, ethyl glycol or diacetone alcohol. If the silk is stretched during this treatment the finished thread shows increased strength; if it is allowed to shrink the thread shows increased extensibility but no material increase in strength.

Finished artificial threads, yarns or films of cellulose ethers[2] which have been treated with a neutral organic swelling agent as 50% aqueous dioxane, or threads spun from a solution containing dioxane, are gradually stretched 200% or more while still in contact with the swelling medium. Previous to, during, or immediately after these operations the threads may be subjected to traverse pressure, e.g., by rolling, and they are finally treated with salt solutions and dried. G. Coudene[3] improves the elasticity of artificial silk by allowing it to take its natural elongation on treatment with water or water vapor as by steaming, and then adjusting the new length by drying under tension.

For increasing the strength of fibers or textiles of methyl-, ethyl- or benzyl-cellulose[4], the filaments are treated with concentrated sulfuric, hydrochloric, phosphoric or nitric acids, the time of treatment depending upon acid concentration and temperature. If the material is primarily composed of cellulose acetate, sulfuric acid of 1.4-1.84 sp. gr. may be used, the time varying from 0.5-12 seconds at 10°. Or sulfonic acids may be used in an analogous man-

1. British Celanese, Ltd., and W. Taylor, E. P. 362939; abst. J. S. C. I. 1932, **51**, 258-B.
2. K. Weissenberg and B. Rabinowitsch, E. P. 352445; abst. J. S. C. I. 1931, **50**, 878-B; Textile Mfr. 1931, **57**, #684, 460. E. P. 352909; abst. Silk J. 1932, **8**, #93, 54. Can. P. 320447.
3. E. P. 340602.
4. H. Dreyfus, E. P. 324662; abst. C. A. 1930, **24**, 3900. G. Müller, E. P. 358501; abst. J. S. C. I. 1932, **51**, 17-B; Textile Mfr. 1932, **58**, #687, 119.

ner[1], sulfacetic acid, ethylenesulfonic acid or methylsulfonic acid being recommended.

In order to render filaments more resistant to hot aqueous media[2], they may first be treated with a swelling agent, and then stretched beyond the elastic limit, the process being continuous if desired[3]. The filaments become materially strengthened[4], if extruded filaments are placed under tension while still containing residual solvent, the applied stretch being confined to those filaments while they still contain residual solvent and hence are in a semi-plastic condition. H. Dreyfus claims that materials composed of or containing cellulose ethers have their tenacity and power of stretching improved by treating them with an agent which has no solvent action or strong swelling action on the cellulose derivative at ordinary temperatures, but swells, plastifies or dissolves at relatively high temperatures. Glycol, glycerol, ethyl lactate, diacetone alcohol or diethyl tartrate are examples of bodies considered suitable for this purpose[5].

W. Harrison is authority for the statement that in the formation of artificial silks of high tensile strength in which the threads are stretched while in a swollen plastic or semi-dissolved condition[6], best results are obtained if the stretching process is carried out on filaments containing the maximum percentage of α-cellulose. Instead of using an initial cellulose of maximum α-cellulose content, he prefers to extract the non-resistant celluloses in an acetated condition by treatment of cellulose acetate with aqueous acetone of 50-80% strength.

In order to render cellulose ether yarns capable of withstanding textile operations involving severe strain on the yarns as knitting, weaving and ring-spinning opera-

1. H. Dreyfus, F. P. 693240; abst. C. A. 1931, **25**, 1686; Chem. Zentr. 1931, I, 2289. F. P. 689800.
2. *Ibid.* Can. P. 293057. 3. *Ibid.* Can. P. 311410.
4. *Ibid.* Can. P. 317108.
5. *Ibid.* F. P. 720867; abst. C. A. 1932, **26**, 4175.
6. E. P. 344873. Holl. P. 22730. See E. P. 229678, 271517, 319291.

tions, a finish is applied to the yarn comprising a lubricating oil[1], the oil acting externally on the yarns to facilitate flexing and increase pliability. Another variant proposed for increasing the tensile strength[2] is to submit the filament, while still in a swollen condition as a gel, to a cooling treatment under tension, and then dry, still under tension. According to Y. Kami[3], the breaking strength of an artificial silk yarn is less than the sum of the strengths of the constituent filaments, and, like the extensibility, which is greater than that of a single filament, decreases as the amount of twist increases. With increasing humidity the strength rises to a maximum and then falls again, whereas the extensibility increases continuously.

Sizing[4]. The application of sizes to filaments, fibers and textiles composed of or containing cellulose ethers and esters, and the composition of the sizes useful for this purpose, may be grouped under the following subdivisions:

1. *Cellulose Ether Sizes.* A good example of the versatility of cellulose derivatives is to be found in the lower etherified methyl- and ethyl-celluloses, which are either soluble in cold or hot water or materially affected thereby. Several applications have been made of this water-soluble capacity in the preparation of sizes for textiles in general, and for cellulose ethers and organic cellulose esters in particular. Colloresin D, a methylcellulose dissolving to a thick opalescent solution in water, has been used as a sizing agent in calico printing, and a methylcellulose preparation known as Tylose S has been used as an emulsifying agent and protective colloid for oils, fats, waxes, pig-

1. British Celanese, Ltd., R. Roberts and S. Welch, E. P. 365621.
2. E. Trachsler, Swiss P. 114677; abst. J. S. C. I. 1927, **46**, 185-B.
3. Bull. Sericulture, Japan, 1931, **4**, #2, 9; abst. J. S. C. I. 1932, **51**, 334-B.
4. E. Sauter, D. R. P. 546213; abst. C. A. 1932, **26**, 3388. See F. P. 710498. W. Bennett, Silk J. 1926, **3**, #26, 66; abst. C. A. 1926, **20**, 3818. P. Sisley, Jr., Russa, 1931, **6**, 803, 965, 1115, 1117, 1535; abst. C. A. 1932, **26**, 1791.

ments, china clay and graphite[1], finding employment in the production of lead pencils, shoe polishes and plastic masses. Tylose S is said to bear a close resemblance in solution to tragacanth, being non-fermentable and uniform in quality. Its aqueous solution coagulates upon heating, but becomes soluble again upon cooling. It comes into the trade in compressed blocks, readily dissolvable by pouring boiling water over the mass and stirring until cool.

The H. Bohne size, recommended as a finish for fibrous materials, and suitable for simultaneous sizing of cotton and artificial filaments, comprises a solution of methylcellulose to which a softening agent as fats, oils, waxes, higher aliphatic alcohols or sulfonated oils may be added[2]. H. Dreyfus[3] sizes and finishes textiles and threads by the application thereto of aqueous solutions or dispersions of cellulose ethers of suitable water susceptibility, or by the employment of cellulose esters as the chloracetate, oxalate, maleate, glycollate, malate, lactate, tartrate, mandelate or glycerate. The I. G. Farbenindustrie[4] size cellulose acetate silk by means of a water-soluble carbohydrate hydroxyalkylether, obtainable by reacting on a carbohydrate with an alkylene oxide in the presence of an aqueous alkali. Oxyethylcellulose, oxypropyl starch and oxybutyl starch are stated as especially applicable. The process is detailed as follows:

1. L. Light, British Plastics, 1932, **4**, #37, 20. See Courtaulds, Ltd., W. Gilles, E. Templeton and E. Smith, E. P. 230187. In the F. Gahlert process (U. S. P. 1847827) the yarn is subjected to a twisting operation and also to the action of an aqueous bath which contains one of the dressings such as a sizing which thoroughly impregnates the yarn so that it swells and is impregnated during the twisting; this is followed by stretching during treatment with a sizing bath, and further stretching of the stretched and sized yarn.

2. E. P. 350409; abst. Textile Mfr. 1931, **57**, #683, 420; Silk J. 1931, **8**, #91, 54. A. Grimshaw (Text. World, 1925, **67**, 320) has given details for the skein sizing of acetate filaments and fabrics, and C. Atkinson (J. Soc. Dyers & Col. 1931, **47**, 5) directions for sizing Seraceta acetate warp yarns.

3. F. P. 700711; abst. C. A. 1931, **25**, 3848. British Celanese, Ltd., H. Dreyfus, W. Dickie and P. Sowter, E. P. 344528.

4. E. P. 341516; abst. C. A. 1931, **25**, 4720; J. S. C. I. 1931, **50**, 486-B; Silk J. 1931, **7**, #84, 54. D. R. P. 523434; abst. C. A. 1931, **25**, 3498.

a. Acetate silk is drawn into a liquor at ordinary temperatures, in which there are dissolved 25 gms. oxypropyl starch per liter, being obtained by treatment of starch with propylene oxide in the presence of NaOH solution. The acetate silk is squeezed out and dried at 50°. The fiber thus sized is very compact and has a good feel. Freeing from size takes place without further additions merely by drawing through water at 60°.

b. Acetate silk is passed at room temperature through a bath of oxyethylcellulose 40 gms. per liter, then squeezed out and dried at 50°. Freeing from size takes place as before.

In another patented method[1], sizing with aqueous solutions of the lower etherified cellulose ether either in the ripened or non-degraded state, best results being obtained by selecting a cellulose ether capable of yielding films on evaporating the aqueous media.

2. *Sizing with Polyvinyl Compounds.* It is well known that vinyl compounds as vinyl esters or vinyl ethers may be converted into polymerization products varying in consistency from liquids to gelatinous masses or coherent solids. Threads or yarns may be sized with these compounds[2] by direct application of a solution, dispersion or emulsion of a partially polymerized vinyl compound, followed by a drying operation. The polymerized compound may be produced on the yarn or textile or by increasing the degree of polymerization of an already partially polymerized vinyl compound. Water-soluble derivatives of polyvinyl alcohol[3], as partly esterified vinyl alcohols ob-

1. British Celanese, Ltd., H. Dreyfus, W. Dickie and P. Sowter, E. P. 344528; abst. C. A. 1932, **26**, 318; J. S. C. I. 1931, **50**, 585-B; Silk J. 1931, **8**, #86, 54.

2. British Celanese, Ltd., H. Dreyfus and W. Taylor, E. P. 346267; abst. C. A. 1932, **26**, 2066; J. S. C. I. 1931, **50**, 674-B; Textile Mfr. 1931, **57**, #680, 305.

3. I. G. Farbenindustrie, A.-G., E. P. 361691; abst. Silk J. 1932, **8**, #97, 56. E. P. 372599, Addn. to E. P. 345207; abst. J. S. C. I. 1932, **51**, 722-B. F. P. 701868; abst. C. A. 1931, **25**, 4136. I. G. Farbenindustrie, A.-G., O. Ernst and K. Sponsel, D. R. P. 523434; abst. C. A. 1931, **25**, 3498.

tained by partial saponification of polyvinyl esters, and products obtained by condensing an aldehyde with a polyvinyl alcohol, may be used instead of the alcohol itself. Aqueous solutions not exceeding 15% strength are used.

3. *Sizing with Cellulose Esters.* A process has been described for the sizing and finishing of all types of textile yarns[1], by the use of aqueous solutions or dispersions of cellulose esters such as cellulose oxalate or maleate which have been esterified in the presence of chloracetic anhydride, or by modification of cellulose acetate by treatment with organic acids. Yarns thus sized may readily be desized by scouring with an aqueous soap solution to which a small amount of alkali may be advantageously added.

4. *Proteid and Albuminous Sizes.* The sizing of dyed yarn, particularly yarn containing organic derivatives of cellulose that have been colored with certain water-insoluble dyes that are solubilized by means of a dispersing agent[2] may be accomplished with a sizing composition containing glue or gelatin that is substantially neutral, the yarn being composed of methyl-, ethyl- or benzyl-cellulose or cellulose acetate. The temperature of the sizing bath should be maintained between 60° and 80°. As an example, a yarn of cellulose acetate is dyed with 1.4-dimethyldiaminoanthraquinone or 2.4-dinitro-4′-aminodiphenylamine dispersed in aqueous suspensions by means of sulforicinoleic acid, the dyed yarn being then sized at 70° with gelatin 9, glycerol 2, castor oil 1.5, sodium benzoate 0.016, water 260.

The Erba A.-G.[3] size artificial filaments by an agent which is afterwards dissipated in the dyeing or bleaching liquid without a special de-sizing operation, collagen being specified as suitable, or albumin, globulins, gelatin, keratin, albuminoids, to which casein may be added[4]. J. Maillon[5]

1. British Celanese, Ltd., H. Dreyfus, W. Dickie and P. Sowter, E. P. 344775; abst. C. A. 1932, **26**, 318; J. S. C. I. 1931, **50**, 535-B; Silk J. 1931, **8**, #86, 54; Rayon Record, 1931, 421.
2. H. Platt, U. S. P. 1870868.
3. E. P. 370407 and Addn. E. P. 371003; abst. J. S. C. I. 1932, **51**, 596-B. F. P. 706685; abst. C. A. 1932, **26**, 318.
4. Erba, A.-G., F. P. 706638; abst. C. A. 1932, **26**, 318.
5. F. P. 705638; abst. C. A. 1932, **26**, 318.

uses a mucilaginous bath of animal gelatin and starch in about equal proportions, while Stein, Hall & Co.[1] specify casein, dextrin and a dextrinized starch with a hygroscopic material as corn sugar, glycerol or glucose. The essence of the H. Platt method[2] is dyeing the cellulose acetate or cellulose ether yarn in a bath containing gelatin and sulforicinoleic acid.

5. *Vegetable Oil Sizes.* F. Munz and M. Zabel[3] describe the application to warps of fibers of cellulose derivatives, castor oil in conjunction with rubber emulsions, and Aceta G.m.b.H.[4], a mixture of linseed oil, blown colza oil with lead and manganese resinates. The L. Cavaillon[5] size particularly suitable for crepe yarns, involves the use of a mixed sulfonated oil obtained by treating a mixture of olive and linseed oil with sulfuric acid at 35-40°, and neutralizing the oil with aqueous alkali. An adherent but non-sticky textile size especially applicable to fibers of cellulose derivatives has been described[6], comprising a drying oil with a semi-drying oil as rape or cottonseed, esterified with glycerol. Linseed oil, in which oxidation is inhibited by associating therewith a non-drying oil, is the novelty basis of K. Swoboda[7], while A. Galvin[8] makes use of drying oils to which less than 1% of a drier has been added.

H. Platt[9] sizes yarn containing organic derivatives of cellulose as methyl-, ethyl- or benzyl-cellulose with a composition containing a substantially colorless drying oil

1. H. Bosland, F. Lapiana and Stein, Hall & Co., Inc., E. P. 359802; abst. J. S. C. I. 1932, **51**, 19-B; Textile Mfr. 1932, **58**, #688, 164.
2. E. P. 315428; abst. C. A. 1930, **24**, 1750. Can. P. 313857; abst. C. A. 1931, **25**, 5301.
3. D. R. P. 539467; abst. C. A. 1932, **26**, 1804.
4. F. P. 710498; abst. C. A. 1932, **26**, 1784.
5. E. P. 370810; abst. J. S. C. I. 1932, **51**, 597-B.
6. Aceta, G. m. b. H., E. P. 371048; abst. J. S. C. I. 1932, **51**, 597-B.
7. Kunstseide, 1931, **13**, 101; abst. C. A. 1931, **25**, 4408.
8. D. R. P. 532004; abst. C. A. 1932, **26**, 318.
9. U. S. P. 1861026.

as linseed or China wood oil, while a German process[1] makes use of linoxyn dissolved in an organic solvent with the addition of an organic soap-forming acid, a suitable mixture being prepared by heating to 200° linoxyn 20, tetrahydronaphthalene 48 and oleic acid 7, and diluting with toluene or cyclohexanol. Less than 1% of a substance retarding the oxidation of the linoxyn may be added, such as *b*-naphthol.

6. *Resinate Sizes.* The employment of sizing solutions composed of one or more salts of resin acids as abietic or of naphthenic acids, associated with a fatty lubricating agent, is the essence of the C. Ryley and G. Awcock invention. Sodium, potassium, ammonium, magnesium, zinc or aluminum resinate, abietate or naphthenate are the organic salts specified as applicable[2]. Or a lubricating agent associated with certain resins as mastic or dammar[3], which give non-sticky combinations when heated together are advocated, ordinary rosin or colophony being unsuitable on account of the fact that it sticks to the cellulose ether yarn.

7. *Sizing with Amino-alcohol Resinates.* A process has been described wherein artificial filaments and textiles made therefrom[4] are sized with resinates or oleates of amino-alcohols in aqueous emulsions or in solution in a volatile solvent, triethanolamine resinate, oleate or stearate being specified. Cloths made from artificial silks treated with such sizes are said to be readily de-sized by immersion in a warm soap solution.

8. *Other Sizing Processes,* applicable to cellulose ether and/or cellulose acetate filaments are treatment of oily or fatty emulsions dispersed with casein or gelatin with the aid of borax, ammonia or alkali[5], sodium silicate being

1. Deutsche Hydrierwerke, A.-G., D. R. P. 537361; abst. C. A. 1932, **26**, 1136.
2. C. Ryley, G. Awcock and British Celanese, Ltd., U. S. P. 1807755; abst. C. A. 1931, **25**, 4414. E. P. 244947; abst. J. S. C. I. 1926, **45**, 189-B.
3. *Ibid.* E. P. 244979; abst. J. S. C. I. 1926, **45**, 189-B.
4. A. I. Kousnetzof, E. P. 363448; abst. Textile Mfr. 1932, **58**, 247. F. P. 709431; abst. C. A. 1932, **26**, 1455.
5. G. Lefranc, E. P. 346055; abst. C. A. 1932, **26**, 606.

added to cause the formation of an irreversible gel on drying; addition of 0.5% pine oil to the size used for cellulose derivative fiber improving materially the strength of the fibers[1]. A 1.5% solution of beeswax with soap or dextrin as dispersing agent is recommended for artificial fibers intended to be creped[2].

To prevent textile materials from sticking together after being sized, the sized material may be treated in a bath containing calcium, aluminum, zinc or lead formates, acetates or thiocyanates, to which acetic acid may be added. Brugere[3] has discussed the troubles caused by the hydrophilic character of cellulose ester and ether fibers, which may result in uneven dyeing, and by traces of bleach residues which convert cellulose into oxycellulose. A method of sizing fibers having a cellulose derivative as a base has been detailed[4], which comprises subjecting the fibers to the combined action of a swelling agent and a sizing material, the first aiding in the penetration of the size.

Acetate or cellulose ether yarn to which a size has been applied[5] is preferably wound into hank form and dried during winding, the drying agency being concentrated in the neighborhood of the hank by a surrounding casing. Particular methods for sizing cellulose ether and acetate yarns have been described by H. Dreyfus[6], J. Paillet[7], J. Chirat[8] and others[9]. J. Sussmuth[10] has pointed out

1. W. Fermazin, Chem. Ztg. 1931, **55**, 613; abst. C. A. 1931, **25**, 5983; J. S. C. I. 1931, **50**, 876-B; Chem. Zentr. 1931, I, 2948.
2. P. Jeanpretre, E. P. 371786; abst. J. S. C. I. 1932, **51**, 676-B.
3. Bull. ann. assoc. chim. ind. text. 1930, 58; Chim. et Ind. 1930, **26**, 407; abst. C. A. 1932, **26**, 311. See Sondermann & Co., E. P. 318211.
4. C. Chandler, Can. P. 304200; abst. C. A. 1930, **24**, 5511.
5. S. Fulton, G. Tyce and British Celanese, Ltd., E. P. 355794; abst. Textile Mfr. 1932, **51**, #686, 79.
6. E. P. 210266; abst. C. A. 1924, **18**, 1757; J. S. C. I. 1924, **43**, 312-B; Chem. Zentr. 1924, I, 2760; Faserstoffe, 1924, **6**, 67.
7. E. P. 353285; abst. Textile Mfr. 1932, **58**, #685, 36.
8. E. P. 353850; abst. Textile Mfr. 1932, **58**, #685, 37.
9. C. Addy, J. Billing and H. Halkyard, U. S. P. 1742568; abst. C. A. 1930, **24**, 1229; J. S. C. I. 1930, **49**, 186-B; Chem. Zentr. 1930, II, 1927. E. P. 264382; abst. J. S. C. I. 1927, **46**, 214-B; Chem. Zentr. 1927, II, 173.
10. Rayon, 1931, **12**, #1, 14.

that in the sizing of acetylcellulose yarns, it is advantageous to immerse the filaments entirely in the size solution, and to regulate the steam temperature to below 80°. Some acetate sizing has a tendency to tape up the ends of the warp, especially when the sley is light. It, therefore, is a good policy to keep a strong tension between the quetsch and the first cylinder, as well as on the take-up. This will tend to pull the ends apart and break the cohesion of the taping. An oscillating roller on the take-up is of assistance.

Desizing. The suitability of a substance as a sizing agent depends not only upon the extent to which it strengthens the warp, but also upon the facility of its removal by the finisher[1]. The size should be selected so that it may be substantially removed by a simple scouring operation, preferably with the aid of soap alone.

Conditioning. Yarns composed partially or wholly of methyl-, ethyl- or benzyl-cellulose[2] may be conditioned by the application thereto of polyhydric alcohols as diethylene glycol, ethylene glycol, propylene glycol and glycerol, or toluene or xylene. It will be rembered that the knitting of yarns made of organic derivatives of cellulose presents certain difficulties, since if attempts are made to form a closely knit fabric from such yarns, defects and faults tend to develop because of the lack of sufficient pliability in the yarn. Fibers other than cellulose ethers and esters may more readily be conditioned since they readily absorb oils,

1. K. Walter, Kunstseide, 1931, **13**, 302; abst. C. A. 1932, **26**, 1791. A. Kunze, Russa, 1928, **3**, 745; abst. C. A. 1928, **22**, 3987. Anon., Rayon Record, 1930, **4**, #14, 749. H. Dreyfus (Can P. 283818) removes sizes, oil or other dressing from woven or knitted fabrics, especially those consisting partially or wholly of organic cellulose derivatives, by treating the fabric, wound on a hollow, perforated beam or pipe, with a cleaning or scouring liquid caused to percolate outwards through the rolled fabric. The Societe Chimiques des Usine du Rhone (E. P. 216113) unsize artificial silk fibers by means of hot soap baths containing potassium chloride or sulfate or dipotassium phosphate. Cellulose acetate fabric is unsized and a mixed artificial and real silk fabric is degummed in hot baths containing the neutral soap "Savon de Marseille," and one of the above mentioned potassium salts.

2. British Celanese, Ltd., E. P. 351084; abst. Silk J. 1932, **8**, #92, 53. See E. P. 333949.

water or other conditioning agents. The solvent for best results should be accompanied by a relatively smaller amount of a lubricant as castor, olive or neatsfoot oils.

The filaments or yarns may be conditioned in the package form to a conditioning agent in the vapor form generated within the package[1], which is preferably enclosed in a relatively impervious wrapping of wax paper. Either water, or volatile restricted solvents or swelling agents may be used.

Loading and Weighting. The tendency of woven fabrics made of yarns of the cellulose ethers or of cellulose acetate to "slip," that is to say for the yarns to become displaced in the fabric, the tendency of circular knitted fabrics to "ladder," and the proneness of warp knitted fabrics to "split," are all considerably reduced, and may be practically eliminated by a judicious loading or weighting operation, which in its entirety involves the deposition or precipitation on the fibers of a metallic salt usually in a water-insoluble condition, the operation being facilitated by treatment of the fiber with a reagent which will cause its swelling and hence increase penetration of loading material therein. Where either cellulose ethers or acetylated cellulose filaments or textiles are employed, the loaded goods may be subjected to higher ironing and calendering temperatures with impunity than the unloaded goods, without melting or becoming sufficiently plastic to endanger their characteristic form or structure.

The various processes which have been applied to textiles of the cellulose derivatives may be conveniently grouped under the following headings:

1. *Tin Phosphate,* either stannous or stannic phosphate, and usually produced by a double decomposition between stannous or stannic chloride and a soluble phosphate as sodium phosphate or of phosphoric acid, has been extensively employed and with uniformly satisfactory results.

1. British Celanese, Ltd., E. P. 359867; abst. Textile Mfr. 1932, **58**, #688, 164. G. Blake, Can. P. 319737.

The H. Dreyfus process[1] treats the filaments or fabric first with an aqueous stannic chloride solution of 40° Tw. strength for 0.5 hr., at 40-50°, then pressing out excess of tin solution, followed by a rinse or not, is plunged into a bath of disodium phosphate of 7° Tw., or into a sodium silicate solution of the same concentration, excess of phosphate or silicate being removed by simple hydro-extraction, usually followed by a light washing. Or[2] the textile may be impregnated as in a padding machine with a soluble metallic salt (as stannic, ferric or chromic chlorides), and after drying, a precipitant of trisodium phosphate is applied, the stannic, ferric or chromic phosphates being deposed in the interior of the filaments and the interstices of the fibers. In the E. Cadgene procedure[3], acetylcellulose silk is treated with a gelling agent (15-20% formic or acetic acids) to open up the fiber, drained, steeped in a stannic chloride solution, washed, again jelled, and the tin fixed by means of sodium phosphate solution at 40-45°, finally the material is washed and soaped. Alternatively, gelling and weighting may occur simultaneously by the addition of acetic acid to the stannic chloride solution. From 30-100% weighting may thus be obtained, the material remaining soft and lustrous, and with an increased affinity for certain dyestuffs. It must be remembered that with

1. E. P. 272982. Belg. P. 352472. U. S. P. 1805467. F. P. 621316. See H. Dreyfus, F. P. 694881. E. P. 259899. As an example, 1 kilo of methyl- or ethyl-cellulose is treated for 1 hr. in a bath of stannic chloride of 33° Be., the bath being maintained at a temperature of about 50°. The yarn is removed from the bath, and washed thoroughly with cold water, and then entered in a bath of disodium phosphate of 3-6° Be. for 0.5 hr. at 40-60°, removed and washed with warm water. The loaded yarn is then dyed in a bath containing about 1% dyestuff and 2-3% acetic acid at 40-60°, in which sodium sulfate may be placed. Methyl- or ethyl-cellulose fabrics may be loaded and prepared for dyeing, stencilling or printing with printing plates, by printing with printing pastes in successive baths of stannic chloride or disodium phosphate as outlined above.

2. British Celanese, Ltd., and G. Ellis, E. P. 329659; abst. J. S. C. I. 1930, **49**, 815-B.

3. E. Cadgene and G. Rivat, E. P. 259899; abst. C. A. 1927, **21**, 3470; J. S. C. I. 1927, **46**, 295-B. G. Rivat, U. S. P. 1631062; abst. C. A. 1927, **21**, 2388. G. Rivat, E. Cadgene and C. Dreyfus, U. S. P. 1871470. E. Cadgene, D. R. P. 492148; abst. C. A. 1930, **24**, 2600. G. Rivat, E. Cadgene and C. Dreyfus, Can. P. 271232.

the deposition of insoluble inorganic salts in general, there is a tendency for the material to increase in opacity and be reduced in luster.

C. Mullin[1] has discussed the continuous tin weighting of piece goods by the Clavel and Lindenmeyer processes, the goods being first swollen and then passed continuously through an acid bath, two stannic chloride solutions, a sodium dihydrogen phosphate bath, then a disodium phosphate bath, the usual sodium silicate bath being given after the final pass. The gain in weight is about 30% in a single pass, 56% weighting by a second, and 85% by a third. The machine handles about 20 yds. per min. with two men.

2. *Tin Silicate.* British Celanese, Ltd.[2], treat fibers and yarns of cellulose ethers or organic esters first by immersion in a 40° Tw. solution of stannic chloride during a half hr. at 55-65°, and then in a 7° Tw. solution of sodium silicate, then washing with or without soap solution and drying. The increment of weight of the artificial silk can be considerably augmented by a second or third treatment. An opening up or swelling of the fibers preliminary to the weighting step is made possible by pretreatment with an aqueous albumin solution and ammonium carbonate[3], or with a relatively high concentration of such protective colloids as glue, gelatin or soap[4], the weighting treatment thereby being considerably shortened and intermediate washings of the fabric avoided.

3. *Zinc, Aluminum, Tin Phosphate.* R. Clavel[5] found that very successful weighting of artificial silk is possible by employing successively impregnating and precipitating

1. Textile World, 1931, **80**, 591, 1522; abst. C. A. 1932, **26**, 310. Textile Colorist, 1930, **52**, 531, 558, 631; abst. C. A. 1932, **26**, 310. A. Hall, Rayon Record, 1931, **5**, 555; abst. C. A. 1932, **26**, 602.

2. E. P. 258874; abst. C. A. 1927, **21**, 3135; J. S. C. I. 1928, **47**, 228-B. C. Dreyfus ,Can. P. 273367; abst. C. A. 1927, **21**, 3743. Compare F. P. 563785.

3. R. Clavel, E. P. 266640; abst. J. S. C. I. 1927, **46**, 295-B; Chem. Zentr. 1927, II, 350.

4. *Ibid.* E. P. 277602; abst. J. S. C. I. 1928, **47**, 154-B; Chem. Zentr. 1928, I, 277. Can. P. 308618.

5. U. S. P. 1826274; abst. C. A. 1932, **26**, 606.

baths, his formula for the weighting bath being zinc chloride 2, aluminum sulfate 1, anhydrous tin chloride 4, water to 100. The goods are passed through the bath, squeezed out, and then led through a 3% solution of sodium phosphate, dried and dyed.

4. *Alkali Metal Stannates.* Textiles containing cellulose derivatives such as the cellulose ethers[1] are treated with sodium or potassium stannates or zincates, the textile absorbing a considerable proportion of the metallic radical, becoming more resistant to heat treatment, and showing an affinity to direct dyes, mordant dyes, and indigoid and anthraquinone vat dyes. Adsorption of the alkaline solutions is favored by adding swelling agents as thiocyanates. Dyestuffs especially suitable in this connection are Caledon Jade Green (dimethoxydibenzanthrone), Indanthrene Red Violet R. R. (3'.4'-dichlor-1.2-anthraquinone-acridone), Algol Scarlet G (1-benzoylamino-4-methoxyanthraquinone), Indigo L L, Alizarin, Hematin, Rhodamine B (diethyl-*m*-aminophenolphthalein hydrochloride), *p*-nitrobenzeneazodiphenylamine, and Leucotrope O (dimethylphenylbenzylammonium chloride). In the loading, mordanting and dyeing of filaments composed of or containing methyl-, ethyl- or benzyl-cellulose, a combination of sodium stannate and a water-soluble thiocyanate has been described, in which a solution is prepared containing 15% commercial sodium stannate (41.6% tin and 15.9% Na) and 25% sodium thiocyanate. The fabric is immersed in this bath (weight 30:1 on the goods) at 25° for 1 hr., drained, washed and soaped. C. Dreyfus and W. Blume[2] combine a partial (about 10%) hydrolysis of acetylcellulose followed by weighting with stannic chloride or tannic acid for the combined purpose of weighting the goods and raising the safe ironing temperature.

1. G. Ellis, U. S. P. 1874176. British Celanese, Ltd., and G. Ellis, E. P. 302775; abst. C. A. 1929, **23**, 4353; J. S. C. I. 1929, **48**, 169-B; Silk J. 1929, **5**, #59, 72; Chem. Zentr. 1929, I, 2718. H. Dreyfus, F. P. 661936; abst. C. A. 1930, **24**, 510. Can. P. 316193.
2. U. S. P. 1818466; abst. J. S. C. I. 1932, **51**, 503-B.

5. *Tin Phosphate and Barium Sulfate.* K. Swoboda[1] recommends a double treatment, first two passes through solutions forming tin phosphate whereby a 25-30% increase in weight is obtained without appreciably affecting the strength or extensibility of the fiber, followed by baths giving barium sulfate by double decomposition, the object of the latter manipulation to combine weighting with delustring[2].

6. *Alkali Metal Zincates,* applicable alike to cellulose ether and cellulose ester filaments and textiles, the fabric being immersed 1 hr. in a cold solution containing 5% sodium zincate (Zn 24.23%, Na 35.06%). The goods are then carefully lifted, rinsed, and given a light soaping for 15 min. in 0.25% soap solution at 45°. The fabric so treated is distinguished by its greater resistance to ironing than that of the untreated fabric, and by its affinity for basic, mordant, acid and direct cotton dyestuffs[3].

7. *Tin Chloride.* According to British Celanese, Ltd.[4], in the weighting of cellulose ethers and organic cellulose esters, it is not necessary to follow treatment of stannic chloride with a phosphate or silicate bath, but the use of stannic chloride alone results in adequate fixation by the weighting metal by decomposition of the tin salt by thorough washing with water containing small amounts of alkalis or alkaline salts or soaps, of concentration of about 0.1% in the wash water. It is said that the results obtained by this simplified and more economic process retain all the advantages obtained by weighting by double decomposition processes.

1. Kunstseide, 1931, **13**, 300; abst. C. A. 1932, **26**, 1791.
2. C. Dreyfus and H. Platt, U. S. P. 1806048; abst. C. A. 1931, **25**, 3849; Chemicals, 1931, **35**, 29.
3. British Celanese, Ltd., and G. Ellis, E. P. 306611; abst. Silk J. 1929, **6**, #61, 72.
4. E. P. 279502; abst. C. A. 1928, **22**, 3052; J. S. C. I. 1929, **48**, 126-B; Rayon, 1928, **6**, #7, 36; 1928, **6**, #4, 13. Cf. E. P. 259899; abst. J. S. C. I. 1927, **46**, 295-B. C. Dreyfus, F. P. 642628; abst. C. A. 1929, **23**, 1266. Can. P. 273366. U. S. P. 1798836.

8. *Zinc Phosphate.* R. Clavel[1] first treats the materials with 2% phosphoric acid and 1% ethyl alcohol, and after squeezing out and without washing, then immerses the goods in a weighting bath of zinc chloride solution. In the mordanting of goods of or containing methyl-, ethyl- or benzyl-cellulose[2], use is made of the assistance of highly water soluble zinc salts as zinc chloride, the usual mordanting with iron, chromium, aluminum or tin salts being carried on in the presence of zinc chloride. The concentration of the mordanting agent and the zinc salt govern the amount of metal absorbed, the concentrations, of course, being so adjusted as not to dissolve or peptize the cellulose derivatives or otherwise damage the permanence, strength, luster or other desirable characteristics of the material treated. In a specific example described in the patent, the increase in weight of the goods treated as above was 7.5-10%, whereas omission of the zinc chloride gave a weighting of only about 2.5%[3].

9. *Zinc Chloride.* C. Dreyfus and H. Platt[4] have detailed a method for the weighting of fibers and knitted and woven fabrics of cellulose ethers or esters by treating with an aqueous solution of metallic salts as zinc chloride alone or with stannic chloride, the cellulose derivatives being exposed to a gelling or swelling action during or before the treatment, the weighting being subsequently fixed in insoluble form by washing or soaping. The chloride may be used of such strength that both the gelling and the

1. D. R. P. 471370, Addn. to D. R. P. 468018; abst. C. A. 1929, **23**, 3356; Chem. Zentr. 1929, I, 2718. D. R. P. 468018; abst. C. A. 1929, **23**, 719; Chem. Zentr. 1929, I, 460. E. P. 283019; abst. C. A. 1928, **22**, 3997; Chem. Zentr. 1928, I, 2027. E. P. 266640; abst. Chem. Zentr. 1927, II, 350. F. P. 634641; abst. C. A. 1928, **22**, 3997.

2. British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 309899; abst. C. A. 1930, **24**, 733; J. S. C. I. 1929, **48**, 596-B; Silk J. 1929, **6**, #63, 66; Chem. Zentr. 1929, II, 1102.

3. British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 309876, Addn. to E. P. 258874; abst. C. A. 1930, **24**, 735; J. S. C. I. 1929, **48**, 596-B; Silk J. 1929, **6**, #63, 66; Chem. Zentr. 1929, II, 1102. H. Dreyfus, F. P. Addn. 35947 to F. P. 634165; abst. C. A. 1930, **24**, 4171.

4. E. P. 279502.

weighting are effected, or a separate gelling agent as formic or acetic acid, phenol, furfural or pyridine may be used either in a separate bath or mixed with the chloride. If desired, precipitation of the tin or zinc may be made as an additional operation, using sodium carbonate or hydroxide, ammonia, or potassium or calcium hydroxides, the latter but little soluble in water.

10. *Aluminum Phosphate.* Artificial silk is given an immersion in an acid solution as phosphoric or chloracetic acids, followed by aluminum sulfate, with or without the addition of glue or other protective colloid[1]. The intermediate washing between impregnation and precipitation is thus rendered unnecessary, no precipitation taking place on the surface of material so treated. Alternatively, acid and/or protective colloid may be added to the impregnating bath or to the fiber before precipitation, the acid being subsequently removed by means of a mild acid bath.

11. *Aluminum Acetate.* Artificial silk fabrics of cellulose derivatives may be impregnated at 40° with a 1-5% solution of *basic* aluminum acetate acidified with acetic acid, resulting in a combined weighting and the raising of the safe ironing temperature of the goods materially, without increase of luster when ironed damp[2].

12. *Metal or Metallic Oxide.* In mordanting and mordant dyeing which also involves weighting[3] there is projected onto the filaments or textile prepared therefrom at relatively high speed a mordant metal or metal oxide or a compound of a mordant metal capable of yielding the oxide or hydroxide or basic salt. Cellulose ethers are particularly amenable to this method of mordanting and weighting. It is preferred to project the metal itself and to oxidize it to the mordant metal oxide either during its passage

1. R. Clavel, E. P. 280094; abst. J. S. C. I. 1928, **47**, 296-B; Rayon, 1928, **6**, #12, 46.

2. British Celanese, Ltd., E. P. 299058; abst. J. S. C. I. 1929, **48**, 716-B.

3. British Celanese, Ltd., W. Dickie and F. Hill, E. P. 337813; abst. C. A. 1931, **25**, 2304; J. S. C. I. 1931, **50**, 197-B. Can. P. 321955. See E. P. 314208.

to the material or after it has embedded in or been deposited on the material, the Schoop apparatus for metallizing being particularly suitable for use.

13. *Aluminum Tannate or Phosphate.* A process has been described by H. Dreyfus for the loading of filaments of cellulose derivatives[1] in which water-soluble salts of aluminum, and alternatively tin or zinc, are followed by a precipitating bath containing tannic acid or a soluble phosphate, thus precipitating the insoluble salt on the fiber. The loading and ladder-reducing agents may be applied separately or simultaneously as a single or a plurality of treatments, depending upon the degree of loading desired. The goods are afterwards washed in soap solution.

14. *Magnesium or Calcium Phosphate.* W. Zänker[2] loads textiles of artificial silk by impregnating them with acidified solutions of heavy metals as calcium chloride or magnesium chloride or sulfate, choosing salts of neutral reaction. A soluble phosphate bath is then applied, and the textile washed free from unfixed salts.

15. *Magnesium Sulfate.* In order to impart the desired luster accompanied by a weighting effect, H. Bertsch[3] treats the fiber with a mixture of magnesium sulfate and dextrin in water to which is added with agitation, a paraffin or wax emulsion produced by the use of dipropylnaphthalenesulfonic acid. The mixture is said to be perfectly homogeneous and does not throw down any clots of magnesia compounds.

16. *Barium Sulfate.* The J. Roscow invention contemplates weighting by the precipitation in the fibers of barium sulfate obtained by first soaking the material in a barium chloride solution[4], hydro-extracting, drying, and then impregnating with a dilute sulfuric acid solution in excess of that necessary to form $BaSO_4$, afterwards wash-

1. E. P. 281084; abst. Rayon, 1928, **6**, #5, 36. E. P. 336621; abst. C. A. 1931, **25**, 1995; J. S. C. I. 1931, **50**, 197-B. See E. P. 258874, 259899, 284798, 285941, 308322, 308323, 309201, 312095, 312096.
2. F. P. 702964; abst. C. A. 1931, **25**, 4415.
3. U. S. P. 1830255.
4. U. S. P. 1602840; abst. J. S. C. I. 1927, **46**, 9-B.

ing out the sulfuric and hydrochloric acids and drying. A 50% barium chloride solution and 10% sulfuric acid are recommended.

17. *Rare Metals.* A German process for the loading of artificial filaments and textiles made therefrom has been described[1], in which the filaments are treated with heavy metal oxides of zirconium and salts of the rare earths in the presence of ammonia, and in solution in an organic solvent, the luster of the filaments not being diminished. The filaments may be dyed before the weighting process. The by-products obtained as the result of the manufacture of thorium nitrate are especially recommended as being suitable loading agents[2], especially in their hydroxide form, being used as such or in conjunction with iron, nickel, chromium or tin hydroxides.

18. *Organic Metal Salts.* H. Dreyfus[3] reports that if mordant materials are applied to cellulose ethers or organic esters in the form of their salts with aliphatic acids and especially with hydroxyaliphatic acids, absorption of the mordant metals takes place and when such mordanted materials are dyed, full lake shades are obtainable with their characteristic fastness. Thus good mordanting accompanied by a weighting is said to be obtainable with any of the following salts: basic chromium or aluminum lactate or sodium aluminum lactate, basic aluminum ammonium citrate or ferric citrate, basic aluminum or chromium glycollate, or aluminum, chromium or ferrous acetate (pyrolignite of iron). Aluminum or chromium acetosulfate, acetonitrate or acetochloride are also equally applicable.

19. *Tannin.* A substantial increase in the weight and volume of cellulose ethers of the water-resistant type and

1. Deutsche Gasglühlicht Auer-Ges. m. b. H., D. R. P. 403990; abst. J. S. C. I. 1925, **44**, 204-B; Chemicals, 1925, **24**, #17, 45.

2. *Ibid.* D. R. P. 402401, Addn. to D. R. P. 338653; abst. J. S. C. I. 1925, **44**, 38-B; Amer. Silk J. 1925, **44**, #9, 50. See E. P. 116103; abst. J. S. C. I. 1920, **39**, 595-A.

3. U. S. P. 1779464; abst. C. A. 1931, **25**, 217; Cellulose, 1930, **1**, #11, 293. E. P. 287204; abst. C. A. 1929, **23**, 528; J. S. C. I. 1928, **47**, 402-B. F. P. 644937; abst. C. A. 1929, **23**, 2046. See E. P. 286761. F. P. 644936.

cellulose esters[1] is described in a process which does not impair the appearance or other qualities of the fiber or textile, and which comprises treating one part of textile with 30 parts of 30% solution of tannin at about 55° for 0.75 hr., but if the material is treated with the tannin solution in the cold, there is less increase in weight. Conversely, treatment with 30% tannin solution for 2 hrs. at 80-85° results in a very marked increase in weight of goods so treated. P. King and A. Sahasranam[2] have studied the power of acetate silks for tannins of various concentrations. Their results indicate that cellulose acetate absorbs about 20% of the tannic acid in a given solution, the difference in percentage absorption between 1 hr., 2 hrs. and overnight being only about 2% in a 50% solution.

20. *Antimony Tartrate.* The familiar mordant composition tartar emetic (potassium antimony tartrate) and tannin has been found to be applicable for loading purposes in the hands of C. Dreyfus and H. Platt[3], who first treat with tannin as outlined above, followed by a bath of 30% aqueous tannin at 80-85° for 2 hrs. According to the disclosures of H. Dreyfus[4] soluble salts of tin, zinc, aluminum, bismuth, tungsten, and antimony, applied to fibers or textiles of or containing methyl-, ethyl- or benzyl-cellulose, induce a loading and weighting of the fiber readily controlled as to weight deposited, especially if the treatment is preceded or succeeded by a swelling treatment of the fibers, using glycollic or lactic acids, ethyl alcohol, acetone, diacetone alcohol, diacetin, phenol or hydroquinone soluble in water.

21. *Metal Thiocyanates.* The thiocyanates of the alkali and alkali earth metals have a direct solvent and swelling action upon the cellulose ethers and acetylcellulose, and

1. C. Dreyfus and H. Platt, E. P. 260290; abst. C. A. 1927, **21**, 3470; J. S. C. I. 1928, **47**, 477-B. G. Ellis, Can. P. 305543.
2. J. Soc. Dyers Colourists, 1930, **46**, 118; abst. C. A. 1931, **25**, 212; J. S. C. I. 1930, **49**, 656-B.
3. U. S. P. 1731298; abst. C. A. 1930, **24**, 238; J. S. C. I. 1929, **48**, 976-B; Cellulose, 1930, **1**, #2, 66.
4. F. P. 634165. E. P. 323180. Can. P. 292893. F. P. 675466.

this property has been taken advantage of in processes of loading textiles in which the initial colloiding action of the thiocyanates results in an opening-up of the fibers thereby augmenting their receptivity for the weighting agent. In one process[1] the goods are first treated with stannic chloride solution at 20°, followed by a bath of ammonium thiocyanate. In another[2], the baths are so adjusted as to contain 280 gms. stannic chloride ($SnCl_4.\%-5H_2O$) and 243 gms. ammonium thiocyanate per liter, these being the stoichiometrical quantities required to yield the salt $Sn(CNS)_4$. After weighting, the goods are lifted, rinsed, and soaped with 0.25% olive oil soap at 50°. An intermediate treatment with sodium phosphate may be introduced, in which case the formation of tin phosphate also liberates alkali thiocyanate which swells the fibers simultaneously with precipitation of insoluble phosphate therein and thereon. Degree of absorption of loading material or mordant by the materials is profoundly influenced by the concentration of the thiocyanate grouping present in the liquor quite apart from the concentration of the metallic radical itself. Thus, by increasing the concentration of the thiocyanate radical compared with that of the metallic radical, a higher degree of absorption of metal is possible[3], explainable on the grounds of the direct swelling and solvent function of the thiocyanate. Iron, aluminum or chromium thiocyanate may be used.

As swelling agents in the weighting of organic cellulose substitution derivatives there have been specified[4]

1. H. Dreyfus, F. P. 642331.
2. G. Ellis, U. S. P. 1817741; abst. C. A. 1931, **25**, 5580. British Celanese, Ltd., H. Dreyfus and G. Ellis, E. P. 285941; abst. C. A. 1929, **23**, 290; J. S. C. I. 1928, **47**, 330-B; Silk J. 1928, **5**, #49, 78; Chem. Zentr. 1928, II, 204. F. P. 702353. Can. P. 276516. Belg. P. 344890.
3. G. Ellis, U. S. P. 1757519; abst. J. S. C. I. 1930, **49**, 555-B.
4. H. Dreyfus, E. P. 284798; abst. J. S. C. I. 1928, **47**, 444-B. See E. P. 281084; abst. J. S. C. I. 1928, **47**, 227-B. In the H. Dreyfus and G. Ellis method (Can. P. 285978; abst. Chem. Zentr. 1932, I, 2242) the metallic mordant is brought onto the fibers in the form of

thiocarbimides, carbimides, cyanate, urea, urethanes, thiourea, thiourethanes, guanidine or their substitution products. Ammonium, sodium or potassium thiocyanates are all suitable for use to increase the weighting and mordanting effect[1], it being necessary, obviously, that the thiocyanate radical present be in excess of that chemically equivalent to the metallic radical[2]. Another method of increasing the absorptive capacity of the loading components is the addition to the weighting bath of an aqueous solution of lactic acid, alcohol, acetone or a phenol[3].

In dyeing effect threads of acetate silk or partially esterified cotton[4], clearer effects are said to be obtained by adding to the dye-bath an organic mordant for basic dyes such as Katanol, or mordanting with salts of hydroxyaliphatic acids as tin, aluminum, chromium or zinc lactates, citrates, glycollates and acetates[5]. The penetration of mordant is said to be facilitated by the simultaneous addition

a thiocyanate, whereby the concentration of thiocyanate radical is greater than corresponds to the equivalent amount of mordant metal radical, and is then dyed with a mordant dyestuff.

1. British Celanese, Ltd., and G. Ellis, E. P. 280698; abst. C. A. 1928, **22**, 3305; J. S. C. I. 1928, **47**, 86-B; Silk J. 1928, **4**, #47, 68; Chem. Zentr. 1928, I, 1096. F. P. 644565; abst. C. A. 1929, **23**, 1759. Organic cellulose ethers or esters may be mordanted according to the process of British Celanese, Ltd., G. Rivat and E. Cadgene (E. P. 273693; abst. J. S. C. I. 1928, **47**, 891-B) in presence of such swelling agents as formic or acetic acids, furfuraldehyde, phenol, pyridine, and especially a mixture of furfuraldehyde with 3-5 parts acetic acid. Mordanting may also be accomplished by spinning together a solution of a cellulose ether or ester containing half as much calcium thiocyanate dissolved in acetone as the cellulose compound. (See E. P. 273692, 273693, 336621.) Or there may be used as a combined dyeing and mordanting bath such substances as aluminum, chromium or ferrous thiocyanates, or aluminum, iron or chromium benzoate, salicylate or phthalate (British Dyestuffs Corporation, Ltd., L. Lawrie and H. Blackshaw, E. P. 240293; abst. C. A. 1926, **20**, 2253).

2. H. Dreyfus, F. P. 638248; abst. C. A. 1929, **23**, 290; Chem. Zentr. 1928, II, 2204. F. P. 642331; abst. C. A. 1929, **23**, 1267. Can. P. 285802, 285978; abst. C. A. 1929, **23**, 1286. Can. P. 306857.

3. *Ibid.* U. S. P. 1821464; abst. C. A. 1931, **25**, 5990. F. P. 634165; abst. C. A. 1928, **22**, 3789. F. P. 34391, Addn. to F. P. 634165; abst. C. A. 1929, **23**, 4581. Belg. P. 345566.

4. I. G. Farbenindustrie, A.-G., D. R. P. 481253; abst. C. A. 1930, **24**, 248; Chem. Zentr. 1929, II, 2375. See E. P. 306876.

5. H. Dreyfus, Can. P. 281195; abst. C. A. 1928, **22**, 3051.

of zinc chloride[1], which has a distinct swelling effect upon the cellulose ethers and esters[2]. C. Dreyfus reports[3] that when ribbons or other mixed fabric containing silk or cotton associated with cellulose ether or ester filaments which have been impregnated with a permanent finish, are subjected to the weighting process, the weighting of the silk in the mixed fabrics can be executed in an economical and successful way without absorption of weighting material by the other fibers, if the non-silk threads have previously been coated with a thin layer of a cellulose derivative[4].

In the mordanting and weighting of cellulose propionate or butyrate filaments in hank form[5], it is recommended to first treat with 33° Be. solution of stannic chloride at 50°, then with disodium phosphate solution of 3-6° Be. strength, afterwards washing with warm water. H. Dreyfus proceeds first to treat the cellulose ether or ester material with a swelling agent as formic, acetic, glycollic or lactic acids, acetone, diacetone alcohol, diacetin, phenol or hydroquinone, and after the fibers have become swollen a mordant solution is applied at temperatures not above 80°[6]. It is advised to use high concentrations of mordants[7], preferably up to 60% solutions. Or[8], the mordant may be applied to the cellulose ether in the form of a suspension, dispersion or colloidal solution, as the oxides of titanium, zinc, aluminum, chromium, iron, cerium or tin. The electric polarity of the dispersed particles is opposite to that of the material.

1. H. Dreyfus, Can. P. 297863.
2. R. Clavel, U. S. P. 1806043; abst. C. A. 1931, **25**, 3847. E. P. 270987; abst. C. A. 1928, **22**, 1693; J. S. C. I. 1927, **46**, 653-B. F. P. 621380; abst. Chem. Zentr. 1927, II, 765. D. R. P. 521613; abst. C. A. 1931, **25**, 3496; Chem. Zentr. 1931, I, 3294.
3. U. S. P. 1508840; abst. C. A. 1924, **18**, 3727.
4. C. Dreyfus, Can. P. 304293.
5. H. Dreyfus, U. S. P. 1805468; abst. Chem. Zentr. 1931, II, 3046.
6. *Ibid.* E. P. 285948; abst. C. A. 1929, **23**, 288. Can. P. 285801; abst. C. A. 1929, **23**, 1267.
7. *Ibid.* E. P. 286761; abst. C. A. 1929, **23**, 528. F. P. 644936; abst. C. A. 1929, **23**, 2046.
8. *Ibid.* F. P. 39164, Addn. to F. P. 703626; abst. C. A. 1932, **26**, 2328. See E. P. 343124.

The British Celanese, Ltd., and G. Ellis[1] treat fabrics containing cellulose ethers or esters without loading to increase the friction between the fibers, e.g., to reduce laddering, with one or more organic substances having a solvent or solute action upon the fibers, as with boiling toluene or methylated spirit and water[2]. Sulfurized compounds of phenols[3] have been advanced as desirable tannin substitutes for mordanting artificial silk.

Waterproofing. Nearly fifty years ago J. Stevens[4] published his method for waterproofing fabric in which a coating of pyroxylin, camphor and *b*-naphthol was applied thereto, and was followed by the method of M. Dickert[5] who waterproofed cardboard shotgun cartridges with successive coatings of balata and cellulose acetate. C. Dreyfus[6] prepares fabrics of increased impermeability of moisture by applying to the fabric a rubber compound and then topping with a cellulose acetate-resin solution.

In the manufacture of fabrics having a basis of cellulose ethers or cellulose esters and possessing waterproof and gas proof properties[7], those fabrics composed of or containing methyl-, ethyl- or benzyl-cellulose are subjected to heat and pressure of a degree sufficient to soften and melt the cellulose ether, thereby closing the interstices between the woven fibers and compacting the mass to a high degree of impermeability. G. Ellis and British Celanese, Ltd.[8],

1. E. P. 280990; abst. Silk J. 1928, **4**, #47, 68; J. S. C. I. 1928, **47**, 85-B.
2. British Celanese, Ltd., and G. Ellis, E. P. 355331; abst. Textile Mfr. 1932, **51**, #686, 78. Can. P. 324228. See F. P. 639196. F. P. 35500, Addn. to F. P. 639196.
3. Soc. Alsacienne de Produits Chimiques, E. P. 224218; abst. C. A. 1925, **19**, 1202; J. S. C. I. 1925, **44**, 588-B.
4. U. S. P. 615319.
5. U. S. P. 1180704; abst. C. A. 1916, **10**, 1710; J. S. C. I. 1916, **35**, 643.
6. Can. P. 310252.
7. British Celanese, Ltd., T. Woodman and W. Dickie, E. P. 249946; abst. C. A. 1927, **21**, 1019; J. S. C. I. 1926, **45**, 532-B; Ann. Rep. S. C. I. 1926, **11**, 131.
8. E. P. 323785, Addn. to E. P. 323501; abst. C. A. 1930, **24**, 3368; J. S. C. I. 1930, **49**, 321-B; Cellulose, 1930, **1**, #9, 246. Can. P. 307040.

waterproof methyl-, ethyl- and benzyl-cellulose by treatment with an emulsion of wax in a soap, and by precipitation of the soap in or on the material under treatment. Tin, aluminum, calcium, barium, lead, iron, chromium, bismuth, zinc and antimony chlorides, sulfates and thiocyanates are used to impregnate the material, and an insoluble soap is precipitated thereon and therein by treatment with fatty acids, sulfonated fatty acids or naphthenic acid.

Proofed cloth for use as printers' blankets may be made by coating a woollen cloth with an acetyl- or nitrocellulose solution[1], followed with castor oil and a pigment. M. Arosio[2] decreases the hygroscopicity of wood, vulcanized fiber or parchment paper surfaces by applying thereto dissolved acetylcellulose containing mineral coloring matter, while A. Nathansohn[3] increases the water resistance of artificial fibers of either acetated cellulose or a cellulose ether as ethylcellulose, by submitting them to a limited esterification treatment with palmityl or stearyl chloride with palmitic or stearic anhydride, thereby producing a cellulose acetostearate or acetopalmitate, or ethylcellulose palmitate or stearate.

Acetate filaments having a high resistance to boiling are said to be obtained by using acetone-soluble acetylcellulose, preferably in the stabilized form and but very slightly soluble in 70% alcohol[4]. Fabrics consisting of or containing methyl-, ethyl -or benzyl-cellulose or cellulose formate, acetate, propionate or butyrate[5] are waterproofed by treatment with an aqueous solution of aluminum acetate, whereby they also may be ironed at a higher tempera-

1. C. Goddard, E. P. 325034; abst. C. A. 1930, **24**, 3912; J. S. C. I. 1930, **49**, 370-B; Chem. Zentr. 1930, II, 3876.
2. E. P. 131911; abst. J. S. C. I. 1921, **40**, 143-A; Chim. et Ind. 1920, **4**, 798; Kunst. 1920, **10**, 69. E. P. 131916; abst. C. A. 1920, **14**, 359; Chim. et Ind. 1920, **4**, 798; Kunst. 1920, **10**, 69.
3. F. P. 693803; abst. C. A. 1931, **25**, 1686; Chem. Zentr. 1931, I, 1385. D. R. P. 535283; abst. C. A. 1932, **26**, 1136.
4. I. G. Farbenindustrie, A.-G., E. P. 319014; abst. C. A. 1930, **24**, 2602; Silk J. and Rayon World, 1930, **6**, #68, 66. F. P. 681696; abst. C. A. 1930, **24**, 4391; Cellulose, 1930, **1**, #9, 246.
5. H. Platt and C. Croft, E. P. 299058; abst. C. A. 1929, **23**, 3111.

ture without the iron sticking to them. Artificial silk stable to boiling and resistant to the action of soap and alkalis (?)[1] is said to result by esterifying a cellulose with propionic or butyric acids so that the resulting cellulose acetopropionate or acetobutyrate contains but about 0.2 mols. of the higher fatty acid.

The M. Dickert method of producing waterproof coatings on objects which are influenced by humidity comprises applying a thin coating of cellulose acetate in chloroform (i.e., a cellulose acetate which has not been partially hydrolyzed). The L. Cavanaugh process for soil-proofing fabrics[2] involves treatment first by impregnation with a volatile liquid as benzine, followed by the application of an acetylcellulose solution[3]. In the R. Lant process[4], textile filaments, fabrics and other coherent structures are subjected to the action of higher fatty acid chlorides in association with pyridine under such conditions that esterification of the cellulose is effected to an extent insufficient to destroy the primary physical character of the structure. With artificial filaments, they may be treated during the course of their manufacture.

Paper pulp may be water-insolubilized by adding to the pulp in the beater, an aqueous suspension or emulsion of cellulose ether-esters derived from substituted fatty acids as ethylcellulose palmitate, oleate or stearate[5], or cellulose dilaurate, the band of paper afterwards being submitted to mechanical pressure at a sufficiently elevated temperature to soften the cellulose derivative, but below its flowing point.

P. Krais and R. Buchheim[6] have made a study of

1. I. G. Farbenindustrie, A.-G., F. P. 662353; abst. C. A. 1930, **24**, 498. F. P. 686922; abst. C. A. 1931, **25**, 814. See F. P. 660804.
2. L. Cavanaugh, U. S. P. 1277695. E. P. 133180; abst. J. Soc. Dyers & Col., 1920, **36**, 27; Kunst. 1920, **10**, 149.
3. P. Dutreillis, Russa, 1932, **7**, 391; abst. C. A. 1932, **26**, 4478.
4. E. P. 343104; abst. Chem. Zentr. 1931, II, 2399.
5. I. G. Farbenindustrie, A.-G., E. P. 289063. F. P. 35906, Addn. to F. P. 648154; abst. C. A. 1930, **24**, 4159.
6. Textile Forschung, 1931, **13**, 94; Chim. et ind. 1932, **27**, 1405; abst. C. A. 1932, **26**, 4478.

waterproofing processes for fabrics, in which three different colored fabrics were subjected to 20 different waterproofing processes, three impermeability tests being applied to each. The absorption of water varied between 27.9-89.5%, and the penetration of water from 0-0.23 cc. per minute.

In the waterproofing of open-mesh fabrics[1], the process of British Celanese, Ltd., may be followed, the fabric comprising cellulose ether or ester yarns, by applying a rubber solution to the under face of the fabric so that it does not penetrate through the face, thereby avoiding spotting with the rubber solution. Or the fabric base may have applied thereto a thin sheet of rubber or rubberized fabric, it being necessary that the rubber solvent is not a solvent of the fabric or of any of its components[2].

Coating. H. Dreyfus[3] smooths and increases the tensile strength of filaments by applying a coating composition thereto as a continuous operation while the filaments are traveling, and subsequently drying them out of contact with frictional surfaces until drying is completed. In the impregnation of textiles[4], they are treated with cellulose ethers or organic esters in volatile solvents together with a bituminous substance, the amount of solvent being sufficiently great to prevent closing of the interstices in the textile. In applying coatings to cellulose derivatives[5], G. Schneider spreads dissolved acetylcellulose or cellulose ether on glass or other rigid surface and the solvent evaporates to form a film. Fabric to be coated is wetted with a dilute solution of a cellulose derivative and the wetted surface then pressed against the film, and the united film and fabric then removed from the film support.

1. E. P. 296450; abst. C. A. 1929, **23**, 2582.
2. British Celanese, Ltd., E. P. 338065; abst. C. A. 1931, **25**, 2305.
3. Can. P. 309595.
4. I. G. Farbenindustrie, A.-G., E. P. 335247; abst. C. A. 1931, **25**, 1392; J. S. C. I. 1930, **49**, 1148-B. See E. P. 322768.
5. U. S. P. 1824690; abst. C. A. 1932, **26**, 319; Chem. Zentr. 1931, II, 3416.

L. Lilienfeld has shown[1] that vegetable textile materials in the form of yarn or fabric acquire a silk-like luster without material loss of softness, by coating or impregnating with solutions in volatile solvents or pyridine of cellulose ethers or of cellulose xanthic esters, or of N-substituted thiourethanes of cellulose, and then subjecting the coated materials to a treatment adapted to cause the materials to shrink. C. Dreyfus[2] has found that when ribbons or mixed fabrics which contain silk associated with cotton yarns and which have been subjected to a permanent impregnation or finish with a cellulose ether or ester, are subjected to a weighting process, the yarns impregnated with the cellulose derivative are immune to the weighting treatment, and differential effects are thus obtainable. Another method for treating fabrics has been described[3], this consisting in precipitating a cellulose derivative on the surface of the fabric by evaporation of a solution in a mixed solvent, the highest boiling portion being a non-solvent of the cellulose compound. When the process is applied to a fabric or film having a basis of a cellulose derivative, a surface of relatively low luster is produced for the reason that as the evaporative process increases so does the increment of non-solvent over solvent, until a point is reached where incipient precipitation of the cellulose compound takes place in an opaque form.

Coated articles may be produced by applying a fabric made of a thermoplastic cellulose derivative to a suitable core and subjecting to heat and pressure so as to secure adherence of fabric to core[4]. The core may be of papier mache, fiber board, compressed paper, or plastic wood, and the fabric applied to the core a woven, knitted type of methyl-, ethyl- or benzyl-cellulose. In order to improve the strength, elongation and dye affinity while diminishing

1. E. P. 357120, 357190; abst. Textile Mfr. 1932, **58**, #687, 116; Silk J. 1932, **8**, #95, 50.
2. U. S. P. 1508840; abst. C. A. 1924, **18**, 3737.
3. British Celanese, Ltd., E. P. 346269; abst. J. S. C. I. 1930, **49**, 685-B.
4. *Ibid.* E. P. 365143.

the luster of cellulose fabrics[1], they are given an all-over treatment with thiocyanate solution of 15-25° Be., and are then washed. With cellulose ether or acetate fabrics the result is not as permanent as with regenerated cellulose rayons.

In the coating of textile materials[2], a solution or dispersion of a polymerized vinyl compound as polyvinyl acetate is applied, in methyl alcohol as solvent. The addition of a softener as oils, fats or soaps is necessary to the treatment bath.

Increasing Heat Resistance. Both cellulose ether and acetylcellulose artificial filaments partake of the defect that they easily fuse or melt when subjected to heat and pressure as in the ordinary ironing operation, temperatures exceeding 200° being dangerous, so that in laundering operations and in the making up of garments where hot pressing is necessary, it would be a definite advantage if the filaments or textile could be subjected to a prior operation or treatment whereby its safe ironing temperature could be materially raised. In the topic "Artificial Horsehair" this property of fusing under heat is taken advantage of in the production of ribbons by cutting fabrics by means of a heated blunt edge, fusing the filaments instead of employing a cutting operation which would leave a ragged or ravelled edge, thus usefully forming selvedges to protect the strip from tearing.

In order to render the cellulose ethers and cellulose acetate more resistant to heat, several methods have been proposed, most of which involve treatment with inorganic salts and weighting and loading agents which are beneficial in that they raise the sintering or fusion point. Some of the processes proposed are only suitable where the textile is to be colored black as in dyeing black with logwood or hematin, followed by oxidation with sodium bichromate[3],

1. Lyons Piece Dye Works, E. P. 361418; abst. Silk J. 1932, 8, #97, 56.
2. H. Dreyfus, F. P. 706130; abst. Chem. Zentr. 1931, II, 3285.
3. C. Dreyfus, U. S. P. 1871047. E. P. 313970.

this treatment being claimed to raise the fusing point by about 40°. A. Hall[1] has observed that cellulose derivatives dyed with aniline black resist hot ironing to a considerable extent, and when such dyed textile is burned no formation of the usual fused beads takes place.

Although the hot ironing properties may be improved by incorporation within the cellulose derivative of organic silicon compounds as methyl, ethyl or amyl silicate[2], there are said to be certain disadvantages of using this method in connection with acetylcellulose filaments. According to a French patent[3], by mordanting the fabric in a special manner with weighting agents as metal salts, under such conditions that there is no apparent swelling of the cellulose derivative as by using a low concentration metallic salt or a low temperature for working in the presence of sodium chloride, the safe ironing temperature may be materially raised, with cellulose acetate for instance, from 220° to 280° and even to 320°. Stannic chloride is preferred as the mordant.

It has also been demonstrated[4] that filaments and fabrics composed of or containing methyl-, ethyl- or benzylcellulose may be ironed safely at a substantially higher temperature, if previously treated with an aluminum salt as the basic acetate, without the iron sticking to them. Sodium or potassium stannates have been advocated for the same purpose[5].

Cellulose ethers, as the methyl or ethyl ethers, may be safely ironed by the C. Palmer process[6] which is based on a double ironing treatment, first by a hot iron or calender at above 100°, only when it is dry, the fabric being never

1. Rayon Record, 1930, **4**, #25, 1299.
2. Courtaulds, Ltd. and C. Diamond, E. P. 317936; abst. J. S. C. I. 1929, **48**, 893-B.
3. C. Dreyfus, F. P. 718725; abst. C. A. 1932, **26**, 3376. British Celanese, Ltd., E. P. 372129; abst. J. S. C. I. 1932, **51**, 597-B.
4. British Celanese, Ltd., E. P. 299058; abst. C. A. 1929, **23**, 3111; J. S. C. I. 1929, **46**, 716-B; Silk J. 1929, **5**, #57, 72; Chem. Zentr. 1929, I, 1168.
5. British Celanese, Ltd., and G. Ellis, E. P. 302775; abst. C. A. 1929, **23**, 4353.
6. U. S. P. 1732340; abst. C. A. 1930, **24**, 249.

permitted to come in contact with the hot iron or calender while it is damp or wet. The fabric is first preferably air dried, and then ironed to remove the creases, the temperature of the iron being kept within the limits of slightly above 100° and well below the fusing point of the cellulose derivative.

The following methods are applicable primarily to cellulose acetate threads and textiles because they involve a superficial or partial saponification, the essential point in such processes being that they shall permit of perfectly even saponification and involve no loss in strength[1]. If cellulose acetate woven goods are simply treated with a dilute sodium hydroxide solution, the regenerated cellulose formed is in a highly dispersed condition, and is thus prone to have but a low wet strength. It is desirable, therefore, that the regenerated cellulose formed should be compact, the degree of dispersion being indicated by the depth of shade resulting from dyeing with direct colors.

A mechanical process for raising the safe ironing temperature of cellulose acetate has been devised by C. Dreyfus and H. Platt[2], the fabric being immersed in 4-7% NaOH solution at 70-85° until the acetate has been saponified only superficially on the filaments, when they are washed and dried. If the saponification is induced by the use of an aqueous alcoholic solution of an alcoholate of a dihydric alcohol such as ethylene glycol, it is alleged the resulting products have a higher tensile strength than before submission to this treatment, and much less alkali is required in the saponification process than where no alcohol is used. Barium hydroxide as the preferred alkali has also been used[3].

1. British Celanese, Ltd., E. P. 313404; abst. J. S. C. I. 1930, **49**, 1107-B. See E. P. 125153.
2. U. S. P. 1866153.
3. A. Hall, Rayon Record, 1930, **4**, 801. Amer. Dyestuff Reptr. 1931, **20**, 583; abst. C. A. 1931, **25**, 5995.

In another advocated method[1], material composed partially or wholly or cellulose acetate is treated at 70-90° with a solution containing 0.3-0.7 gms. per liter of NaOH, the alkalinity being maintained within these limits by additions of soda from time to time, whereby a regular and partial hydrolysis of the cellulose ester takes place, not exceeding 6%. The quantity of alkali solution should be 130-160 times the weight of the materials to be treated[2]. Partial alkaline saponification coupled with a weighting treatment has also been proposed, thus raising the safe ironing temperature to above 270°[3].

A. Hall has studied the partial saponification of acetate filaments in respect to raising the ironing temperature in a quantitative manner, and has arrived at the following results: degree of saponification, 0%, temperature of coalescence (fusion), 215-220°; 0.4%, 240-245°; 0.7%, 230-235°; 3.9%, 250-255°; 7%, 240-245°; 9.8%, 275-280°; 22.6%, 265-270°; 31.5-87%, 275-280°. It appears that the fusion point of cellulose acetate filaments is considerably raised by but a small degree of saponification—a marked advantage. The filaments did not become brown in color until quite near the fusion point.

In a recent process[4] a method has been disclosed for increasing the safe ironing temperature of fabrics containing cellulose esters, and which involves applying to the yarn or fabric a pasty mass containing an alkaline agent as sodium or potassium carbonate, phenolate, silicate, sulfite, or trisodium or tripotassium phosphate. Acacia, tragacanth or British gum is used as a thickener for the paste, which may also contain buffer salts or modifying agents

1. C. Dreyfus, E. P. 304596; abst. C. A. 1929, **23**, 4832; J. S. C. I. 1929, **48**, 1012-B; Silk J. 1929, **5**, #60, 66. See also C. Dreyfus, E. P. 309377; abst. C. A. 1930, **24**, 735.

2. C. Dreyfus and W. Blume, U. S. P. 1818466. E. P. 309377, Addn. to E. P. 304596; abst. C. A. 1930, **24**, 735; Silk J. 1929, **6**, #63, 66.

3. *Ibid.* Can. P. 324414. See H. Dreyfus, F. P. 676127; abst. C. A. 1930, **24**, 2899.

4. C. Dreyfus and G. Schneider, U. S. P. 1884622. Can. P. 317920.

as soap, sodium acetate, borax or ethyl alcohol. Whereas with cellulose acetate, if the calender or iron is above about 220° sticking of the fabric and melting of the acetylcellulose is prone to take place, this treatment raises the safe ironing point to 260° or higher. Water-soluble cellulose ethers as methylcellulose and ethylcellulose of a low degree of etherification may be used as the thickening media in the above process.

The R. Curtis method of "iron-proofing" cellulose acetate fabrics[1] is to run the fabric through an American padder (11° Tw. NaOH solution at 140° F.) at 100 yds. per min., picking up liquid to give 80% increase in weight. The cloth is batched up and then given two ends on the jig, through water at 170° F., after which the dyeing can be carried on as usual. The method involves the partial regeneration of the cellulose due to the alkali treatment.

Modifying Luster. The high luster of artificial silk was originally its chief attribute, but as time went on, this luster which exceeds that of raw silk, was considered a drawback, and many are the attempts which have been made to reduce this luster so that it does not exceed that of degummed silk, or even to so remove the luster that the product resembles natural silk which has been soupled. Remembering that all forms of cellulose ether or cellulose acetate filaments are made either from precipitation into a liquid medium or by evaporation of solvent therefrom until a substantial solid structureless fiber of indeterminate length is formed, these fibers all possess the colloidal structure and properties of gels, and take on the optical properties of glass. Natural silk owes its comparatively lesser luster possibly because less homogeneous in structure than filaments deposited from meticulously clarified solutions, but more probably from the fact that natural silk retains portions of the coating material which breaks up or roughens the surface and thereby diminishes light ray scintillations with the result that the luster is more soft and sub-

1. Textile World, 1929, **76**, 1760; abst. C. A. 1930, **24**, 1743.

dued. Therefore the basic principle of the process of delustering artificial filaments consists in removing the smoothness from the surface and substituting a rough or irregular surface, or else implanting in the pores or interstices of the individual filatures, insoluble inorganic particles whose function is to break up, disseminate and diverge light rays. In those processes for deadening brilliancy which depend upon solvent action or intumescing in the presence of oleaginous materials, diminution in luster is probably explainable upon the assumption of irregularity in expansion and contraction of the filament by virtue of the solvent or softener applied, resulting in a non-homogeneous surface. There is no doubt but what the luster is influenced and determined by the surface structure, filament fineness, and the transparency or arrangement and size of the cellulose particles, together with the existence, in some instances, of minute gas bubbles which are usually ellipsoidal, oval or ovate.

In the earlier phases of trade developments in the artificial filament art and up to comparatively recent processes of manufacture, but little attention was devoted to the specific modification of luster for particular fields of application, but the public taste has changed in the direction of a desire to "tone down" the glassy brightness to a tone simulating natural silk. When the great bulk of the output of artificial silk was used in the form of knitted fabric for underwear this distasteful appearance due to "super-luster" was not so conspicuous, but with application of large quantities in hosiery and glove manufacture, appearance became an important factor.

The methods evolved, processes patented and disclosures published having apparent meritorious features in connection with the general subject of modification of luster, have been collated herein under the four classifications "Preserving Luster," "Relustring," and "Increasing" and "Decreasing" the normal luster, the latter being subdivided into ten separate topics.

Increasing Luster. An excessive glossy shine may be imparted to any fabric by sustained friction, as evidenced by the shine acquired on the seat of our pants when we were lads and not lessened by sliding back and forth on the old horse-hair sofa, but there is a marked difference between luster intentionally imparted and a shine gained by resistance to motion when applied to textiles. All silk-like materials, whether the product of the intuitive cunning of the silkworm or the result of the intellectual strategy of man are more or less lustrous in appearance, but not always of the kind or degree desired. Therefore the introduction of glossing processes to overcome drabness in appearance, and deadening operations to attenuate the intensity in glow of over-brightness.

O. Knecht and E. Stocker have observed that esterified or etherified cotton of which the luster is diminished or removed[1] may again be rendered lustrous or even the original luster augmented, if the treated fibers are steamed, advantageously under pressure. It is immaterial whether the steaming operation be applied to the fibers in the loose state or while under tension, the strength of the fibers being unaltered by the treatment. C. Dreyfus[2] imparts luster to a thread or fabric composed in part at least of an organic derivative of cellulose, by submission to a smoothing treatment in the presence of moisture and at an elevated temperature which is controlled.

The luster of materials containing cellulose ethers or esters[3], which may have been wholly or partially delustered owing to the action of hot aqueous media, is increased or rendered more uniform by subjection to steam superheated 20° or more, preferably at super-atmosphere pressure.

L. Lilienfeld[4] imparts a silk-like luster on vegetable

1. U. S. P. 1856815. E. P. 295936; abst. J. S. C. I. 1929, **48**, 774-B; Chem. Zentr. 1929, I, 326.
2. U. S. P. 1860456; abst. C. A. 1932, **26**, 3938. Can. P. 300046.
3. British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 349980, Addn. to E. P. 332231; abst. Silk J. and Rayon World, 1931, **8**, #90, 62.
4. E. P. 357120. F. P. 719341, 719342; abst. C. A. 1932, **26**, 4185.

fibrous materials by coating with a cellulose ether or cellulosexanthic acid esters, rendering them more pliable and soft to the touch and increasing the luster or sheen. In the case of cellulose ethers where applied to cotton or other vegetable fiber, the latter is first shrunk by a concentrated alkali treatment (mercerized) and then coated with the cellulose ether, or preferably the etherized cellulose in solution is applied directly to the fiber before the alkaline treatment, the cellulose ethers, as well known, being highly resistant to highly concentrated alkali solutions. The process is illustrated by two of the 22 examples contained in the patent:

1. Cotton sateen is coated with an 8% solution of benzylcellulose in pure pyridine and dried at 40°. Then the coated and dried sateen is introduced into a 22.5% NaOH solution at 15°, where it remains for a few minutes, after which it is neutralized with 10% sulfuric acid at 16°, washed and dried.

2. Cotton sateen is coated with an 8% solution of methyl or ethyl cellulose xanthate and dried at 40°. It is then immersed in 50% NaOH solution at 15° for a few minutes, lifted, neutralized with 10% vitriol at 16°, washed and dried.

Materials containing cellulose ethers or esters are modified as to luster, weighted or rendered more resistant to ironing[1] by applying to them fine dispersions or colloidal solutions of white inorganic substances such as the oxides of aluminum, titanium, tin, silicon, zinc or cerium, barium carbonate, zinc sulfide, China clay or bentonite, as by bath, spraying or padding treatments, printing or stencilling. W. Taylor[2] modifies the luster by the application of a substance to the filaments in the course of their formation by the dry or evaporative method, and while they contain a substantial proportion of residual solvent. Improvement

1. C. Dreyfus, H. Platt, R. Parkinson and British Celanese, Ltd., E. P. 343121; abst. C. A. 1931, **25**, 5580.
2. Can. P. 322150.

in brightness in appearance should not be carried to the point where the filaments take on a dazzling appearance.

To avoid increasing the luster during finishing[1] fabrics containing delustered acetylcellulose are ironed or calendered either in the dry condition at around 100°, or first at below 100° until all moisture is removed, and then at or above that temperature. A firm handle and glossy appearance may be conferred upon filaments and fabrics or organic derivatives[2] by steeping in a cold solution of gelatin or casein, followed by treatment with formaldehyde. Yarns and fabrics manufactured so that they contain threads of normal and delustered cellulose acetate silk[3] are said to have special advantages in handle and appearance. Since the process of delustering (treatment with steam at 100°) decreases the affinity of acetylcellulose for basic dyes such as Capri blue, two-color effects may be obtained by suitably dyeing the manufactured products.

Preserving Luster. It has been found[4] that if a suitable organic solvent or gelling agent be incorporated in fibers of organic cellulose derivatives during some stage in manufacture, and then steamed under pressure for about a half hour, the resulting filaments retain their luster when boiled in a soap solution, as is usual. Advantage has been taken of this discovery by weaving or knitting fabrics from yarns of this character which have been treated with a luster-preserving agent together with untreated yarns, and then delustering by boiling the fabric with a soap solution, when it is only the untreated yarns in the fabric which lose their luster[5]. Alternatively, a fabric may be printed or stencilled with a luster-preserving agent, then steamed, and afterwards boiled with a soap solution; the printed

1. C. Dreyfus and C. Palmer, E. P. 295035; abst. C. A. 1929, **23**, 2046; J. S. C. I. 1930, **49**, 370-B.
2. British Celanese, Ltd., G. Langdon, A. Flower and S. Fulton, E. P. 358593; abst. J. S. C. I. 1932, **51**, 19-B; Chem. Zentr. 1932, I, 1024.
3. C. Palmer and S. Fulton, U. S. P. 1777445. E. P. 278116.
4. British Celanese, Ltd., and G. Ellis, E. P. 332187; abst. Chem. Zentr. 1931, II, 2677.
5. *Ibid.* E. P. 335583; abst. Chem. Zentr. 1931, II, 2677.

parts remain bright while the remainder of the fabric becomes dull. Suitable luster-preserving agents include resorcinol, hydroquinone, cresols, diacetone alcohol, *p*-toluenesulfonamide, diethyl tartrate and phthalimide which are relatively non-volatile, and also more volatile substances as phenol, glycol ethers and ethyl lactate.

The I. Budowski method of producing a restoring material[1] comprises grinding oleic acids of high molecular weight with the addition of an emulsifier as casein or saponnes, so that a mass is formed which is emulsifiable in water. Preserving luster may also be brought about by a partial rearrangement of the filaments toward a parallel relation under tension[2]. An improved resistance to the delustering action of hot aqueous media is obtained by employing solutions of cellulose ethers or esters containing proportions of an aliphatic alcohol other than methyl[3], resistance to delustering being increased as the proportion of alcohol is reduced below 5%, or as it is increased from 10-40%. It is advised to have the moisture content of the cellulose compound reduced under 1% before treatment. Although the process is applicable to wet or dry spinning, the latter is preferred, the spinning temperature being higher the larger the proportion of alcohol used.

It is possible to iron, press or calender without appreciably affecting the luster of fabric of cellulose derivatives by subjecting the fabric in a dry state to the action of a hot ironing surface *below* the fusion or sintering point of the cellulose compound[4]. Yarns and fabrics of cellulose ethers or esters have their luster increased or restored, or they are protected from the delustering effect of hot aque-

1. U. S. P. 1809470; abst. Chem. Zentr. 1931, II, 3416.
2. W. Sternberg, U. S. P. 1770047; abst. C. A. 1930, **24**, 4643; Chem. Zentr. 1930, II, 2331.
3. British Celanese, Ltd., E. P. 310045; abst. C. A. 1930, **24**, 25; Chem. Zentr. 1931, I, 1389. E. P. 310046; abst. Chem. Zentr. 930, II, 2722. C. Dreyfus and W. Whitehead, Can. P. 316423.
4. C. Palmer, Can. P. 312667.

ous media[1], by treating with dry or substantially dry steam at 20 lb. per sq. in., at a temperature of 137°.

In the treatment of fabrics containing cellulose ethers or esters[2], the luster may be revived if hot or boiling aqueous liquors are used, by adding to the liquor a sufficient quantity of certain salts to preserve the luster, transparency and appearance, suitable salts being 10-25% solutions of ammonium chloride or bromide, sodium chloride, sulfate or phosphate, magnesium chloride or sulfate, or calcium, barium, strontium or aluminum chlorides, which act as protective agents. It is recommended to stretch cellulose acetate yarn to increase its resistance to delustering in hot, aqueous liquors[3], after treatment with swelling agents has been carried out while the yarn is in the form of "sheet of warp," and after treatment with a swelling agent for an optimum period which varies with the agent used[4]. Ammonium chloride or other inorganic salt of neutral to acid reaction[5] may be used for checking the delustring tendency of substances such as hot aqueous solutions.

In the preservation of luster of cellulose acetate filaments and fabrics[6], the fabric is treated locally with substances as dyes and ester solvents (phenols, cresols, resorcinol, catechol, naphthols), which are mutually soluble with the acetylcellulose, followed by a delustring treatment with moist steam desired to produce variant effects on portions

1. British Celanese, Ltd., and G. Ellis, E. P. 332231; abst. C. A. 1931, **25**, 218; J. S. C. I. 1930, **49**, 944-B; Chem. Zentr. 1931, II, 2677. F. P. 686644; abst. C. A. 1931, **25**, 605; Chem. Zentr. 1931, I, 871. F. P. 37856, Addn. to F. P. 686644; abst. C. A. 1931, **25**, 4719.

2. H. Dreyfus, F. P. 601297; abst. Chem. Zentr. 1927, I, 1219. Can. P. 260319; abst. C. A. 1926, **20**, 3578; Chem. Zentr. 1926, II, 2367. Belg. P. 343504. C. Dreyfus, Ital. P. 265292.

3. British Celanese, Ltd., H. Dreyfus and W. Taylor, E. P. 277089; abst. J. S. C. I. 1927, **46**, 964-B.

4. *Ibid.* E. P. 371461; abst. J. S. C. I. 1932, **51**, 676-B. See E. P. 370430; abst. J. S. C. I. 1932, **51**, 638-B.

5. C. Palmer and S. Fulton, U. S. P. 1808061; abst. C. A. 1931, **25**, 4415. British Celanese, Ltd., C. Palmer and S. Fulton, E. P. 260312; abst. C. A. 1927, **21**, 3471; J. S. C. I. 1927, **46**, 9-B. H. Dreyfus, F. P. 617655; abst. Chem. Zentr. 1928, I, 3015. C. Palmer and S. Fulton, Can. P. 275737.

6. G. Ellis, U. S. P. 1826608; abst. C. A. 1932, **26**, 605; Chemicals, 1931, **36**, 11.

of the fabrics. The luster of cellulose derivatives may be conserved unimpaired and may still be heated to 100° in an aqueous solution[1], provided the solution contains certain salts in solution in an amount greater than a certain minimum, that minimum being for sodium sulfate, a 25% solution, sodium or magnesium chlorides, magnesium sulfate or calcium chloride 10%; sodium phosphate, potassium sulfate or potassium or barium chlorides, 20%; ammonium bromide or chloride, 10%; and aluminum chloride, potassium chromate, sodium sulfite or hydrosulfite, (each) 20%. It is recommended in the dyeing of mixtures of wool and cellulose acetate materials at high temperatures, with acid dyes[2], to add 15 gms. magnesium sulfate per liter dye liquor to preserve the luster of the acetylcellulose.

Delustring. This topic, subdivided under ten separately numbered classifications, aims at a substantially complete synopsis of the many properties which may have been proposed for modifying by subduing the normal luster obtained on both the cellulose ethers and esters. Formerly it was desired to impart the maximum of luster, shininess and glint to the filaments, but in recent years the edict of fashion has changed in this respect, and hence the need for applying treatments to modify the degree of inherent luster.

1. *Delustring with Pigments Before Spinning*[3]. The preparation of filaments or fabrics of methyl-, ethyl- or benzyl-cellulose having a subdued, reduced or modified lus-

1. Silver Springs Bleaching & Dyeing Co., Ltd., and A. Hall, E. P. 246879; abst. C. A. 1927, **21**, 502; J. S. C. I. 1926, **45**, 317-B. U. S. P. 1765581; abst. C. A. 1930, **24**, 4156; J. S. C. I. 1930, **49**, 763-B.

2. K. Wolfgang, Kunstseide, 1928, **10**, 117; abst. C. A. 1928, **22**, 4255; J. S. C. I. 1928, **47**, 744-B. See E. P. 246879. Can. P. 309130.

3. For data of an anticipatory nature as to early efforts at modifying luster, or use of materials which inadvertently reduce luster, most of them of a pigment nature, see: U. S. P. 394559, 569704, 646044, 689337, 724020, 724616, 826351, 834739, 842125, 863793, 879603, 883442, 912812, 960100, 1023295, 1036282, 1213115, 1217028, 1398525, 1404535, 1545144, 1602840, 1653962, 1692372, 1725742. E. P. 2210, 2211, 1886; 2570, 1889; 22022, 1897; 9577, 1899; 9087, 1900; 20398, 1901; 14483, 16604, 18022, 22525, 1903; 16583, 1905; 8045, 1906; 2998, 22371, 1907; 4956, 8742, 24809, 24811, 1908; 12687,

ter[1] is obtainable by incorporating in the solution before spinning, pigments or other insoluble inorganic particles of high covering power, such as 0.5-4% of finely divided titanium oxide (Titanox, titanium white). The pigment is first worked up to a paste by means of a small amount of water, and this gradually incorporated into the solution before spinning. After the addition of pigment, it is advisable to keep the solution under vacuum for a few hours to remove entrained air and dissolved oxygen. Titanium nitride, cyanonitride or phosphate have also been specified for this purpose[2].

H. Hands and Spicers, Ltd.[3], have described an invention particularly applicable to cellulose ethers, and suitable for filaments or for films for photographic supports, in which very finely divided cotton flock is admixed with titanium white and barium sulfate, being first ground in tetrachlorethane to a stiff paste, and then incorporated with the cellulose ether or ester in association with relatively small amounts of cedar oil and boiled linseed oil, acetone being recommended as the direct solvent.

Irrespective of the process employed or the pigment employed, it is of paramount importance that the latter be in such a fine state of subdivision and disaggregation

15306, 1909; 26928, 1910; 25245, 25534, 1911; 1378, 1599, 3042, 15080, 1912; 8283, 23196, 1913; 14675, 1914; 138641, 146367, 162759, 165164, 171125, 184449, 213931, 216307, 230187, 260312, 261046, 261047, 261099, 262741, 290263. F. P. 165349, 172208, 319217, 333835, 349885, 350723, 361319, 371447, 389284, 405430, 408370, 434602, 436087, 443621, 453652, 477493. D. R. P. 7117-Appl. V. 38368, 70999, 75896, 82111, 82112, 82555, 82653, Addn. to 62533, 117461, 125309, 137255, 137461, 152743, 159524, 182773, 200023, 231643, 243068, 248946, 255302, 257459, 262253, 262552, 311557, 397012, 402401, 403990, 460235. Aust. P. 4953, 37137. Aust. Hung. P. 31310. Belg. P. 68890, 76272, 144371, 184456, 191178, 207484, 247990, 255026. Holl. P. 18030. Hung. P. 132522. Ital. P. 17844. Span. P. 7849. Swiss P. 63587, 64683.

1. British Celanese, Ltd., R. Riley, R. Parkinson and H. Sims, E. P. 341897; abst. C. A. 1931, **25**, 5028; J. S. C. I. 1931, **50**, 391-B; Silk J. 1931, **7**, #64, 54; Chem. Zentr. 1932, I, 1600.

2. Native titanium oxide, Brookite, has been used as a pigment in celluloid manufacture, U. S. P. 1365882, as has Rutile and Octahedrite.

3. E. P. 282980; abst. J. S. C. I. 1928, **47**, 213-B; Chem. Zentr. 1928, I, 1824; Kunst. 1929, **19**, 138. D. R. P. 468743; abst. C. A. 1929, **23**, 781; Chem. Zentr. 1929, I, 340. F. P. 625165.

that it readily passes through the minute spinneret orifices without clogging. According to H. Dreyfus[1] who uses an ignited metallic salt as barium sulfate, zinc oxide or barium or zinc silicates, the particles are ground in the presence of a dispersing agent or protective colloid to a uniform diameter of 0.5-2.5 microns. The size of the particles depends, of course, upon the denier of filament spun, the smaller the denier, the finer must the particles be, and it must be assured that there is no agglomeration of separate particles into larger aggregates. J. Singmaster[2] who induces a subdued tone in artificial filaments by incorporation in the spinning solution of titanium oxide surrounded by a non-volatile oleaginous material such as heavy white petroleum oil, has fixed the safe particle size as less than 0.75 microns, and recommends before spinning to pass the solution containing the suspended particles through at least a portion of the usual filtering system in order to increase uniformity of dispersion and remove any flocculated portions that may have adhered.

In order to promote the separation and distribution of the inorganic particles throughout the mass material[3], it has been found advisable to use a distributing agent in making up the spinning mixture, castor oil, dibutyl phthalate and tricresyl phosphate being indicated for this purpose, especially the latter two by virtue of their solvent and softening action upon the cellulose ether or ester, zinc oxide, carbon black, barium sulfate, iron oxide or magnesium oxide being used. Unless it is proposed to obtain colored pigments, carbon black or iron oxide, of course, is contraindicated, the limits of pigment to be used being 0.1-1% of the mass, the latter amount being entirely too

1. E. P. 338490; abst. J. S. C. I. 1931, **50**, 109-B.
2. E. P. 342743; abst. C. A. 1931, **25**, 5559; Silk J. 1931, **8**, #85, 53. F. P. 680493; abst. C. A. 1930, **24**, 3902; Chem. Zentr. 1930, II, 656. E. P. 243350, 290693, 297364, 339603.
3. J. Singmaster, U. S. P. 1725742; abst. Chem. Zentr. 1929, II, 3261. E. P. 339603; abst. C. A. 1931, **25**, 2849; Chem. Zentr. 1931, I, 1699; Silk J. and Rayon World, 1931, **7**, #82, 54. F. P. 680492; abst. C. A. 1930, **24**, 3902; Chem. Zentr. 1930, II, 656. See E. P. 274054, 290263, 290693, 297364.

high. The use of sufficient barium sulfate results in obtaining a filament absolutely devoid of luster[1], but this salt has a very high specific gravity in comparison to its opacity or covering power, so that there is a well definable limit as to the quantity which may be advantageously used.

A mixture of barium and strontium sulfates or strontium sulfate alone[2], or barium sulfate and phosphate[3], or asbestos or asbestine[4] are some of the combinations which have been patented for subduing luster. As artificial silk in the non-textile form is sold by weight, the introduction of an inorganic pigment is also of interest from a pecuniary viewpoint. As applied to filaments of methyl-, ethyl- and benzyl-cellulose, H. Dreyfus incorporates with and in the spinning solution barium sulfate obtained by double decomposition, holding the pigment in suspension by the use of a solution of water-soluble methyl- or ethyl-cellulose or alkylated starch[5].

In the preparation of cellulose ether or ester solutions containing insoluble pigments[6], the latter may be dispersed either in the solvent or in a solution of cellulose derivative which may be the final solution, by passage at very high speed under high pressure through one or more narrow orifices advantageously having the form of slits. The pas-

1. J. Delpech and C. Heinrich, F. P. 679326; abst. C. A. 1930, **24**, 3911; Chem. Zentr. 1930, II, 843; Cellulose, 1930, **1**, #8, 223.

2. A. König, E. P. 350391; abst. Textile Mfr. 1931, **57**, #683, 420; Silk J. 1931, **8**, #91, 54. F. P. 677673; abst. Chem. Zentr. 1930, II, 3221. See E. P. 242240.

3. British Celanese, Ltd., W. Taylor, R. Roberts and L. Gregory, E. P. 334563; abst. C. A. 1931, **25**, 1084; J. S. C. I. 1930, **49**, 1063-B; Chem. Zentr. 1931, I, 1699. See E. P. 258874, 259899, 279504, 281084, 284798, 285941, 329659.

4. Wolff & Co., E. Czapek and R. Weingand, E. P. 274054; abst. J. S. C. I. 1928, **47**, 853-B; Chem. Zentr. 1927, II, 2248.

5. E. P. 338490; abst. C. A. 1931, **25**, 2567; Chem. Zentr. 1932, I, 1600; Chim. et ind. 1931, **25**, 955. F. P. 689800; abst. C. A. 1931, **25**, 1103; Chem. Zentr. 1931, I, 2286. See U. S. P. 1622368. Can. P. 321531. Compare E. P. 259899, 279502, 286761, 300894. F. P. 621316, 634165, Addn. 34391 to 634165, 636057, 636058, 642331, 643323, 644565, 644937.

6. Soc. pour la Fabrication de la Soie Rhodiaseta, E. P. 356740; abst. Silk J. 1932, **8**, #95, 50. F. P. 707330; abst. C. A. 1932, **26**, 843; Chem. Zentr. 1931, II, 2537.

sage may be repeated a number of times until the requisite degree of dispersion is attained. A quantitative study has been made of the relative opacity or light ray absorption of various pigments suitable for delustering purposes[1], and taking the effect produced by incorporating in a filament 0.5% of titanium dioxide as a standard, substantially the same effect is produced by the stated amount of other pigments: titanium dioxide 0.5, titanalba 0.5, titanox 1, zinc sulfide 1, fine texture lithopone 1.5, zirconalba 3, zirconium oxide 3, blanc fixe 4, alumina fume 4, and thorium oxide 3.

It is stated that it is possible to prepare under very economical conditions[2] spinning solutions weighted with barium sulfate and capable of being filtered and spun without difficulty by dry-spinning, by preparing the solutions with cellulose acetate which has been precipitated from its acetylation mixture, whether diluted or not, in which the barium sulfate has been formed by chemical reaction, the secondary products of reaction being eliminated by washing and drying of the cellulose acetate in the usual manner before it is dissolved in condition to be spun. It must be remembered, however, that if acid is eliminaed as the result of the double decomposition leading to the formation of the $BaSO_4$, this may materially affect the process of partial hydration of the acetylated cellulose.

2. *Pigment Addition After Spinning.* The addition of delustring components in solid form to the already formed filament or to yarns and textiles formed therefrom, depends for its efficiency not only upon the particle size of the individual entity which is sought to be imbedded in the filamentous substance, but also to the degree of porosity, capillarity or absorptive power of the filament at the moment of contacting with the insoluble and hence more or less repellent particle, and hence in these processes which mostly involve some form of double decomposition, it is

1. J. Singmaster, U. S. P. 1875894.
2. Soc. Chim. des Usines du Rhone, E. P. 294623; abst. C. A. 1929, **23**, 2034; J. S. C. I. 1929, **48**, 596-B; Chem. Zentr. 1928, II, 2206. F. P. 623448; abst. C. A. 1929, **23**, 278.

advantageous to place the filament in the maximum receptive condition as by a swelling or colloiding treatment. Considerable thought has been expended and ingenuity brought to bear in evolving suitable methods for this class of impregnation processes resulting in diminution of luster in cellulose silks.

H. Dreyfus first impregnates the fiber with an alkali metal zincate as sodium or potassium zincate, and then treats the fiber with an aqueous solution of a salt which gives a white precipitate with the zinc salt as sodium carbonate, phosphate or oxalate, resulting in the formation of zinc carbonate, phosphate or oxalate, all white and insoluble in water[1]. The luster of artificial filaments of organic cellulose derivatives is lowered by adding a solution of borax or boric acid and a fat or free fatty acid in the presence of solvent penetrants as mono- or poly-hydroxy alcohols, inversion sugar, naphthene or terpenes. This treatment is said to also increase the elasticity of the fibers and to impart a superior feel and more uniform dyeing properties[2]. Cellulose artificial fibers may be permanently delustered[3] by immersion for about 15 min. in a hot, very dilute, aqueous solution of colloidal titanium tetrahydroxide, optionally followed by a soaping treatment. Solutions containing 0.001-0.4% titanium dioxide are claimed as suitable.

The H. Gardner method employing titanium is to impregnate with a solution of a titanium salt[4], and subsequently decompose the salt *in situ* so as to deposit insoluble white titanium compound within the material. Titanium sulfate or titanium potassium oxalate are suitable water-

1. Can. P. 293067.
2. Fabrique de Soie Artificielle de Tomaszow Soc. Anon., E. P. 357112; abst. Silk J. 1932, **8**, #95, 50. F. P. 690795; abst. C. A. 1931, **25**, 1380; Chem. Zentr. 1931, I, 1699.
3. R. Speitel and M. Schenk, E. P. 371239; abst. J. S. C. I. 1932, **51**, 597-B. F. P. 720038; abst. C. A. 1932, **26**, 3937.
4. U. S. P. 1692372; abst. C. A. 1929, **23**, 719; J. S. C. I. 1929, **48**, 169-B. E. P. 290263; abst. J. S. C. I. 1929, **48**, 430-B. Chem. Zentr. 1928, II, 1407. F. P. 647013; abst. C. A. 1929, **23**, 2582. D. R. P. 531079; abst. C. A. 1931, **25**, 5580.

soluble impregnates. An invention relating to the delustering of cellulose ethers and esters lays its claim to originality upon the fact that these compounds are susceptible of directly absorbing colloidal solutions when in the swollen condition, the oxides of aluminum, titanium, tin, tungsten, silicon, zinc, lead, uranium and cerium, barium carbonate or sulfate, zinc sulfide, kaolin or bentonite being directly applicable when in a colloidal condition in a dispersion medium[1].

It is claimed that practically permanently subdued luster may be conferred upon a cellulose ether or ester[2] by taking advantage of the solvent and swelling action of zinc chloride in aqueous solution, and after penetration of the zinc in the filament substance, rendering it insoluble by precipitation as the sulfide by treatment with a solution containing sulfide ions. Other suitable swelling agents are formic or acetic acids or acetone. Cellulose ethers, or cellulose esters, after peripheral saponification in filament form may be delustered by impregnating them with water soluble calcium, strontium or barium chlorides or nitrates, and then treatment with a water-soluble sulfate or phosphate to precipitate the corresponding sulfates or phosphates[3]. Or[4], the filaments may be immersed in a cold clear solution of magnesium silicofluoride, which is then gradually heated to 70-90°, whereby silicic acid separates and is deposited within the silk. Alternatively, similar deposition of silicic acid is secured by addition of this salt to the spinning solution. The delustering is fast to soaping at 50-60°, but not to bleaching with hypochlorites.

1. H. Dreyfus, F. P. 703626; abst. C. A. 1931, **25**, 4402.
2. C. Dreyfus and H. Platt, U. S. P. 1756941; abst. C. A. 1930, **24**, 3384; Chem. Zentr. 1930, II, 654; J. S. C. I. 1931, **50**, 17-B. British Celanese, Ltd., E. P. 344093; abst. C. A. 1932, **26**, 319; J. S. C. I. 1931, **50**, 438-B; Silk J. and Rayon World, **8**, #85, 54. C. Dreyfus and H. Platt, Can. P. 324627.
3. C. Dreyfus, F. P. 681060; abst. C. A. 1930, **24**, 4340; Chem. Zentr. 1931, I, 872.
4. C. Zahn, U. S. P. 1845107; abst. C. A. 1932, **26**, 2329. N. V. J. A. Carp's Garenfabr., E. P. 337418; abst. J. S. C. I. 1931, **50**, 243-B; Chem. Zentr. 1931, I, 871. F. P. 679744; abst. C. A. 1930, **24**, 3902. Holl. P. 23648; abst. C. A. 1931, **25**, 3498.

W. Lorimer[1] obtains barium sulfate by precipitation by taking alum and soaking the filaments therein and then immerses in a barium chloride solution until the effect desired has been obtained. C. Dreyfus[2] fabricates artificial straw, ribbons and similar filament aggregates by the union of a plurality of finer filaments with the aid of a solvent of restricted power, and during the manufacture a finely divided filling material as titanium dioxide is incorporated while the filaments are in a swollen and receptive state. The dull-lustring of artificial filaments in any form has been described by R. Clavel[3], who first treats the filaments with alkali metal phosphates and then with water-soluble heavy metal salts, resulting in the precipitation of the corresponding phosphate. C. Baillod[4] proceeds similarly, but the final material deposited is white cadmium sulfide.

The combination of a white pigment with a slightly alkaline latex dispersion constitutes the essence of another patented method[5]. Permanent matt effects are said to be producible upon fabrics comprising organic cellulose derivatives[6] by delustering the fabric and then applying a paste containing cellulose nitrate, a softening agent, zinc oxide and a solvent for the cellulose nitrate which is not a solvent of the filaments constituting the fabric.

A novel method has been evolved by H. Dreyfus for the treatment of filaments and fabrics of cellulose ethers and esters[7], based upon the utilization of a class of organic

1. U. S. P. 1839978; abst. C. A. 1932, **26**, 1455; Chem. Zentr. 1932, I, 1846. See U. S. P. 1839979.
2. F. P. 715184; abst. C. A. 1932, **26**, 1784; Chem. Zentr. 1932, I, 2256.
3. U. S. P. 1845037; abst. C. A. 1932, **26**, 2329. E. P. 300894; abst. J. S. C. I. 1929, **48**, 811-B. F. P. 648508; abst. Chem. Zentr. 1929, I, 1634. Can. P. 291658.
4. E. P. 348094; abst. Silk J. 1931, **8**, #89, 54. Swiss P. 141270; abst. Chem. Zentr. 1931, I, 2824.
5. C. Dreyfus, G. Miles and H. Platt, U. S. P. 1870407. Can. P. 324629.
6. C. Dreyfus and W. Blume, Can. P. 324412.
7. E. P. 343949; abst. C. A. 1931, **25**, 4719; J. S. C. I. 1931, **50**, 486-B. F. P. 702210; abst. Chem. Zentr. 1932, I, 1463.

compounds in which a metal other than an alkali metal is directly united to carbon, or in which such a metal replaces the hydrogen of a hydroxyl group and also the organic esters of metallic acids, but excluding metal carboxylates and sulfonates. The metallic organic compounds may be introduced into spinning solutions or after the fibers have been formed. Members of this group include methyl, ethyl, phenyl and similar compounds as zinc diethyl, lead tetraethyl (exceedingly toxic), or similar organic compounds. Especially advantageous have been found metal alcoholates or phenolates such as zinc and aluminum ethylates, aluminum *iso*propylate, butylate, phenolate or *o*-cresolate, or tetraethyl titanate. Compounds containing two or more of the above groupings may also be used, such as methyl zinc methylate (or ethylate) or ethyl zinc methylate (or ethylate). These compounds may be used in the dissolved form, either in the spinning solution, or by direct contact with the filaments after formation, the latter having been rendered more porous and receptive by a previous treatment with alcohols or hydrocarbons. Tetraethyl titanate is soluble in benzene, and the solution mixed with an acetone solution of the cellulose derivative, containing water, titanium being precipitated in the form of titanic acid. It is especially applicable to the delustring of methyl-, ethyl- and benzyl-cellulose.

3. *Addition of Oils, Hydrocarbons, Waxes and Soaps.* Dull cellulose ether fibers or acetylcellulose filaments may be made in a similar manner to those produced from viscose, by adding mineral oil or petroleum jelly (vaseline)[1] preferably emulsified with cyclohexanol, lanolin[2], purified wool fat in benzene, acetone, benzine, turpentine or pine oil in the form of an emulsion[3], unsaponifiable oil or diffi-

1. W. Stokes, U. S. P. 1823769. Courtaulds, Ltd., W. Glover and G. Heaven, E. P. 273386; abst. Chem. Zentr. 1927, II, 2035. W. Stokes and Courtaulds, Ltd., E. P. 290693; abst. Chem. Zentr. 1928, II, 1282. Courtaulds, Ltd., and J. Taylor, E. P. 294805; abst. Silk J. 1927, **5**, #54, 90; Chem. Zentr. 1928, II, 2205.

2. Breda-Visada, Ltd., and R. Jones, E. P. 348743; abst. Textile Mfr. 1931, **57**, #682, 380; Silk J. 1931, **8**, #89, 56.

3. A. Lely, E. P. 370512; abst. J. S. C. I. 1932, **51**, 595-B.

cultly saponifiable wax[1], or by impregnation with a solution of carnauba, montan or candelilla wax or beeswax[2], in solution in an organic solvent which is afterwards removed by evaporation.

H. Gardner[3] has described subdued luster filaments obtained by combining a cellulose ether or ester with a relatively small proportion of a synthetic resin of the *p*-toluenesulfonamide-aldehyde type, in association with an inorganic pigment as titanium oxide, while Borvisk Syndicate, Ltd.[4], induces a matt appearance on artificial silk by a combination of oils as olive or castor with a hydrogenated hydrocarbon as tetrahydronaphthalene. Paraffin-proteid emulsion[5], high boiling carbocyclic hydrocarbons[6], mineral, animal and vegetable oils in the presence of aniline, tetrahydronaphthalene, or nitrobenzene[7], or paraffin, wax or spermaceti homogenized with the cellulose ether or cellulose carboxylic ester solution at a temperature above the melting point of the wax, the homogenized solution maintained at that temperature until it passes through the spinning jet[8], are some of the other processes which have been accorded patent protection.

When dry-spinning in acetone[9], the introduction of 1% arachis oil before filament formation followed by treatment of the fibers with a hot soap solution, is said to induce an opacifying effect which may be modified within

1. N. V. Hollandsche Kunstzijde Industrie, E. P. 348910; abst. Textile Mfr. 1931, **57**, #682, 381; Chem. Zentr. 1931, II, 1788.
2. J. Hirschberger, U. S. P. 1819241; abst. J. S. C. I. 1932, **51**, 503-B; Chem. Zentr. 1931, II, 2950; Silk J. 1932, **8**, #97, 45.
3. U. S. P. 1768401; abst. C. A. 1930, **24**, 4392; Chem. Zentr. 1930, II, 2333. U. S. P. 1864426, 1864428. E. P. 290263; abst. C. A. 1929, **23**, 719. See U. S. P. 1564664.
4. E. P. 273647; abst. Chem. Zentr. 1927, II, 2025.
5. Kirklees, Ltd., A. Bennet and W. Tong, E. P. 355015; abst. Textile Mfr. 1932, **51**, #686, 77; Silk J. 1932, **8**, #94, 53; Chem. Zentr. 1932, I, 1736.
6. J. Bourgeois, E. Nieuviarts and C. de Clercq, F. P. 434602.
7. E. Heymann, F. P. 637309; abst. C. A. 1929, **23**, 513; Chem. Zentr. 1928, II, 205.
8. Courtaulds, Ltd., and C. Diamond, E. P. 360626; abst. Chem. Zentr. 1932, I, 1736.
9. *Ibid.* E. P. 338269; abst. C. A. 1931, **25**, 2305; Chem. Zentr. 1931, I, 1699; J. S. C. I. 1931, **50**, 110-B.

wide limits. Turkey red oil has been suggested[1], but it is water-soluble. Carnauba wax emulsions induce a dull luster effect on artificial filaments by virtue of the fact that upon evaporation they leave a rough and hence a non-glossy surface, but the use of a heavy organic solvent with the wax is said to obviate this undesirable tendency to roughness[2].

The formation of tin, aluminum, iron, chromium, bismuth, zinc or antimony oleates, palmitates or stearates (insoluble metallic soaps)[3], the fibers being preliminarily or conjointly treated with specified swelling agents as glycollic or lactic acids, ethyl alcohol, acetone, diacetone alcohol, diacetin, phenol, hydroquinone, urea, urethanes, thiourethanes or guanidine, is the manipulative process of British Celanese, Ltd., and G. Ellis. The H. Dreyfus procedure is similar[4]. O. Muller combines treatment of the filaments with an emulsion containing paraffin, soap, glue and an abrasive material as chalk, kaolin, zinc oxide and fuller's earth[5].

4. *Delustring With Organic Compounds.* A number of processes have been exploited for producing a subdued effect upon cellulose ether and ester filaments and textiles have been advocated, many of them depending upon differential solubility characteristics, in which at some stage of the evaporative process the introduced solvent either liquid or solid either is thrown out of solution, incipiently precipitates the cellulose compound, crystallizes or other-

1. British Celanese, Ltd., and W. Taylor, E. P. 333504; abst. J. S. C. I. 1930, **49**, 986-B; Rayon Record, 1930, **4**, 1062.

2. J. Meyer, Rayon, 1929, **10**, #2, 19, 24, 40; abst. C. A. 1930, **24**, 2598.

3. British Celanese, Ltd., and G. Ellis, E. P. 323501; abst. C. A. 1930, **24**, 3119; J. S. C. I. 1930, **49**, 281-B; Chem. Zentr. 1930, II, 1140.

4. F. P. 677263; abst. C. A. 1930, **24**, 3119; Chem. Zentr. 1931, I, 871.

5. U. S. P. 1705490; abst. J. S. C. I. 1929, **48**, 640-B; Chem. Zentr. 1929, II, 511. U. S. P. 1769850; abst. J. S. C. I. 1931, **50**, 346-B; Chem. Zentr. 1930, II, 2331. Nyanza Colour & Chemical Co., Inc., E. P. 315432. E. P. 360876; abst. Silk J. 1932, **8**, #97, 55.

wise changes its form or reaction in order to induce opacity in the fiber with which it has been associated.

In one method[1] delustering is accomplished in a very simple and technically easily workable method by applying to or printing on a paste comprising urea or a urea derivative and a thickening agent as tragacanth, drying, and steaming for 5-10 min. A beautiful milky matt effect is said to be produced on a glossy ground. Or carbonic acid dianilids, or dialkylanilids as diethyl-*o*-tolyl urea may be used[2], the amide being dissolved away in the spinning bath or other treating liquid. White or colored matt effects on cellulose ethers or esters are also obtainable by printing on the yarn or fabric a paste or thickened solution containing glycollic acid or sodium glycollate[3], or lactic acid or sodium lactate, either as such or accompanied by urea or a ureide.

The cellulose derivative filaments may be treated with aqueous suspensions of aliphatic esters as ethyl oxalate[4], and then with ammonia, whereby oxamide is formed within the material, thus reducing the luster and imparting a scroop handle. The delustring is fast to soaping, and it is alleged the process may readily be adapted for dyeing or printing methods. Substituting aniline for ammonia, oxanilid results. H. Dreyfus[5] incorporates in cellulose ether or ester filaments or in fabrics prepared therefrom,

1. I. G. Farbenindustrie, A.-G., E. P. 309194; abst. J. S. C. I. 1930, **49**, 859-B. F. P. 672217; abst. C. A. 1930, **24**, 2291. D. R. P. 512399; abst. C. A. 1931, **25**, 1393.

2. *Ibid.* E. P. 345405; abst. C. A. 1932, **26**, 306. F. P. 37800, Addn. to F. P. 669686; abst. Chem. Zentr. 1931, I, 2557.

3. *Ibid.* E. P. 345673, Addn. to E. P. 309194; abst. C. A. 1932, **26**, 2067; J. S. C. I. 1931, **50**, 534-B; Textile Mfr. 1931, **57**, #680, 304; Silk J. 1931, **8**, #87, 54. F. P. 39168, Addn. to F. P. 672217; abst. C. A. 1932, **26**, 2329. A. Baumert and R. Fischer, D. R. P. 519983; abst. Chem. Zentr. 1931, II, 777.

4. Silver Springs Bleaching & Dyeing Co., Ltd., and A. Hall, E. P. 316638; abst. C. A. 1930, **24**, 1992; J. S. C. I. 1929, **48**, 938-B; Chem. Zentr. 1930, I, 777; Silk J. 1929, **6**, #66, 70.

5. E. P. 346678; abst. C. A. 1932, **26**, 2055; J. S. C. I. 1931, **50**, 715-B; Chem. Zentr. 1932, I, 1463; Silk J. 1931, **8**, #88, 54. F. P. 702174; abst. C. A. 1931, **25**, 4125; Chem. Zentr. 1931, II, 3419. Cf. F. P. 686330, 688625. C. Dreyfus, Can. P. 323604.

organic substances in quantity greater than is soluble in the base, being preferably insoluble in water or relatively so, including dilute acids or alkalis or reagents with which the materials are liable to be treated in commercial practice. He has demonstrated that best results are to be had by means of organic substances of melting point above about 240°, such as *sym-a*-dinaphthyl urea, *b*-tetranaphthyl urea, *b*-dinaphthyloxamide, acetylbenzidine, dibenzoylbenzidine, diacetyltolidine, carbobenzidine, thiocarbobenzidine, 4.4′-dithioureidobiphenyl, succinic-*a*-naphthalide, *p*-nitrophenylphthalimide, anthraquinone, 2.6-dichloranthraquinone, acenaphthenequinone, or substances of lower melting point as anthracene, carbazole, phenanthrene, *sym-a*-dinaphthyl thiourea, and diphenyloxamide.

It is preferred to incorporate these bodies in the spinning solution, and the method of incorporation is an important feature, being particularly important for incorporation with acetone solutions of the cellulose derivatives, for, although insoluble in acetone, they are held in the spinning solution in a high state of subdivision. They are all said to be suitable for association with methyl-, ethyl- or benzylcellulose solutions for filament formation in order to impart a subdued, reduced or modified luster.

A. Hall treats the filaments with a suspension or solution of anthraquinone[1], and then oxidizes the absorbed anthraquinone with hydrogen dioxide, the original leuco compound producing a dull effect. The anthraquinone must be introduced into the spinning solution or brought into contact with the artificial fibers in the unoxidized condition. An analogous effect is said to be introduced by saturating the fibers with phenol or a phenolic body as the cresols or xylenols, resorcinol or monochlorphenol[2]. Similar chemi-

1. E. P. 316169; abst. C. A. 1930, **24**, 1750; J. S. C. I. 1929, **48**, 938-B; Silk J. 1929, **6**, #66, 68.

2. British Celanese, Ltd., G. Ellis and R. Storey, E. P. 358574; abst. J. S. C. I. 1932, **51**, 19-B; Chem. Zentr. 1932, I, 763; Textile Mfr. 1932, **58**, #687, 119; Silk J. 1932, **8**, #96, 49. F. P. 717449. See F. P. 623554.

cally to monochlorphenol is the treatment with mono- or di-chlorbenzene or -xylene and hydrogenated naphthalenes as unfolded by G. Bonwitt[1], who also uses with filaments of alkyl-, aryl- and aralkyl-cellulose, monochlorbenzene, xylene and high boiling mineral oils[2]. Especially applicable are mono- and di-chlorbenzene when in a very fine state of colloidal suspension[3], the largest allowable diameter of the particles ranging from 6.9 microns where 6 denier elemental fibers are to be spun, to 0.8 micron for 1 denier.

Delustered threads also result when there is incorporated in the spinning solution or the formed threads are treated with a compound of a hydroxylamine with a fatty acid as hydroxyethyl oleate[4], the product being afterwards treated with hot soap solution, or when a monohydric aliphatic ester of a higher fatty acid as amyl stearate[5], an organic acid ester of a saccharide soluble in organic solvents as glucose penta-acetate[6], or the above in association with a small proportion of titanium dioxide[7] is employed, all being afterwards treated with a soap solution at or near the boiling point.

A chlorinated aliphatic hydrocarbon with soluble protective colloids as agar agar, gelatin or acacia[8], mono- or di-chlorbenzene suitably homogenized[9], water-insoluble

1. E. P. 285066; abst. Chem. Zentr. 1928, II, 2523; J. S. C. I. 1929, **48**, 203-B; Kunst. 1929, **19**, 162.
2. E. P. 285863; abst. Chem. Zentr. 1929, I, 327; Silk J. 1928, **5**, #49, 78.
3. G. Bonwitt, E. P. 288222; abst. J. S. C. I. 1929, **48**, 353-B. See E. P. 285066.
4. Courtaulds, Ltd., and C. Diamond, E. P. 356299; abst. J. S. C. I. 1931, **50**, 1044-B; abst. Chem. Zentr. 1932, I, 1736; Textile Mfr. 1932, **58**, #686, 79; Silk J. 1932, **8**, #94, 54.
5. *Ibid.* E. P. 352412; abst. J. S. C. I. 1931, **50**, 878-B; Chem. Zentr. 1932, I, 1736; Textile Mfr. 1931, **57**, #684, 450.
6. *Ibid.* E. P. 352610 (Patent opposed); abst. J. S. C. I. 1931, **50**, 878-B; Chem. Zentr. 1932, I, 1736. Addn. E. P. 338269.
7. *Ibid.* E. P. 352611 (Patent opposed); abst. J. S. C. I. 1931, **50**, 878-B; Chem. Zentr. 1932, I, 1736. Addn. E. P. 338269.
8. Lustrafil, Ltd., and S. Barker, E. P. 349658; abst. Textile Mfr. 1931, **57**, #682, 383; Chem. Zentr. 1932, I, 161.
9. T. Koch, U. S. P. 1748014; abst. Chem. Zentr. 1931, I, 1699. U. S. P. 1781018; abst. Chem. Zentr. 1931, II, 1791. G. Bonwitt, F. P. 640644; abst. Chem. Zentr. 1928, II, 2523. F. P. 34041, Addn.

terpenes or terpene alcohols emulsified by the presence of sulfonated castor oil[1], and a small proportion of caramel or caramel-containing material[2], have been described as efficient for imparting that desirable quiet gloss to synthetic filaments. Treatment with sodium phenolate or aniline hydrochloride followed by hot dilute inorganic acid or alkali, according as the delustering agent is acidic or basic, to decompose the salt and set free the delustering component[3], or difficultly hydrolyzable esters of a hydrogenated phenol and a mono- or poly-carboxylic acid as methylcyclohexanol cinnamate, methyl adipate, oleate, stearate or palmitate, alone or in company with an emulsifying agent, are indicative of other bodies which induce diminished luster when applied to cellulose ether or ester filaments or fabrics[4].

Casein or albumen corneated by a subsequent application with aqueous barium hydroxide[5], ethanolamines as triethanolamine[6], incorporation of caoutchouc latex[7], and the addition of softer resins (copal, Manila, congo, kauri, Alberto) and certain synthetic resins and phenolic-aldehyde condensates having a softening or melting point above 200°[8], have also been advocated. The addition of a solvent or gelling agent as resorcinol, hydroquinone, cresols,

to F. P. 640644; abst. Chem. Zentr. 1929, II, 2130. Can. P. 280291. N.-V. Algemeene Kunstzijde Unie., Holl. P. 24570; abst. C. A. 1932, **26**, 1440.

1. N.-V. Hollandsche Kunstzijde Industrie, E. P. 356749; abst. Textile Mfr. 1932, **51**, #686, 80. F. P. 693411; abst. C. A. 1931, **25**, 1672.

2. *Ibid.* E. P. 219898; abst. Chem. Zentr. 1924, II, 2715.

3. Calico Printers' Assoc., Ltd., and J. Whinfield, E. P. 275357; abst. C. A. 1928, **22**, 2279; J. S. C. I. 1927, **46**, 776-B; Chem. Zentr. 1927, II, 2574.

4. Breda-Visada, Ltd., H. Sagar, E. Weyenbergh and R. Jones, E. P. 344288; abst. C. A. 1932, **26**, 305. F. P. 714124; abst. C. A. 1932, **26**, 1784.

5. B. Borzykowski, E. P. 292627, Addn. to E. P. 273647; abst. Silk J. 1928, **5**, #53, 108; Chem. Zentr. 1928, II, 1406. F. P. 35451, Addn. to F. P. 636090; abst. C. A. 1930, **24**, 3901.

6. British Celanese, Ltd., E. P. 355466; abst. J. S. C. I. 1931, **50**, 1008-B; Textile Mfr. 1932, **51**, #686, 78; Silk J. 1932, **8**, #94, 53.

7. J. Stockley and E. Witte, U. S. P. 1875185.

8. H. Dreyfus, E. P. 346793; abst. J. S. C. I. 1931, **50**, 799-B. Can. P. 315360. See E. P. 346678.

aniline, diacetone alcohol, diacetin, *p*-toluene (or -xylene) sulfonamide and their methyl or ethyl derivatives, diethyl tartrate, phenol, ethyl lactate, acetic acid or acetone[1] are some of the compounds which have been recommended as desirable additions to the cellulose ethers and esters to attenuate their normal luster. With the above, an after treatment with dry steam is said to enhance the luster-diminishing effect.

A process has been amplified[2] for treating knitted fabrics composed of or containing cellulose derivatives in which a shrinking agent as nitric acid is applied, which reduces tendency of the fabric to develop faults such as laddering, running or splitting, and incidentally reduces the luster to some extent. The incorporation with the fibers of solid bodies such as rice starch added in the form of a cold emulsion[3], ground cellulose[4] or finely divided cotton flock or other fibrous materials of high divisibility[5], induces reduced luster when attached to or imbedded in cellulose ether or ester filaments or filament aggregates.

H. Altwegg and A. Eichler[6] have disclosed manipulative details for producing delustered threads which involve spinning a cellulose derivative solution having a substance of the anhydride-acid type dissolved therein to form a thread of normal luster, and then subjecting the finished lustrous thread to a solution of a substance which reacts with the first named substance to form an insoluble, opaque compound.

5. *Solvent Delustring.* Many of the liquids and solids

1. British Celanese, Ltd., and G. Ellis, E. P. 332187, 332231; abst. C. A. 1931, **25**, 205; J. S. C. I. 1930, **49**, 944-B; Chem. Zentr. 1931, II, 2677. H. Dreyfus, F. P. 686644, Addn. F. P. 37856; abst. C. A. 1931, **25**, 605, 4719. See E. P. 269605, 277089.

2. British Celanese, Ltd., E. P. 335139; abst. C. A. 1931, **25**, 1393; J. S. C. I. 1930, **49**, 1105-B; Chem. Zentr. 1931, II, 1787.

3. Lustrafil, Ltd., and S. Barker, E. P. 347396; abst. J. S. C. I. 1931, **50**, 799-B; Chem. Zentr. 1932, I, 161.

4. F. Nonamaker, U. S. P. 1822416; abst. J. S. C. I. 1932, **51**, 675-B; Silk J. 1932, **8**, #97, 45; Chem. Zentr. 1931, II, 3178.

5. H. Dreyfus, E. P. 344510; abst. C. A. 1932, **26**, 306; Silk J. 1931, **8**, #86, 54.

6. Can. P. 322075.

mentioned in the topic preceding may be regarded as solvents, in that they exert a swelling and colloiding action in affiliation with other solvents. By creating at the region of the spinning jets an atmosphere laden with solvent vapors[1], particularly for the purpose of obtaining non-scintillating filaments and withdrawing the solvent-laden atmosphere by suitably located heating means from the lower part of the cell and delivered to the region of the spinning jets, fibers of attenuated luster are formed.

By applying to a textile material containing an organic cellulose derivative a mixture containing a solvent and a non-solvent for the cellulose compound[2], the non-solvent portion being of considerably higher boiling point and hence lower speed of evaporation, the mixture as a whole is not a solvent, as the filament or fabric dries after treatment, a subdued appearance being observable. A mixture of acetone 80-95% and xylene 20-5% applied to cellulose ether or ester filament aggregates[3] causes the individual filaments to coalesce and to be reduced in luster. A mixture of acetone 70 and xylene 30 is also claimed as efficient[4].

The delustring of threads, films and fabrics made of or containing cellulose ethers or esters[5] is carried on in one process by treating the material at 40-80° in an aqueous emulsion of organic substances which swell or dissolve it, but which are substantially insoluble in water. Such substances include cyclohexanone, cyclohexanol, di- and triacetin, methyl phthalate, amyl acetate, ethyl benzoate, anisole, nitrobenzene, ethyl acetoacetate, benzyl alcohol, phene-

1. Chatillon Soc. Anon. Italiana per la Seta Artificiale and E. Orioli, E. P. 344385; abst. J. S. C. I. 1931, **50**, 582-B.
2. C. Dreyfus and W. Whitehead, Can. P. 324632.
3. British Celanese, Ltd., E. P. 364020; abst. J. S. C. I. 1932, **51**, 258-B.
4. *Ibid.* E. P. 363426; abst. J. S. C. I. 1932, **51**, 258-B; Textile Mfr. 1932, **58**, 247; Silk J. 1932, **9**, #96, 45; Rayon and Synthetic Yarn J. 1932, **13**, #7, 24. C. Dreyfus, F. P. 703002; abst. C. A. 1931, **25**, 4415; Chem. Zentr. 1932, I, 470.
5. Soc. pour la Fabrication de la Soie Rhodiaseta, E. P. 313072; abst. C. A. 1930, **24**, 977; J. S. C. I. 1930, **49**, 1107-B; Silk J. 1929, **6**, #64, 68. F. P. 655435; abst. C. A. 1929, **23**, 4071.

tole, nitroanisols, nitrophenetols, guaiacol, benzaldehyde or salicylic aldehyde, the concentration not exceeding 10%.

According to the S. Dunlop disclosure[1], artificial silk of reduced luster is obtained by extruding a solution of a cellulose ether or ester in a volatile solvent into a spinning cell in which a current of air or gas is set up by mechanical means inside the spinning cell, and directed in the vicinity of the spinning nozzle obliquely to the issuing filaments so they are exposed to unequal lateral pressures. These disturbances in evaporation of the solvent result in solidified filaments the outer surfaces of which display two or more re-entrant surfaces. Such filaments are less lustrous than those with a dumb-bell cross-section which result when evaporation of solvent proceeds normally[2].

6. *Water or Steam Delustring.* W. Taylor and British Celanese, Ltd.[3], apply a luster-modifying liquid to filaments of organic cellulose derivatives while they still contain a relatively large proportion of solvent, hot water, benzine and paraffin reducing the luster, and toluene and xylene increasing it if properly applied. A silk having a dull finish may be made from ether-cellulose or ester-cellulose by carrying out the dry or evaporative process in the presence of steam[4], by passing steam into the spinning chamber or leading the thread not completely freed from solvent, into a chamber containing steam. A little water may be added to the spinning solution with benefit. Filaments may also be partially delustered by treatment with moist steam or hot water or aqueous alcohol[5], wetting

1. E. P. 359385; abst. Textile Mfr. 1932, **58**, #688, 162.

2. Courtaulds, Ltd., and C. Diamond, E. P. 365178; abst. J. S. C. I. 1932, **51**, 336-B; Textile Mfr. 1932, **58**, #691, 287. Can. P. 308126.

3. E. P. 327740; abst. C. A. 1930, **24**, 5169; Chem. Zentr. 1930, II, 1305. H. Dreyfus, F. P. 681806; abst. C. A. 1930, **24**, 4391; Chem. Zentr. 1930, II, 3666.

4. N.-V. Nederlandsche Kunstzijdefabriek, F. P. 640446; abst. C. A. 1929, **23**, 982; Kunst. 1929, **19**, 163; Chem. Zentr. 1928, II, 2523. Algemeene Kunstzijde Unie, D. R. P. 514400; abst. C. A. 1931, **25**, 1673; Chem. Zentr. 1931, I, 1203.

5. British Celanese, Ltd., and W. Taylor, E. P. 333504; abst. C. A. 1931, **25**, 592; Chem. Zentr. 1931, I, 1858.

agents being incorporated with the spinning solution before extrusion in order to increase the moisture capacity of the filaments towards the water-obtaining mixture.

Fabrics composed of cellulose ethers or esters are delustered by the action of wet steam[1], then treated uniformly or locally with a paste containing a water-insoluble thickening agent as nitrocellulose, an effect material as zinc oxide or barium sulfate, together with a dye and plasticizer if desired, including also a solvent for the thickening agent which is a non-solvent of the cellulose derivative. The S. Vles process for delustring cellulose derivatives[2] comprises dissolving in a volatile solvent such as acetone, the solution being used in a spinning cell in which the solvent is evaporated and the spun material passed into an atmosphere in which a suitable proportion of water is introduced from outside the cell, the proportion of water determining the degree of delustring.

It is claimed that the actual temperature of the spinning solution just prior to extrusion, as opposed to the temperature of the evaporative medium in the immediate vicinity of the spinning nozzles[3], controls to a large degree the luster of the filaments. Ordinarily the temperature of the spinning solution has been to a large extent dependent upon the temperature of the evaporative medium in the immediate vicinity of the spinning nozzles, and with increased speeds of spinning this temperature has been steadily increased. It has been found that under any given set

1. British Celanese, Ltd., E. P. 314396, Addn. to E. P. 274841; abst. J. S. C. I. 1930, **49**, 1106-B; Chem. Zentr. 1930, I, 439. E. P. 314414; abst. Chem. Zentr. 1930, I, 2657. H. Dreyfus, F. P. 664064; abst. C. A. 1930, **24**, 963; Chem. Zentr. 1929, II, 3262. F. P. 664065. Can. P. 303277, 303278. Belg. P. 327478.

2. U. S. P. 1838121; abst. C. A. 1932, **26**, 1440. Can. P. 278904; abst. Chem. Zentr. 1932, I, 318.

3. British Celanese, Ltd., W. Taylor and R. Roberts, E. P. 334195; abst. C. A. 1931, **25**, 1084; J. S. C. I. 1930, **59**, 1023-B; Chem. Zentr. 1931, I, 2141. E. P. 320632; abst. J. S. C. I. 1930, **49**, 53. E. P. 198023, 315729, 333504. H. Dreyfus, F. P. 38319, Addn. to F. P. 690432; abst. C. A. 1932, **26**, 1120. F. P. 690432; abst. C. A. 1931, **25**, 1084; Chem. Zentr. 1931, II, 1792.

of spinning conditions, e.g., concentration of spinning solution and viscosity of cellulose derivative therein, speed of spinning, denier being spun and evaporative power of the drying medium, a certain definite minimum temperature for the spinning solution just prior to extrusion exists for the production of high luster filaments, but that with this set of spinning conditions, by decreasing the temperature of the spinning solution prior to filament extrusion, filaments of any degree of reduced luster may be produced.

7. *Delustring in Hot Baths.* According to C. Dreyfus and H. Platt[1] delustring by means of hot baths such as boiling aqueous liquids, may be controlled or prevented by the addition of ammonium or calcium thiocyanates of about 1% strength, the fabric being boiled for 0.5-0.75 hr. The process is applicable to the treatment of films, fibers and fabrics made of or containing ethylcellulose, the treatment increasing the density and softness of the fiber.

8. *Delustring During Dyeing.* According to British Celanese, Ltd.[2], fabrics made of yarns of cellulose ethers or cellulose acetate have their luster reduced by subjecting them to a delustring treatment while suspended in the length or piece or in the form of hanks, and may contain dyes or swelling agents for the fabric, while the fabric may be dyed before, during or after the delustring treatment. Another method of delustring consists in treating cellulose derivative silk so as to absorb leuco-compounds of anthraquinone and such of its derivatives as are color-

1. U. S. P. 1740889. E. P. 282272. F. P. 644985. Can. P. 285048. Belg. P. 354978. W. Stahl, Seide, 1931, **36**, 358, 360, 402, 409; abst. C. A. 1932, **26**, 1792, has studied the effects of sodium, potassium and ammonium hydroxides, sodium carbonate, sulfuric acid and hydrochloric, acetic and tartaric acids on the delustring of acetate silks in hot baths, using temperatures of 20°, 40°, 75° and 100°, and has shown that in all cases delustring becomes apparent at about 70° and increases up to the boiling point of the solution. Although the luster of acetate silk is destroyed by boiling in distilled water there is no evidence of hydrolysis. Delustring may be decreased by lowering the temperature of the treating bath, adding protective salts, or modifying the acetate silk.

2. E. P. 345509; abst. Textile Mfr. 1931, **57**, #680, 304; Silk J. 1931, **8**, #87, 52.

less in the fully oxidized state[1], and is then suitably oxidized, thereby depositing the fully oxidized anthraquinone compound within the silk which becomes reduced in luster. Anthraquinone and 2-chloranthraquinone are particularly suitable, and are applied from an alkaline reducing liquor containing ammonia and sodium hyposulfite. The silk may be delustered and dyed simultaneously if use is made of dyes such as Hydron Pink FF.

In the preparation of threads, cords and fabrics[2] new effects are to be obtained by combining normal lustrous artificial silk with yarns which have been wholly or partially delustered, the two threads being doubled to form a cord suitable for knitting or weaving, differential effects being obtainable by taking advantage of the different dyeing effects of the two materials.

9. *Mechanical or Abrasion Delustring.* Either yarns or fabrics[3] may be modified as to luster by treatment with abrasive materials such as pumice powder, carborundum, silica, emery or powdered glass, being applied to the fabric in the form of paste or as a film on brushes or rollers. For the production of a pattern effect a stencil is interposed between the abrasive and fabric. W. Cameron and C. Croft[4] deluster knit fabrics containing yarns of organic cellulose derivatives by subjecting the fabric of a delustring agent preferably of the abrasive type, while the yarn is held in such position that distortion or wrinkling is substantially prevented.

In delustring fabrics such as "shiny" worn garments[5],

1. Silver Springs Bleaching and Dyeing Co., Ltd., and A. Hall, E. P. 316169; abst. C. A. 1930, **24**, 1750; J. S. C. I. 1929, **48**, 938-B; Chem. Zentr. 1930, I, 776; Silk J. 1929, **6**, #66, 68.

2. British Celanese, Ltd., C. Palmer and S. Fulton, E. P. 278116; abst. Chem. Zentr. 1928, I, 755. H. Dreyfus, F. P. 637468; abst. C. A. 1929, **23**, 705; Chem. Zentr. 1928, II, 2754.

3. British Celanese, Ltd., W. Taylor and C. Dreyfus, E. P. 335204; abst. C. A. 1931, **25**, 1393; Rayon Record, 1930, **4**, 1260; J. S. C. I. 1930, **49**, 1147-B; Chem. Zentr. 1931, II, 2239. Compare E. P. 328247.

4. Can. P. 305535.

5. A. English and S. Stamoulis, U. S. P. 1823192; abst. C. A. 1932, **26**, 319; Chem. Zentr. 1932, I, 470.

removal of the shine may be accomplished by friction after wetting the fabric with the supernatant liquid from a mixture of macerated raw potato and water. According to W. Taylor and British Celanese, Ltd.[1], who have patented a process for so doing, all types of artificial filaments may be delustered to any desired degree by subjection to a process of abrasion in which the threads are led over an abrasive surface or loose abrasive material, or in which a stream of the abrasive material dispersed in a liquid medium impinges on the moving threads. Suitable abrasives comprehended in the invention include kieselguhr of at least 120-mesh fineness, pumice powder, powdered glass, carborundum and emery. Other abrasives which are soluble in solvents and which may thus be removed by a washing treatment are sodium sulfate, alum and sodium chloride.

10. *Other Processes.* Yarns, bristles, films and fabrics made of cellulose derivatives as cellulose ethers[2] are delustered and rendered opaque without crinkling or distortion by delustring while the material is under tension or stress, as by loading with weights or by winding under tension from one reel to another. The luster of cellulose ether fabrics may also be subdued by subjecting the fabric to a delustring operation while the fabric is suspended vertically in the form of hanks to prevent distortion or wrinkling. While greater advantages accrue from its use in the treatment of circular or warp knitted fabrics, it is also said to be beneficial when applied to woven fabrics. They should be completely immersed[3]. The usual delustring methods of boiling in a soap solution or precipitation of a metallic salt are then applied[4].

1. E. P. 328247; abst. C. A. 1930, **24**, 5512; J. S. C. I. 1930, **49**, 763-B; Chem. Zentr. 1930, II, 2462; Rayon Record, 1930, **4**, 711.
2. British Celanese, Ltd., E. P. 318642; abst. Chem. Zentr. 1930, I, 3375; Silk J. 1930, **6**, #68, 66. C. Dreyfus, Can. P. 297853, 305535.
3. *Ibid.* E. P. 345509, Addn. to E. P. 343698; abst. C. A. 1931, **25**, 5580; J. S. C. I. 1931, **50**, 584-B.
4. *Ibid.* E. P. 343698; abst. J. S. C. I. 1931, **50**, 486-B; Chem. Zentr. 1931, II, 3059; Silk J. 1931, **8**, #85, 54.

In reduction of luster where the filaments are formed by a dry method of spinning[1], a small fan is placed in the spinning cell near the nozzle, a current of air or gas is directed at right angles to one side of the liquid filaments so that evaporation of solvent proceeds irregularly, the result being the production of filaments exhibiting two or more re-entrant surfaces. According to L. Clement and C. Riviere[2], silks, films, varnishes and artificial leathers of ethylcellulose or benzylcellulose, are obtained with a matt surface by mixing a solution of the cellulose *ether* in one or more volatile solvents with a solution of a cellulose *ester* also in a volatile solvent or solvent combination, an especially pronounced matt surface resulting from a mixture of acetylcellulose in acetone and benzylcellulose in a mixture of acetone, benzene and methyl or ethyl alcohols. Cellulose ether or ester threads or fabrics may have their luster materially reduced by impregnating them with a solution of ordinary cellulose in zinc chloride, a thiocyanate or by a copperammonia solution, or the filaments may be treated with a dilute viscose solution and then with an acid to precipitate the cellulose[3]. If in the spinning of cellulose ether filaments they are extruded into an atmosphere containing one or more organic precipitants for the cellulose compounds, the filaments become delustered[4]. E. Jordan[5] has described a method for controlling the delustring process for cellulose derivative silks, by examining from time

1. S. Dunlop, E. P. 359385; abst. J. S. C. I. 1932, **51**, 17-B.
2. F. P. 700477; abst. C. A. 1931, **25**, 3834; Chem. Zentr. 1931, II, 3178.
3. H. Dreyfus, F. P. 678399; abst. C. A. 1930, **24**, 3646.
4. British Celanese, Ltd., R. Payne and R. Roberts, E. P. 314404; abst. C. A. 1930, **24**, 1509; J. S. C. I. 1929, **48**, 714-B; Silk J. 1929, **6**, #65, 80; Chem. Zentr. 1930, II, 2657. H. Dreyfus, F. P. 664064; abst. C. A. 1930, **24**, 963. F. P. 664065; abst. Chem. Zentr. 1929, II, 3262.
5. Textile World, 1932, **81**, 2007; abst. C. A. 1932, **26**, 4478. See also: J. Bennett, U. S. P. 1633160; abst. J. S. C. I. 1927, **46**, 776-B. British Celanese, Ltd., E. P. 334198, Addn. to E. P. 334195; abst. C. A. 1931, **25**, 1084; J. S. C. I. 1930, **49**, 1023-B; Chem. Zentr. 1932, I, 1848. Soc. of Chemical Industry in Basle, E. P. 349322; abst. Textile Mfr. 1931, **57**, #682, 381; J. S. C. I. 1931, **50**, 714-B. E. P. 300998, 320363. H. Dreyfus, Can. P. 303277.

to time either the fiber or cross-sections of it mounted in anhydrous glycerol by means of a microscope.

If cellulose acetate materials are steeped in cold or warm 40-50% aqueous solutions of 15-35% formaldehyde and 10-30% of methyl, ethyl, propyl or butyl alcohol capable of forming an acetal-like compound with the formaldehyde[1], and are then washed and dried, they become softer, less lustrous, more voluminous and shrinkage takes place. If it is desired to produce luster pattern effects, two types of cellulose ether or ester yarns may be woven together[2], one type being readily delustered by treatment with boiling water or soap solution and the other being more resistant to this treatment, then subjecting the mixed fabric to a delustring process such as immersion in a boiling soap bath.

In the treatment of thermoplastic fabrics such as prepared from the cellulose ethers[3], mottled or printed effects exhibiting a difference in luster on the surface may be induced and their luster restored by ironing or calendering while still damp, mottled effects being produced by dampening only portions of the materials. The luster may also be reduced on materials composed of the cellulose ethers by first applying an aqueous 10% solution of triethanolamine, then immediately subjecting the fabric to the action of steam at 5 lbs. pressure for 15 min. in a cottage steamer[4]. Textiles containing ethylcellulose or cellulose acetate may be made so that a part of the cellulose derivative is more resistant to the action of warm, delustring agents than the rest[5], by applying a solvent or swelling agent locally, and then submitting the whole fabric to steaming.

1. K. Beck, E. P. 361200. F. P. 710299. See F. Bayer & Co., Ital. P. 167228.
2. British Celanese, Ltd., E. P. 310845.
3. *Ibid.* E. P. 295043; abst. C. A. 1929, **23**, 2046.
4. C. Dreyfus and H. Platt, U. S. P. 1836527.
5. British Celanese, Ltd., and G. Ellis, E. P. 335583. C. Dreyfus and W. Whitehead, U. S. P. 1838663. H. Dreyfus, F. P. Addn. 37906 to 686644.

In the knitting of yarns of continuous filamentous structure, and especially in circular knitting operations as in the manufacture of hosiery[1], the stitches and loops do not always have exactly similar shapes. This variation from the normal is known as "stitch distortion" where the stitches do not form a straight line along the rib of the fabric, or as "pin holes" where the stitches are so formed that there are holes of unequal size. One opinion is that this is due to non-uniformity in the coefficient of friction between the filaments of the yarn and also between the yarn and needles. It has been found that this may be remedied if the filaments are roughened in any suitable manner, the roughening reducing the luster of the fabric produced.

In order to deluster cellulose ether or ester fabrics[2], H. Platt and C. Dreyfus precipitate white insoluble salts in the material in the presence of swelling agents, as by treatment with barium thiocyanate and sulfuric acid, or with a 20% formic acid solution, then with barium chloride solution and finally with a 1% solution of phosphoric acid, thus forming barium phosphate[3]. The luster of filaments containing cellulose ethers or esters is diminished by treating them with phenolic substances of low concentration, as an $N/30$ solution of phenol[4]. Cellulose acetate silk is said to be delustered with perfect regularity without deleteriously affecting the strength, elasticity and other desirable qualities[5], by soaking the yarn for 2-24 hrs. at the ordinary temperature in a 10-30% aqueous solution of calcium, lithium or magnesium chloride and then treating the impregnating fabric, after squeezing, for 1-20 min., in boiling $0.1N$ hydrochloric acid or boric acid, or $0.02N$ benzoic acid, or $0.01N$ salicylic or *b*-naphthalenesulfonic acids.

1. C. Dreyfus and W. Whitehead, U. S. P. 1883349.
2. E. P. 318467; abst. C. A. 1930, **24**, 2311.
3. W. Taylor and R. Roberts, Can. P. 321721, 321723.
4. H. Dreyfus, F. P. 717449; abst. C. A. 1932, **26**, 2876.
5. Soc. Fabr. Soie "Rhodiaseta," E. P. 301335. D. R. P. 512637; abst. C. A. 1931, **25**, 1391. F. P. 638795; abst. C. A. 1929, **23**, 530. G. Lardy, U. S. P. 1778327.

Cellulose acetate silk of reduced luster may be prepared by the introduction of water vapor, as such, into the spinning cell. Alternatively, the filaments may be formed in the usual manner[1], and before the threads are wholly deprived of solvent, they are passed into a second cell to which water vapor is supplied, the degree of delustring depending upon the amount of water vapor introduced. The presence of one or more protective agents as readily ionizable neutral salts, especially cane sugar, is said to restrain, retard or even prevent delustring by boiling water[2].

Matt effects are producible on cellulose acetate silk by dissolving in the spinning solution a small quantity of stearic acid or a soluble anhydride, and treating the filaments obtained with aqueous solutions of salts which form difficultly soluble salts with the acid used[3]. Glycerol is also effective for this purpose, especially in conjunction with a small amount of stearic acid[4].

Relustring, or the recovery, partially or completely, of luster already lost, may be applied to cellulose ether or organic cellulose ester filaments or textiles prepared therefrom, by treatment with an aqueous solution or dilution of one or more swelling agents which are soluble in or miscible with water, the goods being afterwards treated for removal of water contained by evaporation, without reduction of the ratio of solvent to water in the solution retained by the filaments. Examples of useful solvent and swelling agents are: acetic acid, phenol, benzyl alcohol, triacetin, cyclohexanone and ammonium or other thiocyanates. The treatments should be carried out under such conditions of concentration, temperature and treatment duration so that in no case is the solvent action sufficiently energetic to

1. N. V. Nederlandsche Kunstzijdefabriek, Belg. P. 354883. E. P. 291067.
2. C. Palmer and S. Fulton, U. S. P. 1808061.
3. Soc. Pour la Fabrication de la Soie "Rhodiaseta," F. P. 695490. D. R. P. 502320. M. Theumann, Can. P. 284275.
4. *Ibid.* F. P. 695491; abst. C. A. 1931, **25**, 2849.

cause the filaments to fuse or stick together[1], or become contorted or permanently deformed. By suitable adjustment of conditions, the luster may be restored to a modified degree so as to resemble that of natural silk or other fibers.

Delustered threads or fabrics of methyl- or ethyl-cellulose[2], either alone or admixed with silk, cotton or wool, may have the luster restored by ironing or calendering them while in the wet or damp state. Mottled effects are producible by damping the materials in parts.

In the treatment of threads or knitted or woven fabrics of organic cellulose derivatives[3], in which the filaments are in a partially delustered condition, boiling with a 2-3% solution of ammonium sulfate or a 1-6% solution of sodium sulfate is said to gradually restore the luster. 10-40 min. boiling is usually sufficient, but depends upon the degree of relustring desired. The goods are rinsed in water to remove the salts, and dried. G. Lardy[4] claims that cellulose acetate threads or fabrics which have been accidentally or intentionally tarnished under the action of certain agents, may have the luster restored by bringing in contact in the wet condition with a surface heated above 125°. The rapidity of restoration of luster depends on the temperature, and to the degree of moisture in the fabric. When the temperature is too low, restoration of luster is too slow for commercially working.

The luster of delustered cellulose ether and ester yarns may be restored by application of ethyl lactate[5] or ethylene-

1. British Celanese, Ltd., J. Briggs, C. Palmer and J. Kidd, E. P. 259265. Can. P. 276514; abst. C. A. 1928, **22**, 2068. U. S. P. 1808098.

2. British Celanese, Ltd., E. P. 295043; abst. J. S. C. I. 1930, **49**, 370-B; Chem. Zentr. 1928, II, 2512.

3. C. Palmer and S. Fulton, U. S. P. 1774184; abst. C. A. 1930, **24**, 5168; J. S. C. I. 1930, **49**, 495-B. British Celanese, Ltd., C. Palmer and S. Fulton, E. P. 259266; abst. C. A. 1927, **21**, 3461. C. Palmer and S. Fulton, Can. P. 285049; abst. C. A. 1929, **23**, 996. See E. P. 165164.

4. U. S. P. 1803672; abst. C. A. 1931, **25**, 3849; Chem. Zentr. 1931, II, 798.

5. Bleachers' Assoc., Ltd., W. Kershaw, F. Barrett and R. Gaunt, E. P. 301567; abst. J. S. C. I. 1929, **48**, 127-B; Chem. Zentr. 1929, I, 2828.

glycol monomethyl ether[1] and drying. For the production of pattern effects, the silk is completely delustered by padding with a soap solution and steaming, then printing with a thickened paste containing ethyl lactate or ethyleneglycol monomethyl ether, drying, and afterwards washing, the printed parts taking on a higher luster than the non-printed. Dyes may be added to the printing pastes so the silk may be dyed simultaneously. If cellulose acetate yarns have been delustered[2], as by treatment in a boiling soap solution, the luster may be brought back by steaming for a half hour at a pressure of 20 lbs. per sq. in. in excess of atmosphere pressure and at a temperature of 175-185°. Or[3], the dulled acetylcellulose filaments, threads or fabrics may be wetted and hot calendered at between 125-170° and a pressure of 0.1-0.5 kgm. per sq. cm.[4].

Cellulose acetate yarns that have been delustered either to produce a wool-like effect[5] or by accident[6], may be relustered by treating them with swelling agents as formic or acetic acids, ethyl acetate or calcium thiocyanate, and then exposing them in a dry condition to the action of substantially dry steam, preferably under slight pressure, under such conditions as preclude the deposition of moisture. Dyestuffs, salts and mordants may be added to the swelling agents, and by using suitable resists, lustrous designs on a dull background may be produced. When a high-boiling solvent has been used in the manufacture of the

1. Bleacher's Assoc., Ltd., W. Kershaw, F. Barrett and R. Gaunt, E. P. 301568; abst. J.S.C.I. 1929, **48**, 127-B; Chem. Zentr. 1929, I, 2828.
2. British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 349980, Addn. to E. P. 332231; abst. J. S. C. I. 1931, **50**, 838-B. E. P. 332231; abst. C. A. 1931, **25**, 218; J. S. C. I. 1930, **49**, 944-B.
3. Du Pont Rayon Co., Can. P. 304199.
4. R. Clavel, D. R. P. Anm. C-37609.
5. *Ibid.* E. P. 206818; abst. J. S. C. I. 1924, **43**, 743-B.
6. *Ibid.* E. P. 269605; abst. C. A. 1928, **22**, 1474; J. S. C. I. 1927, **46**, 473-B; Rayon, 1927, **5**, #3, 32; Kunstseide, 1927, #9, 471. See U. S. P. 1844204. F. P. 604786; abst. Chem. Zentr. 1927, I, 1219. F. P. 31830, Addn. to F. P. 604786; abst. Chem. Zentr. 1927, II, 1205. D. R. P. 451110, Addn. to D. R. P. 446486; abst. Chem. Zentr. 1928, I, 259. D. R. P. 446486; abst. Chem. Zentr. 1927, II, 1316. Can. P. 275559; abst. C. A. 1928, **22**, 1243.

filaments, exposure to dry steam is sufficient to restore the luster.

The British Celanese, Ltd.[1], reluster delustered fabrics by applying thereto the methyl or ethyl ethers of ethyleneglycol, diacetone alcohol, benzyl alcohol, triacetin, cyclohexanone or potassium or ammonium thiocyanate, or sugar, phthalimide or xylenemonomethylsulfonamide. In selecting the particular agent to be employed if the goods are to be printed, due regard should be taken to the other constituents of the printing paste with which the relustering agent should be compatible both physically and chemically. For instance, if the printing paste is alkaline, an acid relustering agent tends to neutralize the alkali in a disadvantageous manner and should be avoided.

Mildewproofing. The occurrence of mildew or mould fungi on fabrics made from cellulose ether or ester yarns is a fruitful cause of troublesome complaints, there being little definite information as yet on the subject[2]. Growths on such fabrics were originally observed on textiles dyed black or navy blue, but it has been shown that growths may occur on fabrics of this nature dyed any color. Seams, pleats and flounces and such protected portions seem to be an especially suitable nidus for fungi growth. While such spots may readily be removed by simple brushing, new growths readily reappear, the usual ones being *Aspergillus, Rhizopus, Penicillium, Mucor, Fusarium* and *Alternia.* Since these fungi are microscopic plants without chlorophyl, they do not depend upon sunlight for existence. Since moisture is necessary for their incubation and growth, and the cellulose ethers and esters absorb relatively only about half the normal moisture as does cotton, danger from mildewing is not so great.

In the proofing of fabrics against fungi, the oxyaryl-

1. E. P. 306534; abst. C. A. 1929, **23**, 5048; J. S. C. I. 1930, **49**, 702-B; Chem. Zentr. 1929, II, 221.
2. J. Eccles, Am. Dyestuff Rep. 1931, **20**, 633; Textile Mfr. 1931, **57**, 184; abst. C. A. 1932, **26**, 310.

methanes have been recommended as efficient fungicides[1], a hydroxydi- or hydroxytri-arylmethane as the condensation product of formaldehyde with *p*-chlorphenol, or methylene-bis-2'4-chlorphenol and condensation products of formaldehyde with *m*-chlorphenol, 6-chlor-3-cresol, or condensation products from *p*-chlorbenzaldehyde or *p*-diethylaminobenzaldehyde and two molecular proportions of *p*-chlorphenol. Arylamides of salicylic acid have also been put forward as acceptable for this purpose[2], being ground or milled in water in the presence of wetting agents to produce aqueous pasty dispersions suitable for proofing against mildew and other fungoid growths. As an example, 25 parts anhydrous salicylic anilid (salicylanilid) are ground with 25 parts water and 2.5 parts of a 50% solution of the sodium salt of a sulfonated naphthalene-formaldehyde condensation product. Coating with a pyroxylin dope containing zinc resinate or other metallic soaps has also been proposed[3].

Imparting Scroop. The rustle and swish and swirl of silken raiment, usually when adorning a fair woman of aristocratic and patrician mien, has filled many a page of history with glamour and illusionary fascination. Scrooping or avivage is the treatment which imparts to textiles qualities simulating natural silk, and is a process usually applied after the dyeing operation. The materials primarily used for this purpose are starch products, glue, gelatin, diastafor, malt preparations and similar "feel" and "handling" materials[4]. The scrooping bath usually contains an acid substance as formic, acetic or lactic acids, together with emulsified or saponified vegetable oil, usually olive.

Often it is desirable to increase the scroop of fabrics containing methyl-, ethyl- and benzyl-cellulose or cellulose

1. I. G. Farbenindustrie, A.-G., E. P. 336244.
2. Imperial Chemical Industries, Ltd., A. Hailwood and A. Stewart, E. P. 350642; abst. Textile Mfr. 1931, **57**, #683, 421.
3. R. Harvey and H. Day, U. S. P. 1827083; abst. C. A. 1932, **26**, 606.
4. W. Alterhoff, Kunstseide, 1927, 368; abst. Rayon, 1927, **5**, #3, 24.

acetate, and this is particularly true in the case of fabrics as taffeta. H. Platt[1] has found that if such fabric is treated with polybasic aliphatic acids or their salts, and the acids or salts permitted to remain in the fabric, an appreciable increase in scroop results. The fabric is treated with a liquid containing sodium, potassium, ammonium, barium or calcium tartrates, oxalates or citrates, and to still further increase the scroop effect, the treating reagent also should preferably contain an emulsion of olive, neatsfoot or mineral oil. The amounts used are about 0.4% of acid or salt and 0.6% of oil emulsion based on the weight of the fabric, the treatment being 15 min. at 45°, after which the fabric is removed, excess liquid extracted and the fabric dried while stretched on a tenter or frame. Fabric treated with sodium tartrate and olive oil emulsion is said to have the highest scroop, while sodium oxalate alone imparts the minimum of increase in scroop.

Carbonizing. It has been discovered that fibers of cellulose ethers and organic esters of cellulose are unaffected by the usual carbonization agents used to remove vegetable and animal fibers and reconstituted cellulose (regenerated cellulose) and upon this observation have been devised several processes of carbonization of lace, mixed fabrics and filaments in which the cellulose ethers are present[2]. Rayon or artificial silk of the regenerated or "cellulosic" type is completely removed by the usual carbonization operation of treatment with aluminum chloride or hydrochloric acid and subsequent drying at a pre-determined maximum temperature.

1. U. S. P. 1857163; abst. C. A. 1932, **26**, 3920. British Celanese, Ltd., E. P. 354200; abst. Textile Mfr. 1932, **58**, #685, 38. Can. P. 324630.

2. C. Dreyfus, R. Dort and H. Platt, U. S. P. 1725857, 1834338, 1834339; abst. C. A. 1929, **23**, 5049; J. S. C. I. 1929, **48**, 848-B. British Celanese, Ltd., E. P. 274074; abst. C. A. 1928, **22**, 2066; J. S. C. I. 1928, **47**, 811-B. E. P. 310936; abst. C. A. 1930, **24**, 734; J. S. C. I. 1930, **49**, 318-B. C. Dreyfus, F. P. 636608; abst. C. A. 1929, **23**, 719. C. Dreyfus, R. Dort and H. Platt, Can. P. 285047; abst. C. A. 1929, **23**, 995. Compare Silver Springs Bleaching & Dyeing Co., Ltd., and A. Hall, E. P. 246879; abst. J. S. C. I. 1926, **45**, 317-B.

Formerly it was thought only real or natural silk could be used in mixed fabrics to obtain a striped or two-color effect, because of the facility with which rayon of the regenerated cellulose type is removable by carbonization treatment. It is now known that the cellulose ethers and organic cellulose esters may be successfully used as a substitute for real silk to obtain such effects. It would appear that the wearing, dyeing and dye-resisting properties of such fibers are less affected by the carbonization treatment than are the similar properties of real silk. Furthermore, the cellulose ethers are less affected by the carbonization process than are the acetylated celluloses.

While the luster of acetate silk is usually somewhat affected by the carbonization treatment and requires the use of sodium sulfate as a delustering preventative, the luster of the cellulose ethers is not modified by the treatment. The method is illustrated by the following examples:

1. A woolen fabric containing cellulose ether or cellulose acetate fibers is treated in a solution of aluminum chloride of 6-13° Be. at 90°F., excess of aluminum salt removed by pressing or squeezing the fabric on a jig, after which the fabric is hydro-extracted, and then passed through a carbonization dryer at 235° F., the fabric coming out bone dry. If cellulose acetate textile has been used, there is a slight delustering due to the deposition of aluminum oxide on the surface, but this may be removed by a soaping operation. The above process results in all the vegetable fibers being removed, leaving only the wool and cellulose ether or acetate filaments.

2. This unique property of resistance to carbonization is of great importance in the production of embroidery, the cellulose ether or acetate fibers being used to embroider on a cotton or jute canvas. Formerly the cotton or jute backing was removed by hand, but may now be manipulated by passing the fabric through a bath of 1-2% HCl at 120° F., excess solution squeezed out and then passed through a carbonizing dryer at 240° F. After carbonization the fabric

is rinsed and given a scouring treatment with soap, thus removing the cotton background and leaving the cellulose derivative fibers unaffected.

In an improvement on this process[1], the mixed fibers are heated in solutions of inorganic acids or salts sufficiently diluted to have no deleterious effect on the non-cellulosic materials, to render the cellulose fibers removable without drying in the presence of a carbonizing agent. Ornamental effects may be produced by use of colored or other reserves. The N. McLeod carbonizing apparatus appears suitable[2].

The following process which involves a partial saponification of the fibers is useful only for cellulose acetate fibers[3], and is carried out by treating the mixed fiber textile with an alkaline paste with thickeners as tragacanth or acacia in water as used in printing pastes, the latter being applied to the fabric in any suitable manner as by means of embossed or engraved rolls or plates, or by brushing, spraying or stencilling. The printed design may be of any desired configuration. The fabric is passed through a bath of sulfuric acid, aluminum chloride or sodium bisulfate maintained up to a maximum of 212° F., excess solution removed and then the fabric passed through a carbonizing dryer at 215-250° F., the fabric leaving the chamber bone

1. H. Dreyfus, E. P. 339300; abst. C. A. 1931, **25**, 2578; Silk J. 1931, **7**, #82, 54. F. P. 698418; abst. C. A. 1931, **25**, 3177. He soaks cellulose ether or ester fabrics first in a solution of cold monomethylurea, then in stannic chloride solution (E. P. 284798) for loading purposes. C. Dreyfus (Can. P. 320249) treats fabrics with a predetermined pattern of mixed cellulose ether or ester fabric with cotton or other fiber, with a carbonizing solution or a carbonizing promoting compound, and then subjects the fabric to a carbonizing temperature. See Can. P. 296741.

2. U. S. P. 1375714; abst. J. S. C. I. 1921, **40**, 427-A. The G. Rivat and C. Dreyfus (U. S. P. 1818505) comprises treating fibers containing cellulose ethers or cellulose acetate with a mineral acid material (sulfuric acid, acid sodium sulfate, aluminum oxide) and a solvent or swelling agent for the cellulose derivative as phenol, acetone, pyridine, lactic acid or diethyl phthalate, then heating the material to an elevated temperature and removing the effected cellulose material.

3. C. Dreyfus, U. S. P. 1804529; abst. C. A. 1931, **25**, 3849; Chem. Zentr. 1931, II, 1766. Can. P. 314909.

dry. The usual finishing treatments of brushing, steaming and dyeing are then applied.

Wetting. The cellulose ethers of a high degree of etherification, and the partially hydrated cellulose acetates, are both insoluble in water and little affected thereby, therefore, on account of this non-solubility in water accompanied by a low degree of porosity they wet with difficulty unless aided by a special agent. Permeability to liquids, of course, is necessary for dyeing and other impregnating operations. It is, therefore, always desirable that spun artificial products from cellulose derivatives should be easily wetted by water, so that the products or the fabrics may be readily scoured, dyed or given any other finishing treatment. Glycols are excellent wetting agents because of their solvent and swelling capacity[1]. In the case of dry spinning of filaments the polyhydric alcohols employed should obviously be substantially non-volatile, and it is often advantageous to associate with them a body of pronounced hygroscopicity as glycerol or an acetated glycerol, both of which are water-soluble. In order to obtain products easily wetted[2], there is added to the spinning solution of cellulose ether or ester used for the production of yarns and textiles, a substance which is relatively non-volatile and is soluble in water, particularly a non-volatile water-soluble alcohol or ester in conjunction with a water-miscible oleaginous material as the sodium salt of sulforicinoleic acid.

Wetting out or emulsifying agents, according to another process[3] may be obtained by sulfonating a mineral oil fraction and condensing the product with an alcohol, or by condensing a mineral oil with an alcohol and then sulfonating. According to one example, a petroleum fraction obtained by extracting Borneo petroleum with liquid sulfur dioxide is first sulfonated, and then heated with a mixture

1. British Celanese, Ltd., E. P. 313885; abst. C. A. 1930, **24**, 1218; J. S. C. I. 1930, **49**, 1146-B; Silk J. 1929, **6**, #65, 78.
2. *Ibid.* E. P. 333504. See E. P. 177868, 179234.
3. Imperial Chemical Industries, Ltd., F. P. 683728; abst. Cellulose, 1930, **1**, #10, 270. Cites E. P. 274611, 309964.

of *iso*propyl alcohol and sulfuric acid. Instead of *iso*propyl alcohol there may be used *n*-propyl alcohol, *iso*butyl alcohol, cyclohexanol or benzyl alcohol, forming the corresponding esters of the petroleum acid. Methylcyclohexanone, hexalin acetate or butyl propionate are also claimed as appropriate. Potassium, sodium or ammonium ricinoleate, oleate or stearate or triethanolamine stearate or oleate form the basis of the preferred wetting out agent of British Celanese, Ltd.[1]. Ethyleneglycol, propyleneglycol or glycerol in conjunction with toluene or xylene form the basis of another patented formula[2].

G. Miles[3] permanently incorporates in the organic cellulose derivative a substantially inert hydroscopic substance, solidifying the mixture and then allowing the mass to absorb such water as the substance may absorb and retain. Zinc chloride is specified for this purpose, calcium or magesnium chlorides being also water-absorbent and water-retentive. Diacetone alcohol, monoacetin and glycol ether are other appropriate substances.

Wetting and dispersive agents are said to be improved by the addition thereto of lower aliphatic esters (up to the cetyl esters but excluding the glycerides) of fatty sulfonic acids[4]. The Twitchell Process Co.[5] have described certain mineral ("mahogany") sulfonates obtained in the refining of mineral oil with oleum or sulfur trioxide[6], which after purification, are suitable as dispersing agents for cellulose ether or ester dyes. Both types of mahogany sulfonates may be used, viz., those recovered from the acid sludge, and, more particularly, from the oil layer. Dispersion of these sulfonates in water is facilitated by the addi-

1. British Celanese, Ltd., E. P. 367830, Addn. to E. P. 333504; abst. J. S. C. I. 1932, **51**, 416-B.
2. *Ibid.* E. P. 351084; abst. Textile Mfr. 1931, **57**, #684, 458.
3. Can. P. 312024.
4. H. Böhme, A. G., E. P. 316132; abst. Chem. Zentr. 1929, II, 3188; British Plastics, 1931, **3**, #27, 55. See E. P. 313160, 315832.
5. E. P. 354326; abst. J. S. C. I. 1931, **50**, 922-B.
6. Twitchell Process Co., E. P. 127159; abst. J. S. C. I. 1919, **38**, 493-A.

tion of small quantities of low-viscosity mineral oils, aromatic, hydrogenated, or chlorinated solvents.

There have been described as dispersive agents for use with the cellulose ethers in the dyeing and printing operations[1], certain aryl-sulfonic acid anions, which added to the dye-bath in paste form, greatly assist in tinctorial deposition, benzene-, naphthalene- and anthraquinone-sulfonic acids, and their derivatives substituted by one or more oxy-, alkyl-, chlor- or nitro-groups. As examples, methylene green with 2% sodium diphenylaminosulfonate, fuchsine with *b*-naphthalenesulfonic acid, Pyronine G with sodium *b*-anthraquinonemonosulfonate, Setoglaucine with 2.7-naphtholsulfonic acid, and Malachite Green with sodium 1-chlor-4-naphthalenesulfonate. The susceptibility of acetylcellulose for dyes is said to be materially augmented by the addition of a small amount of nitrogenous material as gelatin to the dye-bath[2]. A mixture of gelatin and glycerol has also been proposed[3].

Synthetic resins of the naphthalene-resin or sulfonated resin type have been proposed to give wetting and dispersive properties to cellulose ether and ester insoluble dyes[4]; or the replacement of naphthalene by carbazol, phenol, or halogenized phenols have been disclosed. J. Leaper[5] claims that water-miscible refined white mineral oil, made soluble by adding a mixture of potassium oleate and oleic acid, is superior to sulfonated castor oil as a wetting agent. Waste sulfite liquor alone[6], or with naphthalenesulfonic acids or

1. H. Hoz, W. Bernoulli and A. Link, U. S. P. 1613228; abst. C. A. 1927, **21**, 655; J. S. C. I. 1927, **46**, 139-B. See E. P. 213593, 231897; abst. J. S. C. I. 1925, **44**, 588-B, 708-B.
2. H. Livsey, G. Holden and J. and J. M. Worrall, Ltd., E. P. 313980; abst. C. A. 1930, **24**, 1227.
3. S. Tootal, Can. P. 316728.
4. British Celanese, Ltd., G. Ellis, H. Olpin and W. Kirk, E. P. 323788; abst. C. A. 1930, **24**, 3332; J. S. C. I. 1930, **49**, 362-B; Chem. Zentr. 1930, I, 2634.
5. Textile Mfr. 1931, **57**, #683, 414. Textile Colorist, 1931, **53**, 550; abst. C. A. 1931, **25**, 5994.
6. W. Jaeck and J. Lang, U. S. P. 1796028, 1796029; abst. C. A. 1931, **25**, 2576. Soc. Chem. Ind. in Basle, E. P. 249549; abst. C. A. 1927, **21**, 1017; J. S. C. I. 1927, **46**, 650-B; Chem. Zentr. 1926, II, 649. E. P. 263579; abst. C. A. 1928, **22**, 171; J. S. C. I. 1927, **46**,

synthetic tans[1], gives a combination of saponaceous and penetrative properties which make them excellent wetting and dispersing agents for cellulose ether and ester dyestuffs.

The J. R. Geigy A. G.[2] advise dispersing aminoazobenzene by grinding with soap; the indophenol from *p*-aminomethylaniline and *α*-naphthol is stirred with a solution of soap; 1.4-diaminoanthraquinone is ground with naphthalene sulfonic acid and formaldehyde condensate and British gum; and dianisidine ground with saponin or sodium ligninsulfonate and starch. It is claimed that improved results in dyeing organic cellulose derivatives are obtained with the aid of dispersing agents comprising the sulfonated condensation products of saturated or unsaturated higher alcohols with naphthalene or other aromatic or carbocyclic compounds[3]. Naphthalene and carbazole are especially valuable when condensed with *sec*-octyl alcohol, *n*-octodecyl alcohol, ceryl alcohol, myricyl alcohol, *n*-dodecyl alcohol, and particularly with *n*-cetyl alcohol. Thus, a mixture of naphthalene and cetyl alcohol is condensed in the presence of chlorsulfonic acid at 70°.

Various amino-, alkylamino-, or aralkylamino-substituted derivatives have been described as suitable for dyeing the cellulose ethers in the presence of various dispersing agents[4], for instance 2.5-diaminobenzoquinone dispersed by means of Turkey-red oil yields a yellow shade[5].

186-B; Chem. Zentr. 1927, I, 2359. W. Jaeck and F. Felix, Can. P. 265027; abst. C. A. 1927, **21**, 1017; Chem. Zentr. 1927, II, 1622. See E. P. 219349.

1. R. Metzger, D. R. P. 480298; abst. C. A. 1930, **24**, 6033.
2. E. P. 272896; abst. C. A. 1928, **22**, 1859; J. S. C. I. 1929, **48**, 316-B; Chem. Zentr. 1927, II, 2233.
3. British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 305560; abst. C. A. 1929, **23**, 4831; Chem. Zentr. 1929, II, 355. British Celanese, Ltd., E. Stanley, H. Olpin and G. Ellis, E. P. 365170; abst. J. S. C. I. 1932, **51**, 503-B. H. Dreyfus, Can. P. 293052. Belg. P. 357944. G. Ellis and T. Ellison, Can. P. 314448. See E. P. 298699, 298993.
4. E. P. 219349, 224925, 242393, 242711, 269960, 273819, 273820.
5. British Celanese, Ltd., G. Ellis, H. Olpin and W. Kirk, E. P. 321401; abst. C. A. 1930, **24**, 2897; J. S. C. I. 1930, **49**, 54-B.

J. Bloom[1] has described a process and illustrated an apparatus for the electrical treatment in the dyeing of cellulose compounds, in which sundry dispersoids and adsorbable dispensoid and irreversible colloidal substances are caused to pass through fields of alternating electric, magnetic or electro-static stresses or fields, aiding in the deposition and absorption of the dyestuff.

The wetting properties of the alkalis in solution for the treatment of fibers of organic cellulose derivatives[2] is improved by adding thereto mixtures of phenols and hydrogenated phenols together with aliphatic or ketone alcohols, or the water-repelling properties may be diminished in cotton[3] by precipitating on the fiber a small amount of viscose and then de-esterifying. Sulfonates, acids[4], or the application to yarn of cellulose ethers a hygroscopic solid in an alcoholic medium, materially facilitates the wetting-out process[5], sodium or potassium acetates being suitable, especially in conjunction with glycols as ethylene glycol, propylene glycol and butylene glycol.

Solubilizing Agents. Due to the lack of porosity and water-insolubility of the higher etherified celluloses, dye penetrativeness is usually small. In order to aid in the dyeing, and penetration of other bodies into the cellulose ethers in order to induce specifically desired properties, various "solubilizing" agents, which function as swelling or softening bodies for the cellulose ethers have been proposed, and incorporated as an integral part of the dyeing, softening, cleansing and other treatments to which the filament or fabric made therefrom is subjected.

They are encompassed in the following classes:

1. *Resin and Fatty Acid Soaps.* G. Ellis[6] has pointed

1. U. S. P. 1333700; abst. J. S. C. I. 1920, **39**, 514-A.
2. Chemische Fabrik vorm. Sandoz, E. P. 350018.
3. H. Dreyfus, E. P. 323521.
4. G. Ellis, U. S. P. 1686149.
5. British Celanese, Ltd., S. Welch and R. Roberts, E. P. 365566. See also E. P. 365621.
6. U. S. P. 1716721. British Celanese, Ltd., and G. Ellis, E. P. 273820; abst. C. A. 1928, **22**, 2066; J. S. C. I. 1927, **46**, 650-B; Chem.

out the usefulness in dyeing, printing and stencilling operations involving the use of cellulose ethers and esters, of applying to the fibers to increase their tractability of the sodium, potassium or ammonium salts of resin acids, ammonium, sodium and potassium resinates—the so-called "resin soaps," readily soluble in cold or hot water. Sodium ricinoleate obtained by the saponification of castor oil[1] or ammonium sulforicinoleate as an aid to the penetration of 5.7-dibrom-3-indole-2′-thionaphtheneindigo have been recommended. The soluble sulforicinoleates are especially applicable in solubilizing coloring matters of the "azo" class, as the monazo, disazo, trisazo, and tetrakisazo dyes[2]. Sodium, potassium or ammonium oleate, stearate or palmitate, preferably with the minimum of free alkali therein[3], are used with unsulfonated or other insoluble or relatively insoluble dyestuffs.

2. *Sulfo-aromatic Acids.* The sulfoaromatic ricinoleic acids as sulfobenzene-, sulfophenol-, sulfonaphthalene-ricinoleic acids or their sodium, potassium or ammonium salts[4], have been found especially helpful where hard water is used in making up the dyebath. Likewise the sulfoaromatic stearic acids, as sulfobenzene-, sulfophenol-, or sulfonaphthalene-stearic acid also in the form of their Na., K and NH_4 salts[5]. These "Twitchell reagents" are used as

Zentr. 1927, II, 2715. H. Dreyfus, F. P. Addn. 33247 to F. P. 568655; abst. C. A. 1929, **23**, 1513. See U. S. P. 1600277, 1618413, 1618415, 1641965.

1. G. Ellis, U. S. P. 1723271; abst. C. A. 1929, **23**, 4580; J. S. C. I. 1930, **49**, 238-B. British Celanese, Ltd., and G. Ellis, E. P. 284376; abst. C. A. 1928, **22**, 4834; J. S. C. I. 1928, **47**, 229-B. H. Dreyfus, F. P. 642330. Belg. P. 344889.

2. *Ibid.* U. S. P. 1618414; abst. C. A. 1927, **21**, 1361. E. P. 224925; abst. C. A. 1925, **19**, 1952. F. P. Addn. 27953 to F. P. 568655.

3. *Ibid.* U. S. P. 1618413; abst. C. A. 1927, **21**, 1361; J. S. C. I. 1927, **46**, 249-B. British Celanese, Ltd., and G. Ellis, E. P. 219349; abst. C. A. 1925, **19**, 579; J. S. C. I. 1924, **43**, 906-B. Can. P. 265238; abst. C. A. 1927, **21**, 1018. See E. P. 211720. Can. P. 307038.

4. *Ibid.* U. S. P. 1840572. E. P. 273819; abst. C. A. 1928, **22**, 2066; J. S. C. I. 1927, **46**, 650-B; Chem. Zentr. 1927, II, 2574. Can. P. 285801; abst. Chem. Zentr. 1932, I, 2242. Can. P. 293050. Cites E. P. 224681, 237943.

5. *Ibid.* U. S. P. 1694413; abst. C. A. 1929, **23**, 718. Can. P. 269849; abst. C. A. 1927, **21**, 2384. E. P. 242393; abst. C. A. 1926, **20**, 3822. F. P. Addn. 31071 to F. P. 568655.

solubilizing bodies for those relatively insoluble dyestuffs which otherwise would show weak penetrative power for the organic cellulose derivative.

3. *Soaps with Organic Compounds.* The combination of soaps with bodies having a direct solvent or colloiding action upon the cellulose ether or ester have been described, such as soap solutions containing such organic compounds as amyl alcohol, glycerol, glycerol monochlorhydrin, cyclohexanol, phenol, *p*-toluenesulfon-amide or -anilide, being bodies which form easily dissociated salt-like alkali derivatives[1]. Ethylene chloride, methylene chloride, trichlorethylene, tetrachlorethane and pentachlorethane are bodies also indicated for this purpose.

4. *Naphthenic Acid Esters.* Certain carbocyclic solubilizing agents have been brought forward to facilitate the dyeing and increase the depth of color deposited in the cellulose derivative in a given time, as the naphthenic acids and sulfonaphthenic acids, and their ammonium, sodium and potassium salts. Ammonium naphthenate and sulfonaphthenate just over the alkali line in neutrality have been described[2], combining an unusually unctuous action with a blandness toward the dyestuffs, lakes and pigments used. Furthermore, their alkali solutions are of relatively low viscosity.

5. *Hydrocarbons and Sulfonated Mineral Oils.* G. Ellis and W. Goldthorpe[3] have pointed out the usefulness of hydrocarbon bodies in association with sulfonated fatty

1. A. Aurednicek, E. Keiner and R. Krech, D. R. P. 439111; abst. J. S. C. I. 1927, **46**, 964-B.

2. G. Ellis, U. S. P. 1818541, 1818542, 1818543. E. P. 224925; abst. C. A. 1925, **19**, 1952; J. S. C. I. 1925, **44**, 39-B; Ann. Rep. S. C. I. 1925, **10**, 136; Chem. Zentr. 1925, I, 1653. Belg. P. 311612, 311613.

3. U. S. P. 1803008; abst. C. A. 1931, **25**, 3847; Chem. Zentr. 1931, II, 1766. E. P. 242711; abst. C. A. 1926, **20**, 3822; J. S. C. I. 1926, **45**, 50-B; Ann. Rep. S. C. I. 1926, **11**, 154; Chem. Zentr. 1926, I, 2970. Belg. P. 328117. U. S. P. 1690481; abst. C. A. 1929, **23**, 528; J. S. C. I. 1928, **47**, 926-B. E. P. 269960; abst. C. A. 1928, **22**, 1482; J. S. C. I. 1927, **46**, 475-B; Chem. Zentr. 1927, II, 1205. Can. P. 271278, 276515; abst. C. A. 1928, **22**, 2067. Ital. P. 222812. Belg. P. 340536.

acids and their alkali metal salts, as auxiliary solvents and swelling bodies to place the fiber in condition of maximum dye receptivity. There is included aromatic hydrocarbons (benzene, toluene, cumene, propylbenzene, *o*-methylethylbenzene, mesitylene, diphenylmethane, naphthalene); paraffin hydrocarbons (heptane, triethylmethane, A-nonane, nonane); naphthene hydrocarbons from petroleum (cycloheptane, decanaphthene, tetradecanaphthene, undeca-, dodeca-, tetradeca-, pentadeca-naphthene, duodecylene); terpenes (pinene, sylvestrene); unsaturated hydrocarbons (butylethylene, methylcyclopentene, tetramethylethylene, cyclohexadiene, cyclopentene, cymene, 1.1.2-trimethylcyclopentene).

R. Metzger[1] dyes cellulose ether and ester silk with insoluble dyes in conjunction with a sulfonated mineral oil.

6. *Formaldehyde Condensates.* In solubilizing and dispersing insoluble or relatively insoluble coloring matters[2], use is made of sulfonated naphthalene-formaldehyde condensation products, in amounts less than 1% of the dyestuff. For instance, with a 10% paste of aminoanthraquinone, 0.25% of the above dispersing agent is said to be ample.

7. *Aliphatic Alcohols.* A combination of glycerol and ethyl alcohol[3], the former being 5-10% of the latter, and the use of glycerol or glycol on account of their combined hygroscopic and softening properties[4], are the bases of two patented processes for facilitating dye penetration. Glycerol esters, as mono- di- or tri-acetin (glyceryl acetates) are also efficient, and in general exert a greater swelling and solvent action on the cellulose ethers. Similar

1. U. S. P. 1738660; abst. C. A. 1930, **24**, 973; J. S. C. I. 1930, **49**, 944-B.

2. British Dyestuffs Corp., Ltd., J. Baddiley, A. Shepherdson, H. Swann, J. Hill and L. Lawrie, E. P. 246984, Addn. to E. P. 224077; abst. J. S. C. I. 1926, **45**, 317-B; Chem. Zentr. 1926, II, 2350. D. R. P. 453938; abst. Kunstseide, 1928, #1, 17; Chem. Zentr. 1928, I, 851.

3. Soc. Lyonnaise de Soie Artificielle and P. Chevalet, F. P. 621376; abst. Rayon, 1928, **6**, #1, 24.

4. J. Michael A. G. für Chemische & Metallurgische Industrie, F. P. 668369; abst. C. A. 1930, **24**, 1509; Cellulose, 1930, **1**, #4, 126.

in action[1] is the molasses or concentrated sulfite cellulose waste liquor proposed by R. Metzger, but the color and odor of the latter are decided drawbacks to its extended use for this purpose.

8. *Use of Direct Solvents.* Soluble thiocyanates associated with a water-soluble colloid[2], or formic, acetic, propionic, glycollic, or lactic acids, or such nitrogeneous bases as urea, urethanes, thiourea, thiourethanes and guanidines, are efficient, but all require a thickener in order to exert the penetration and softening uniformly and with minimum loss by evaporation where volatile acids are used[3].

Swelling and Softening Cellulose Ether Fibers. The softening and swelling of cellulose ether and organic cellulose ester fibers often are synonymous, swelling being advantageous in order to increase facility of penetration of dyestuffs and other materials in the cellulose derivative substance and to increase their absorptive capacity. Those cellulose ethers of not maximum etherification, especially the methyl- and ethyl-celluloses, are naturally more readily affected by aqueous reagents than those of maximum etherification, the sensitivity for water being in adverse ratio to the percentage of alkyl or aralkyl combined with the cellulose in ether form. Likewise, the receptivity of cellulose ethers and esters for solutions, whether aqueous or non-aqueous, may be considerably augmented by submission to a softening, colloiding or intumescing treatment in order to increase their capillary absorption. A softening operation applied to filaments often increases their elasticity and diminishes tendency to rupture during operations of transforming the individual filament into the finished textile, the softener acting as a direct lubricant to diminish friction.

1. U. S. P. 1666715; abst. C. A. 1928, **22**, 2067; J. S. C. I. 1928, **47**, 365-B. I. G. Farbenindustrie A.-G., E. P. 271550; abst. C. A. 1928, **22**, 1693; J. S. C. I. 1927, **46**, 553-B.
2. H. Kesseler and E. Döring, D. R. P. 444961; abst. J. S. C. I. 1928, **47**, 229-B.
3. H. Dreyfus, Can. P. 287598; abst. Chem. Zentr. 1932, I, 2646.

Softness or handle is usually a very desirable property in the artificial filament industry and textiles and fabrics prepared therefrom, and the impregnation of all types of cellulose derivatives with true sulfonic acids prepared from carboxylic acids of aliphatic substituted hydrocarbons containing more than eight carbon atoms or their salts is alleged to solve the problem[1]. The alkali salts (sodium, potassium and ammonium) of sulfonated palmitic, stearic, lauric and myristic acids are especially efficacious[2], such as sodium palmitosulfonate (sodium sulfopalmitate) and potassium stearosulfonate.

The properties of threads and textiles are improved by applying to, or incorporating with them derivatives of di- or poly-hydric alcohols in which some of the OH groups have been esterified by higher fatty acids. Glyceryl monooleate either alone or with lecithin is especially recommended[3]. Amides, alkylamides or substituted alkylamides of oleic, palmitic or other higher fatty acids are useful for lubricating, softening, finishing and otherwise improving the properties of textiles of cellulose derivatives[4], oleyl- and palmityl-dimethyl(or diethyl)ethylenediamine being particularized. Cellulose di- and poly-fatty acids as cellulose diacetic acid and its sodium salt have received patent protection as useful dressing agents for artificial silk[5].

Oily or resinous products suitable as softening agents[6] for cellulose ethers, as resins or "water-swelling substances" are obtained by prolonged heating of urea, thiourea, acetylurea or urethane with an excess of an alcohol or ketone such as benzyl alcohol or butylene glycol, ethyl

1. I. G. Farbenindustrie, E. P. 339858; abst. Silk J. 1931, **7**, #81, 49.
2. *Ibid.* E. P. 288612; abst. J. S. C. I. 1928, **47**, 865-B.
3. C. Dreyfus and W. Whitehead, U. S. P. 1872913. F. P. 715183; abst. C. A. 1932, **26**, 1803.
4. H. Dreyfus, F. P. 713183; abst. C. A. 1932, **26**, 1803.
5. I. G. Farbenindustrie, E. P. 317117; abst. C. A. 1930, **24**, 1992. D. R. P. 505629; abst. C. A. 1931, **25**, 606. Belg. P. 381313.
6. *Ibid.* E. P. 278390; abst. C. A. 1928, **22**, 2673; J. S. C. I. 1928, **47**, 648-B; Chem. Zentr. 1928, I, 864. Cites E. P. 209697; abst. C. A. 1924, **18**, 1759; J. S. C. I. 1924, **43**, 224-B.

alcohol, acetophenone, glycerol or the cyclic acetal produced by treating glycerol with acetaldehyde. The methyl acetal of ethyleneglycol has also been recommended as an efficient softener[1], as has a mixture of olive oil, olein, cocoanut fat, butter fat and earthnut oil[2]. The residues obtained by distilling ricinoleic acid (as the fatty acids obtained from castor oil)[3], either used alone or esterified, have been put forward as efficient softening and swelling bodies of etherified celluloses. Glyceryl 9.11-octadecadiene-1-acid is specified.

The pliability and softness of cellulose acetate and cellulose ether yarn may be enhanced so that it may satisfactorily be used in knitting fabrics, containing 60 or more courses per inch[4], by impregnating with a mixture of lubricating and softening agents dispersed in a suitable solvent. Suitable lubricants include castor, olive and neatsfoot oil and petroleum oils; softening agents include ethyl and butyl alcohols, benzyl alcohol and xylene. Usually, equal parts of lubricant, softener, and solvent are used. Artificial silk fibers may also be softened by impregnation with water-soluble products as oleyl- and stearyl-sarcosines, obtained from aliphatic primary or secondary aminocarboxylic acids by substituting a H atom attached to a N, by a saturated or unsaturated fatty acid of C_8 or above, impregnation being effected during dyeing or finishing[5]. Ammonium fatty sulfonate has been used as a cellulose ether softener[6].

Difficultly soluble thiazoles are excellent cellulose ether

1. Imperial Chemical Industries, Ltd., and W. Lawson, E. P. 318989.
2. Algemeene Kunstzijde Unie N. V., Swiss P. 140049; abst. Chem. Zentr. 1931, I, 388.
3. J. Scheiber, E. P. 316538. See E. P. 306452.
4. British Celanese, Ltd., E. P. 351084; abst. J. S. C. I. 1931, **50**, 802-B.
5. I. G. Farbenindustrie, E. P. 360982; abst. J. S. C. I. 1932, **51**, 226-B.
6. L. Lilienfeld, U. S. P. 1217028; abst. J. S. C. I. 1917, **36**, 383-A. F. P. 459972.

softeners[1], a mixture of benzylcellulose with mercaptobenzothiazole or 5-methylmercaptobenzothiazole and methylglycol acetate being described. The manufacture of water-soluble sulfonated products have been described[2], obtained by effecting reaction between an aromatic compound whether carbocyclic or heterocyclic, a sulfonating agent and a natural resin, yielding a soap said to have especially desirable softening effects on cellulose derivatives in the fiber or textile form. Tallow oil distilled at about 4 mm. pressure or less[3] is separable into two components, fatty acids and resin acids (?), which are said to impart a desirable softness and pliability to cellulose derivatives in the filament or woven condition.

H. Dreyfus[4] has described a softening treatment for cellulose ethers, comprising concentrating upon the ether a substance having a solvent or swelling action, but initially present in insufficient concentration to exert such action, removing the same from the filaments while the filaments are incipiently tacky[5], afterwards setting the filaments by evaporating the solvent or softener therefrom[6]. He softens cellulose ethers[7], specifying methyl-, ethyl- and benzyl-cellulose, by the use of ammonium cyanate, isocyanate and isothiocyanate in conjunction with urea, thiourea, urethanes and thiourethanes, or their alkyl or aralkyl substitution products. In another process for softening cellulosic materials[8], it is recommended to use chloroform in the vapor form as an ethylcellulose softener, or a mixture

1. I. G. Farbenindustrie, D. R. P. 537626; abst. C. A. 1932, **26**, 1439.
2. G. Ellis, H. Olpin and E. Kirk, Can. P. 324635, 324636.
3. Oel & Fett-Chemie, G. m. b. H., Aust. P. 118235.
4. E. P. 359971; abst. Textile Mfr. 1932, **58**, #688, 164. See E. P. 277089, 323790.
5. H. Dreyfus, E. P. 359975; abst. Textile Mfr. 1932, **58**, #688, 164.
6. *Ibid.* E. P. 359976; abst. Textile Mfr. 1932, **58**, #688, 164.
7. *Ibid.* F. P. 34391, Addn. to F. P. 634165; abst. C. A. 1929, **23**, 4581.
8. Soc. pour la Fabrication de la Soie "Rhodiaseta," F. P. 705359; abst. C. A. 1931, **25**, 5287. D. R. P. 508070; abst. C. A. 1931, **25**, 814; Chem. Zentr. 1930, II, 3104. Swiss P. 131560; abst. Chem. Zentr. 1929, II, 1755.

of nitromethane and dioxane for cellulose acetate, the process being applied especially to threads.

A finishing treatment for textile materials made of or containing a cellulose ether[1] comprises treatment with an albuminoid substance as gelatin or casein which has a high water retentivity, followed by hardening of the mixture by means of formaldehyde vapor[2]. The chemical compound of H. Bertsch for textile finishing[3] comprises a sulfonated castor oil admixed with butyric acid, whereby it is claimed no deleterious action arises due to splitting off of small amounts of sulfuric acid in use. In the lubrication of textile fibers or threads, materials of cellulose ether or ester composition treated with an oxidized semi-drying oil such as oxidized rapeseed oil[4], or a mixture of mono- or di-ethyleneglycol with glycerol[5], have been made the basis of patent issuance. A hygroscopic solid as sodium or potassium acetate with a cellulose ether plasticizer[6]; a chemically inert mineral oil with true mahogany sulfonate[7]; or treatment of the cellulose ether before dyeing with a softening agent comprising an amide or *N*-substituted amide (other than an oxyalkylamide), including a carboxylic acid containing more than 4-C atoms, and which is not a dye or dye component, are some of the colloiding and swelling agents recommended. Suitable compounds given are amides of lauric, myristic, stearic, palmitic and oleic acids[8].

1. G. Langdon, A. Flower and S. Fulton, E. P. 358593; abst. Silk J. 1932, **8**, #96, 50.
2. H. Chadwick, Amer. Dyestuff Reptr. 1931, **20**, 812; abst. C. A. 1932, **26**, 1448.
3. U. S. P. 1848819.
4. G. Lecomte, U. S. P. 1856713; abst. C. A. 1932, **26**, 3680.
5. W. Whitehead, U. S. P. 1852891. British Celanese, Ltd., S. Welch and R. Roberts, E. P. 365566; abst. J. S. C. I. 1932, **51**, 418-B.
6. British Celanese, Ltd., R. Roberts and S. Welch, E. P. 365621; abst. J. S. C. I. 1932, **51**, 338-B.
7. Twitchell Process Company, E. P. 349962; abst. Textile Mfr. 1931, **57**, #683, 419; Chem. Zentr. 1931, II, 3689. A. Reilly, U. S. P. 1794342; abst. J. S. C. I. 1931, **50**, 1137-B. D. R. P. 536886; abst. C. A. 1932, **26**, 1135.
8. British Celanese, Ltd., G. Ellis, H. Olpin and E. Kirk, E. P. 355726; abst. C. A. 1932, **26**, 4186.

To counteract the tendency of cellulose ether and acetate threads to show electrification phenomenon[1], it is desirable in the softening and treatment of such fibers and textiles, to choose a composition tending to counteract or offset this effect, as well as dress the fibers. These advantages are claimed to be overcome by using a dressing composition of an oxidizing semi-drying oil as oxidized cottonseed oil dissolved in heavy gasolene[2].

In the dyeing, printing or stencilling of cellulose ethers and esters in the yarn or fabric form, certain solubilizing agents having oily or fatty characteristics are indicated. G. Ellis and H. Dreyfus have listed the compounds determined by them as suitable for this purpose[3].

In the stiffening of fabrics composed of wool or cotton, a stiff fabric of methyl-, ethyl- or benzyl-cellulose is prepared[4], using yarns of high twist and preferably of 200-300 denier, by flowing, spraying or immersion of the cellulose ether fabric in a solvent or softener of the same, and this is applied to the fabric to be stiffened while still in the soft or tacky condition[5].

1. G. Lecomte, U. S. P. 1856713.
2. V. Freeland, Textile Mfr. 1931, **57**, 284; abst. C. A. 1932, **26**, 310.
3. Can. P. 293052. Suitable solubilizing agents specified are the higher fatty acids or sulfonated derivatives as sulforicinoleic acid or their alkali or ammonium salts; sulfobenzenestearic acid, sulfophenolstearic acid, sulfonaphthalenestearic acid, sulfonaphthalenericinoleic acid; tetrachlorethane, trichlorethylene, cyclohexane, heptane, triethylmethane, nonane, cresols, alkylanilines, toluidines, chlorphenols, chlorbenzenes, chlornaphthalenes, benzene, toluene, xylene, cumene, propylbenzene, *o*-methylethylbenzene, mesitylene, diphenylmethane, naphthalene, hexahydrophenol, hexahydrocresols, 1.4-hydrobenzene, decahydronaphthalene, dodecanaphthalene, tetradecanaphthalene, pentadecanaphthalene, duodecylene (occurring in Canadian petroleum), pinene, sylvestrene, butylethylene, methylcyclopentene, tetramethylethylene, cyclopentene, cymene and 1.1.2-trimethylcyclopentene.
4. C. Dreyfus, U. S. P. 1828397. Can. P. 311185.
5. See: N. White, Cotton, 1930, **94**, 575; abst. C. A. 1931, **25**, 596; Chem. Zentr. 1930, I, 3612. J. Anderson, Textile World, 1931, **80**, 1204; abst. C. A. 1931, **25**, 5995. J. Sterling, Textile World, 1932, **81**, 856. A. Hall, Textile Colorist, 1930, **52**, 809; abst. C. A. 1931, **25**, 1089. A. Tate, Melliand, 1930, **2**, 111; abst. C. A. 1930, **24**, 3376.

The I. G. Farbenindustrie[1] have discovered that hexahydroaniline or a substituted product constitute excellent swelling and softening agents for the cellulose ethers and esters, specifically hexahydroethyl-(or methyl)-aniline, hexahydro-*o*-(or -*m*-)toluidine, hexahydro-*m*-xylidine and hydrogenated 1.5-naphthylamine diamine, especially applicable in dyeing operations. Sulfobenzenestearic acid, sulfophenolstearic acid, sulfonaphthalenestearic acid, and sulfobenzene-, sulfophenol- and sulfonaphthalene-ricinoleic acids or their corresponding sodium salts are also useful dispersing and swelling agents[2]. If the cellulose ether or ester solution contains a common solvent, then the addition of animal and vegetable oils is recommended for incorporation, imparting in addition to a swelling effect, an enhanced toughness and pliability to the yarns so treated[3].

Another method which has been proposed for softening filaments, yarns and ribbons made of or containing the cellulose ethers or esters[4], is by treatment with 40% aqueous acetone for 10-60 min., and then stretching in from 2-5 stages with a rest period of about 5 sec. between, during which time the tension is released. The stretch at each stage is 15-20%. Swelling and dyeing may be accomplished in one operation by spraying upon the material a dye placed in solution in a solvent for the yarn or textile to be sprayed[5], or if differential effects are desired[6], a

1. E. P. 293766; abst. C. A. 1929, **23**, 1759; J. S. C. I. 1930, **49**, 185-B; Chem. Zentr. 1928, II, 2064. F. P. 656995; abst. C. A. 1929, **23**, 4351. D. R. P. 486696, Addn. to D. R. P. 439004; abst. C. A. 1930, **24**, 1521. See D. R. P. 445979. Schultz, "Farbstofftabellen" 6th Ed. 1923, #145.

2. British Celanese, Ltd., and G. Ellis, E. P. 280989; abst. Silk J. 1928, **4**, #47, 68; J. S. C. I. 1928, **47**, 85-B; C. A. 1928, **22**, 3537. U. S. P. 1686149; abst. J. S. C. I. 1928, **47**, 854-B. Can. P. 281189; abst. C. A. 1928, **22**, 3051. F. P. 637764; abst. C. A. 1929, **23**, 1290; Chem. Zentr. 1928, II, 2085.

3. British Celanese, Ltd., E. P. 359910; abst. Textile Mfr. 1932, **58**, #688, 164.

4. British Celanese, Ltd., H. Dreyfus and W. Taylor, E. P. 370430; abst. J. S. C. I. 1932, **51**, 638-B.

5. W. Whitehead, Can. P. 308605; abst. C. A. 1931, **25**, 1685.

6. C. Dreyfus and H. Platt, Can. P. 324631. Imperial Chemical Industries, Ltd., F. P. 713635.

portion only, depending upon the pattern effect, of the cellulose ether or ester is treated with ethanolamine, followed by a hot aqueous medium.

H. Dreyfus[1] has disclosed a method for the dyeing, printing or stencilling of fabrics of methyl-, ethyl- or benzyl-cellulose in which the following swelling agents are recommended as suitable: formic, acetic, glycollic or lactic acid; ethyl alcohol, acetone, diacetone alcohol, diacetin, phenol, hydroquinone or diethyldiphenyl urea. In the dyeing of organic cellulose derivatives[2], a dispersed dye may be used, provided the dye bath contains sufficient of a solvent for both the dye and the cellulose compound, a wetting or equalizing agent being also present.

Increasing Affinity for Dyestuffs. On account of their water-insolubility in the higher stages of etherification, the alkyl- and aralkyl-celluloses have but little affinity for dyestuffs, usually insufficient to produce shades of great depth, and therefore it is necessary to treat them in order to increase their affinity for, or receptivity to, organic coloring matters. One of the methods which have been proposed for effectuating this is the addition of water-soluble thiocyanates or zinc chloride, which exert a swelling and solvent action[3], another being a sulfurized phenol where aminoanthraquinone base dyes are used[4]. In the latter method sulfur is allowed to act upon phenol[5], and 5% of the products obtained is dissolved in the dye liquor. With *a*-aminoanthraquinone dissolved in concentrated sulfuric acid, bright orange tones are obtained; *b*-aminoanthraquinone gives a beautiful yellow; 1.4.5.8-tetra-aminoanthra-

1. E. P. 285942; abst. C. A. 1929, **23**, 288; J. S. C. I. 1928, **47**, 331-B; Chem. Zentr. 1928, I, 3117. See E. P. 280990; abst. Rayon, 1928, **6**, #5, 36. E. P. 284376. F. P. 642473; abst. C. A. 1929, **23**, 1286. F. P. 643323.
2. A. Fischesser, D. R. P. 547348; abst. C. A. 1932, **26**, 3679; Chem. Zentr. 1932, I, 3231.
3. I. G. Farbenindustrie, A.-G., F. P. 674761; abst. C. A. 1930, **24**, 2883.
4. R. Heidenreich, D. R. P. 473454; abst. C. A. 1929, **23**, 3110; Chem. Zentr. 1929, I, 2827.
5. See D. R. P. 348530.

quinone a blue; 1.4-diaminoanthraquinone a bright violet; and α-methylaminoanthraquinone a gorgeous red.

Ammonium, sodium, magnesium, calcium, zinc or aniline nitrates or chlorates, monomethylamine, dimethylamine, guanidine, pyridine or piperidine markedly increase the affinity of the cellulose ethers and esters for dyestuffs[1], being especially applicable with Methylene blue, Rhodulin red B, Saffranine, Auramine, Bismark brown, Rhodulin yellow, Rhodulin blue 6G (nitrate), Turquoise blue G, Rhodamine 6G, and Methylene blue F. Sulfonated naphthalene or condensation products of naphthalene with formaldehyde are said to markedly increase affinity of fibers of cellulose derivatives for dyestuffs[2], and likewise sodium dicresyl phosphate[3]. Hydroquinone or 2.5-dihydroxytoluene[4], cyanacetic acid[5], and phosphorous trichloride[6] have likewise been advocated.

H. Berthold and P. Rabe[7] have described the application of a series of hydrogenated carbocyclic bases having a benzene or naphthalene nucleus, the N atom being attached to a C atom in the nucleus, which greatly facilitates the dyeing of acetylcellulose without any harmful secondary effects. Such bases are hexahydromethylaniline, hexahy-

1. P. Rabe and W. Schepss, U. S. P. 1645450; abst. C. A. 1928, **22**, 171; J. S. C. I. 1927, **46**, 875-B. E. P. 216838; abst. J. S. C. I. 1925, **44**, 627-B; Chem. Zentr. 1924, II, 2789; C. A. 1925, **19**, 183. See E. P. 179384. D. R. P. 355533. P. Rabe, Textilber, 1928, **9**, 665; abst. J. S. C. I. 1929, **48**, 92-B. Farbenfabriken vorm. F. Bayer & Co., E. P. 215873; abst. C. A. 1924, **18**, 3481; J. S. C. I. 1925, **44**, 801-B.

2. J. Baddiley, A. Shepherdson, H. Swann, J. Hill and L. Lawrie, U. S. P. 1534019; abst. C. A. 1925, **19**, 1781. E. P. 246984; abst. C. A. 1927, **21**, 501; J. S. C. I. 1926, **45**, 317-B. Ital. P. 253044. See E. P. 4648, 1911; 7137, 1913; 211720. E. P. 224077; abst. C. A. 1925, **19**, 1202.

3. R. Metzger, U. S. P. 1532427; abst. Chem. Zentr. 1926, II, 351.

4. H. Dreyfus, F. P. 706620; abst. C. A. 1932, **26**, 317.

5. Lonza Electrizitätswerke und Chemische Fabriken A.-G., F. P. 713908; abst. C. A. 1932, **26**, 1802. Can. P. 316549.

6. Heberlein & Co., E. P. 261792; abst. C. A. 1927, **21**, 3752; J. S. C. I. 1927, **46**, 473-B; Silk J. 1927, **3**, #34, 71; Chem. Zentr. 1927, I, 2360. E. P. 261794; abst. J. S. C. I. 1927, **46**, 552-B; Chem. Zentr. 1927, I, 2357.

7. U. S. P. 1855278.

droethylaniline, hexahydrotoluidines, hexahydro-*o*-(and *m*-)toluidine, hexahydro-*m*-xylidine and hydrogenated naphthalenediamines as 1.5- and 1.7-naphthalenediamine. The amount added is 1-3% calculated on the amount of the bath. For example, sodium 1-amino-4-hexahydroanilidoanthraquinone-2-sulfonate with hexahydroaniline gives clear blue shades.

The R. Clavel processes[1] involve the addition of formic or acetic acids to increase dyestuff affinity, or certain salts as magnesium, zinc or stannous chloride, the cellulose derivative being suspended in a foam apparatus. J. Briggs and C. Palmer[2] use straight ammonium thiocyanate in a 10-15% aqueous solution, and M. Bouvier[3] a mixture of crystallized sodium sulfate and sodium carbonate.

Dyeing of Cellulose Ethers[4]. While the majority of the processes for dyeing the organic cellulose esters which do not involve a superficial saponifying treatment are applicable—and most of them equally so to the cellulose ethers, especially those of substantially maximum etherification, yet, on account of the fact that the cellulose organic esters

1. U. S. P. 1378443; abst. C. A. 1921, **15**, 3213; Chem. Zentr. 1921, IV, 518. E. P. 176535; abst. C. A. 1922, **16**, 2417; J. S. C. I. 1922, **41**, 276-A, 325-A; Caout. et Gutta. 1922, **19**, 11496; Chem. Tech. Uebers. 1922, **46**, 259. E. P. 182830, 182844; abst. J. S. C. I. 1922, **41**, 666-A. F. P. 528230; abst. Chim. et Ind. 1922, **8**, 879. F. P. 542892; abst. Chem. Zentr. 1923, II, 999. D. R. P. 355533; abst. Chem. Zentr. 1922, IV, 552; Chem. Tech. Uebers. 1922, **46**, 259. Swiss P. 92375. See E. P. 102310, 176535.

2. U. S. P. 1398357; abst. C. A. 1922, **16**, 836. E. P. 158340; abst. Chim. et Ind. 1922, **7**, 131; Caout. et Gutta. 1922, **19**, 11334.

3. U. S. P. 1489814; abst. C. A. 1924, **18**, 1914; J. S. C. I. 1924, **43**, 465-B.

4. For general data on dyeing of cellulose ethers and organic esters see: H. Brandenburger, Kunstseide, 1929, **2**, 98, 144; abst. C. A. 1929, **23**, 4575; Kunstseide, 1929, **2**, 300, 338, 425, 459; abst. C. A. 1930, **24**, 1985. Melliand Textilber. 1929, **10**, 215; abst. C. A. 1929, **23**, 4575. Jentgen's Rayon Rev. 1930, **2**, 78, 122, 186, 209; abst. C. A. 1930, **24**, 550. Kunstseide, 1930, **12**, 140; abst. C. A. 1930, **24**, 5501. Kunstseide, 1930, **12**, 173, 223; abst. C. A. 1931, **25**, 209. Kunstseide, 1930, **12**, 267; abst. C. A. 1931, **25**, 1677. Rayon and Rayon J. 1930, **10**, #12, 10. Jentgen's Rayon Rev. 1930, **2**, #6, 250. E. Greenhalgh, Silk J. 1927, **4**, #42, 53. C. Keyworth, J. Soc. Dyers Col. 1927, **43**, #11, 343. H. Remaek, Rayon J. 1926, **1**, #4, 29; abst. C. A. 1926, **20**, 2908. J. Reynolds, Textile Colorist, 1927, **49**, 687; abst. C. A. 1928, **22**, 1044. E. Robertson, Rayon Record, 1930, **4**, 479;

as the acetylcelluloses are better known that the cellulose ethers, the illustrative examples for exemplifying the specific process usually read upon the organic cellulose esters. The following processes for dyeing filaments, yarns and fabrics made therefrom are especially for employment with the etherized celluloses.

L. Lilienfeld[1] deposited in the Austrian Patent Office on June 13, 1921, a document outlining methods for the dyeing of alkylcelluloses which are water-insoluble, by the use of substantive (direct dyeing), acid, vat or sulfur dyestuffs to any desired shade of color by proceeding as follows: The alkylcellulose compound in filament, textile or film form must be insoluble in water at 16° and above, but may swell in water below that temperature, particularly below 10°. In dyeing, water is allowed to act upon the alkylcelluloses at a temperature at which they swell to some extent but do not disintegrate or dissolve, and the swollen filaments or articles are treated in this condition with dyestuffs in the usual manner. The temperature of the water used for swelling the alkylcellulose will depend upon the degree of etherification of the cellulose and the alkyl introduced. Thus, if an ethylcellulose which swells in water at 5-8° but dissolves in water below 5° is to be dyed, then water at 5-8° is used for swelling. The time allotted to the swelling operation depends upon the thickness of the

abst. C. A. 1930, **24**, 4161. W. Weltzien, Kolloid Zts. 1930, **52**, 110; abst. J. S. C. I. 1930, **49**, 815-B. H. Müller, U. S. P. 1717242; abst. C. A. 1929, **23**, 3817. Farbenfabriken vorm. F. Bayer & Co., E. P. 215373. British Dyestuffs Corp., Ltd., W. Perkins and C. Hollins, E. P. 244267. Chem. Works formerly Sandoz, E. P. 306877, 323011. F. P. 663053. Imperial Chemical Industries, Ltd., F. Lodge and W. Tatum, E. P. 322576, 323026. F. P. 682268, 716208. I. G. Farbenindustrie, A.-G., D. R. P. 439004. H. Dreyfus, Belg. P. 356606. H. Dreyfus, G. Ellis and W. Miller, Belg. P. 363782.

1. E. P. 181391; abst. C. A. 1922, **16**, 3763; J. S. C. I. 1923, **42**, 1127-A; Ann. Rep. S. C. I. 1923, **8**, 174; Chem. Zentr. 1922, IV, 841; Caout. et Gutta. 1023, **20**, 11687. E. P. 181394; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1923, **42**, 1126-A; Caout. et Gutta. 1923, **20**, 11687; Chem. Zentr. 1922, IV, 771. F. P. 552769; abst. Chem. Zentr. 1924, I, 2742; J. Soc. Dyers, 1923, **39**, 231; Chim. et Ind. 1923, **10**, 944. Aust. P. 97660. Can. P. 249774.

filament, textile or film, with thin fibers or filaments a few minutes sufficing in ordinary circumstances.

By way of example, an article made from a methyl or ethyl ether of cellulose soluble in water at 5-8° and below, but insoluble in water above 8°, will preferably be swelled in water at 10-12°, while an article manufactured from an alkylcellulose only slightly swelling in water at 9-10°, but distinctly swelling in water between 5-8°, and disintegrating in water at 1-5°, should preferably be soaked in water at 5-8°.

On Nov. 30th of the same year (1921) H. Dreyfus deposited in the British Patent Office a statement of the results of his experiments in the dyeing of the cellulose ethers, including the aralkyl ethers (benzylcellulose) as well as the alkylcelluloses limited by the Lilienfeld process. In spite of the well-known water-repellent properties of these fibers, especially when prepared from cellulose ethers of the higher stages of etherification, especially of methylcellulose, ethylcellulose and benzylcellulose, and though the OH groups in the cellulose molecule suffer steric hindrance by virtue of the etherifying groups present, such materials may be dyed in the usual manner by means of direct cotton and also acid dyestuffs[1] in a neutral bath such as Nigrosine B, Alizarine Astrol B, Azo Yellow 3G, and Orange II, the fastness of the shades being improved when necessary by an after-treatment of the dyed materials with solutions containing copper or chromium salts; ice colors and colors produced by oxidation of amino compounds on the fiber, such as Aniline Black and Paramine Brown[2]; basic dyestuffs (no mordant being necessary) as Magenta, Malachite Green, Methyl Violet, Thioflavine T, and Methylene Blue

1. H. Dreyfus, E. P. 196952; abst. C. A. 1923, **17**, 3794; J. S. C. I. 1923, **42**, 713-A; J. Text. Inst. 1923, **14**, 204-A; J. Soc. Dyers, 1923, **39**, 291; Chem. Zentr. 1923, IV, 619; Faserstoffe, 1924, **6**, 10. F. P. 558917; Chem. Zentr. 1924, I, 1109.

2. *Ibid.* E. P. 196953; abst. C. A. 1923, **17**, 3794; J. S. C. I. 1923, **42**, 713-A; J. Text. Inst. 1923, **14**, A-204; J. Soc. Dyers, 1923, **39**, 291; Faserstoffe, 1924, **6**, 10; Chem. Zentr. 1923, IV, 619.

B[1]; and vat dyestuffs of the indigo and anthraquinone series[2]. The affinity of the cellulose ethers for basic and acid dyestuffs is good, and when dyeing is carried out in an acid or alkaline bath, no hydrolysis of the cellulose ether takes place under the usual conditions of dyeing.

The following quantitative examples illustrate the carrying out of the process:

1. *Congo Red.* The cellulose ether material may be dyed in a bath containing, relative to the weight of the goods, about 1% of Congo Red and 20% sodium chloride, with water in amount of 15-25 times the weight of the goods. The dyeing may be performed at ordinary temperatures, but preferably at about 60° and the bath raised gradually to the boil, boiling being continued until the desired shade is obtained. The goods are then washed and dried.

2. *Diazo Fast Black.* The goods are dyed in a bath containing about 1% by weight of the dyestuff and 15-20% of their weight of common salt. Dyeing temperatures as before.

3. *Nigrosine B.* The bath should be 15-25 times the weight of water of the goods and containing 1% of dyestuff, 15-20% sodium sulfate, operation of heating as before.

4. *Alizarine Astrole B.* Similar to Ex. 3, using similar quantities of dyestuff and Glauber's salt.

5. *Azo Yellow 3G, or Rocelline, or Orange II.* The goods are dyed in a dyebath of about 15-25 times their weight containing about 1% of either dyestuff. It is preferable to enter the goods at 45-50° and the temperature slowly raised to 60-70°, and after the desired depth of color has been obtained, the cellulose ether material is rinsed and dried, preferably at relatively low temperatures.

6. *Indigo.* A stock solution is prepared of 5 kilos 20% indigo paste. 10 liters water, 875 gms. hydrosulfite powder

1. H. Dreyfus, E. P. 196954; abst. C. A. 1923, **17**, 3794; J.S.C.I. 1923, **42**, 713-A; J. Soc. Dyers, 1923, **39**, 291; J. Text. Inst. 1923, **14**, A-204; Faserstoffe, 1924, **6**, 10; Chem. Zentr. 1923, IV, 619.

2. *Ibid.* E. P. 197281; abst. C. A. 1923, **17**, 3794; J. S. C. I 1923, **42**, 713-A; Chem. Zentr. 1923, IV, 619; Faserstoffe, 1924, **6**, 10.

and 3 liters NaOH solution 40.5° Be, and reducing by heating. A dye vat is made up with the required quantity of the stock solution, after first treating the water of the dye vat with a small quantity of hydrosulfite powder. The cellulose ether filaments or fabrics are dipped or otherwise impregnated with the vat at 50° and the color developed by oxidation in the air. The goods are then washed successively with water and hot soap solution, and finally well washed with water.

Yarns, fabrics or films of ethylcellulose and other cellulose ethers[1] may be dyed, printed or stencilled with an aqueous dispersion of an insoluble or relatively insoluble coloring matter prepared by pretreating the color with a dispersing agent such as sodium, potassium or ammonium sulforicinoleate, carbocyclic compounds containing in their structure one or more salt forming group as naphthenic acids or other carboxylic or sulfonic acids of the cycloparaffins, phenols or phenolsulfonic acids or salts. Secondary or auxiliary solvents include tetrachlorethane, trichlorethylene, cyclohexane, heptane, triethylmethane, A-nonane, nonane, chlorphenols, chlornaphthalenes, benzene, toluene, xylene, cumene, propylbenzene, *o*-methylethylbenzene, mesitylene, diphenylmethane, naphthalene, hexahydrophenol, hexahydrocresols, 1.4-hydrobenzene, decahydronaphthalene, decanaphthene, undeca-, dodeca-, pentadeca-, and hexadecanaphthene, duodecylene, turpentine, pinene, sylvestrene, butylethylene, methylcyclopentene, tetramethylethylene, cyclopentene, 1.1.2-trimethylcyclopentene and amylethylene.

The process is said to be especially applicable in the dispersion of highly insoluble colors which would otherwise require excessive quantities of oily or fatty bodies for their dispersion and practical application, examples of such highly insoluble coloring materials which are suitable being azo- and polyazo-compounds, anthraquinone and indigoid derivatives and nitrodiarylamine compounds. The latter

1. H. Dreyfus, E. P. 285104; abst. C. A. 1928, **22**, 4834; J.S.C.I. 1928, **47**, 364-B; Chem. Zentr. 1928, I, 2874. See E. P. 196952, 196953, 196954, 197281.

include 2.4-dinitrobenzeneazo-*b*-naphthol, *p*-nitrobenzeneazo-*p*-naphthol, benzeneazobenzeneazo-*b*-naphthol, *sym*-di-*p*-tolyl-1.4- diaminoanthraquinone, 1-hydroxy-4-p-tolyaminoanthraquinone, pyridone, 2.4-dinitrodiphenylamine, di-*p*-methoxybenzoyldiaminoanthrarufin, and the unreduced, so-called vat colors.

Cellulose ethers may also be dyed by coloring with an azo dyestuff obtainable by coupling *p*-cresol with a diazo-compound of the benzene series containing an alkoxyl group in *p*-position to the diazo group[1]. Dyeing is said to be unusually fast to light. The following examples are illustrative:

1. 4-5 parts 4′-methoxy-2-oxy-5-methylazobenzene are dissolved in 1000 parts finished nitrocellulose varnish. When the solution thus obtained is coated in thin layers on a support (metal, glass, silk, celluloid) a transparent covering is left on drying, the intensely pure yellow color of which is fast to light. By incorporating pigments and lakes a matt appearance is obtainable.

2. 10 parts 4′-ethoxy-2-oxy-5-methylazobenzene are mixed with a suitable dispersing agent as sulfite cellulose liquor and stirred to a uniform paste of 20% strength. One part of this paste is intimately mixed with 10 parts water at 50° and with sufficient of a concentrated soap solution of 0.2% strength. The whole is then diluted with cold water to about 300 parts. In the emulsion thus prepared, 10 parts yarn are entered and handled for 45 min. at 75°. The artificial silk is then rinsed and brightened as usual. There are obtained vivid green-yellow dyeings of very good fastness.

The Farbenfabriken vorm. F. Bayer & Co.[2] have described a method for dyeing the cellulose ethers with special reference to ethylcellulose, with basic dyestuffs by means

1. Soc. Chem. Industry in Basle, E. P. 344884; abst. C. A. 1932, **26**, 317; J. S. C. I. 1931, **50**, 674-B. E. P. 263579, 269934, 271898. F. P. 685956; abst. Chem. Zentr. 1931, I, 527.

2. E. Schnabel and H. Bruns, D. R. P. 365078; abst. J. S. C. I. 1923, **42**, 264-A; Ann. Rep. S. C. I. 1923, **8**, 174; Chem. Zentr. 1923, II, 338; Chem. Tech. Uebers, 1923, **47**, 47.

of organic solvents especially the aminoanthraquinones, giving excellent fastness to light. Their process is synopsized in the following examples:

1. To a solution of ethylcellulose (cellulose ethylate) in benzene is added to the amount of 0.8% of the dry content of the solution, 1-amino-2-brom-4-*p*-toluidoanthraquinone, likewise dissolved in benzene. After evaporation of the solvent there results vivid blue, perfectly transparent objects of exceptional light stability.

2. Instead of the anthraquinone product in Ex. 1, 0.5% of 1.4-diamino-2.3 phenoxyanthraquinone is added to the ethylcellulose solution, a violet-red, transparent coloration forming upon evaporation of the solution to dryness.

3. Instead of the color in Ex. 1, 0.5% of 1.4-di-*p*-toluidoanthraquinone is applied, a pure green, transparent solution resulting, which yields transparent, highly colored films upon evaporation.

Instead of applying the invention solely to the cellulose ethers in solution, the ethylcellulose may be swollen in any appropriate manner to increase its dye receptivity, and a solution of the dyestuff in a non-solvent of the cellulose ether applied, giving similar effects without the cellulose ether passing into solution.

In a patent published under the auspices of the I. G. Farbenindustrie[1] in 1927, is described the production of a dyestuff especially designed for the coloration of the cellulose acetates, by the addition of ammonium thiocyanate to the dyebath. It was further found[2] that the cellulose ethers likewise, especially the benzylated celluloses, also dyed heavy shades when this salt or other water-soluble thiocyanate was a component of the dye-bath. Also bases which have been diazotized show good results after treatment with soluble thiocyanates. The following examples indicate the trend of the method:

1. I. G. Farbenindustrie, E. Müller and A. Schaeffer, D. R. P. 438378; abst. Chem. Zentr. 1927, I, 1216; Silk J. 1928, **5**, #52, 53.
2. E. Müller, D. R. P. 453215, Addn. to D. R. P. 438378; abst. Chem. Zentr. 1928, I, 754; Die Kunstseide, 1928, #1, 16; J. S. C. I. 1927, **46**, 964-B.

1. One kilo benzylcellulose is placed in a dye-bath of 20-25 liters in which 20 gms. Malachite Green (Schultz-Julius, 5th Ed., No. 631) and 500 gms. ammonium thiocyanate are in solution, and treated at 50°. The mixture is slowly heated and dyed for 1 hr. at 70-75° and then dried.

2. One kilo benzylcellulose is further treated in a dye-bath of 20-25 liters in which 20 gms. Chromium Blue BMI (Schultz-Julius No. 141) and 300 gms. ammonium sulfate are made soluble, held at a temperature of 50° and treated in the above manner.

3. One kilo benzylcellulose is placed in a bath with 20-25 liters of water in which 30 gms. dianisidine and 300 gms. ammonium sulfate are dissolved, and the bath heated to 70-75° for 45 min. The benzylcellulose is then diazotized and developed with resorcinol, washed and dried.

Identification Tints. In the textile industry, the application of a fugitive dye to fabrics is frequently resorted to in practice for the purpose of conferring on the fibers a temporary coloration to enable fibers of a different nature to be distinguished one from another, or the textile fibers of the same nature but possessing different characteristics as variations in grade, torsion or direction of twist, this temporary coloration and means of identification being removed when the time is deemed suitable.

Similitude in the appearance of threads of varying composition necessitates some distinctive marking as otherwise the thread is apt to cause confusion and give rise to mixtures or substitutions which are more objectionable than the threads of different chemical nature of varying physical properties, especially as to dye receptivity, and different susceptibilities to other methods of treatment[1].

It is proposed to overcome this objection in various

1. G. Lardy, U. S. P. 1693759; abst. C. A. 1929, **23**, 996. Soc. pour la Fabrication de la Soie Rhodiaseta, E. P. 251580; abst. J. S. C. I. 1926, **45**, 975-B; Rev. Gen. Mat. Plast, 1927, #1, 45; Chem. Zentr. 1927, I, 1251. D. R. P. 480899; abst. C. A. 1929, **23**, 5048; Chem. Zentr. 1929, II, 1993. F. P. 597394; abst. Chem. Zentr. 1926, I, 1743. Swiss P. 123891; abst. Chem. Zentr. 1928, I, 2147. Swiss P. 131327.

ways, one process being to apply colorations to the fibers before their assemblage into threads, or upon the threads during the process of spinning or winding. Employment of color in solution, emulsion or paste is distributed by means of a roller or other suitable manner. In another method[1], solutions of dyestuffs in liquids of boiling points above 100° are employed for the temporary coloration of textile filaments and yarns of cellulose ethers and esters, regenerated cellulose and cotton, such liquids being ethyleneglycol (b. pt. 197.5°), diethyleneglycol (b. pt. 135.5°), diethyleneglycol monoethyl ether (187.5°) and the corresponding di-ethers. Certain of the above liquids are also applicable for lubricating or softening of the fabrics and fibers prior to such textile operations as winding, cap spinning, ring spinning, flyer spinning and hanking.

Also applicable are tinting fluids comprising coloring matters in an oil or sulfonated oil with or without water[2], for temporary colorations. The process is applicable to cellulose ether filaments and yarns, suitable oils being non-drying animal or vegetable oils, as neatsfoot, castor, cottonseed or olive, or Turkey red oil or sulfonated olive oil. Fugitive colors for temporary identification may also be applied by using a dyestuff having no affinity for the fiber and the application of a lubricating liquid[3]. Acid Green G, Acid Red 3B with colloidal olive oil and soft water are examples. The lubricating agent may be a light mineral oil as a spindle oil, a heavy mineral oil or an animal or vegetable oil. The treatment is effected by immersing hanks of the yarn in one liquid and then in the other, or may be applied to yarn passing from one package to another[4].

Where cloths are woven constructed of cellulose ether

1. British Celanese, Ltd., E. P. 308173; abst. C. A. 1930, **24**, 247; J. S. C. I. 1930, **49**, 1062-B; Silk J. 1929, **6**, #62, 70; Chem. Zentr. 1929, II, 657. W. Whitehead, Can. P. 317113.

2. *Ibid.* E. P. 308733, Addn. to E. P. 282036, 308173; abst. C. A. 1930, **24**, 510; J. S. C. I. 1930, **49**, 1063-B; Silk J. 1929, **6**, #62, 72; Chem. Zentr. 1929, II, 657.

3. *Ibid.* E. P. 350056; abst. J. S. C. I. 1931, **50**, 838-B; Textile Mfr. 1931, **57**, #683, 420; Silk J. 1931, **8**, #91, 54.

4. R. Simmonds, Can. P. 301872. O. Gunnell, U. S. P. 1677475.

or ester yarns and those of viscose (regenerated cellulose), acid colors must be used which do not stain viscose under scouring conditions[1].

Direct Dyes. The majority of the direct or substantive cotton dyes have no affinity for cellulose ether or ester filaments, or at least not sufficient affinity to be commercial successes in this field, although certain members of the acid and mordant classes of colors when applied by the direct method have been found satisfactory in a limited sense. Among the direct cotton dyes which have been found suitable are the sodium salt of diphenyldisazobisresorcinol (Pyramidol Brown 3G), sodium *p*-nitrobenzenedisazoaminosulfobenzenylaminothiocresol (Orange G and Paramine Orange R), sodium *p*-sulfobenzeneazo-*m*-phenylenediamineazosalicylate (Paramine Brown G), and sodium benzeneazo-3.6-disulfo-8-amino-1-naphthol-7-azodiphenylazo-*m*-phenylenediamine (Chlorazol Black E).

In a patented process[2], direct dyeing is effected with or without the use of a dispersing agent as of Turkey-red oil, with products formed from mono-, di- or poly-aminoanthraquinones or their substitution products except sulfonic acids, by complete acylation with non-aromatic acyl groups followed by nitration, or with the compounds formed by hydrolyzing or reducing such products. Thus, dinitro-*b*-acetamidoanthraquinone dyes acetylcellulose brown, as do 2-nitro- and 4-nitro-anthraquinonylurethanes. It is claimed[3] that cellulose acetate products may be dyed by means of direct cotton dyestuffs after treatment for 0.25-2 hrs. at 50-70° in an aqueous solution containing 1 kilo barium hydroxide and 1 kilo barium chloride per 100 liters.

To correct or overcome the lack of affinity of cellulose

1. H. Chadwick, Dyer, Calico Printer, 1931, **65**, 677; abst. C. A. 1931, **25**, 5295.

2. British Dyestuffs Corp., Ltd., W. Perkin and C. Hollins, E. P. 244267; abst. C. A. 1927, **21**, 330; J. S. C. I. 1926, **45**, 124-B; Chem. Zentr. 1926, I, 2970. See E. P. 224077; abst. C. A. 1925, **19**, 1202.

3. Teinturerie de La Rize, F. P. 590738; abst. J. S. C. I. 1926, **45**, 154-B; Chem. Zentr. 1926, I, 242. Farberci de la Rize, F. P. 590733; abst. Rayon, 1927, **5**, #6, 24.

ethers for substantive and acid dyes[1], L. Lilienfeld claims that if a definite (as to composition) alkylcellulose is produced, specifically that variety of class which is insoluble in water at 16° or above, but which under 10° is capable of swelling or even dissolving in water, artificial filaments may be prepared therefrom which may be directly dyed with substantive dyestuffs, or with vat and sulfur dyes. Such an alkylcellulose (especially an ethylcellulose) is dissolved in suitable solvents or solvent mixtures as benzene, alcohol, benzene-alcohol, trichlorethylene-alcohol, chloroform-alcohol, and then spun in the usual manner. Such fibers are dyed in the usual manner with direct dyestuffs, the pertinent point being that the alkylcellulose will swell sufficiently in the water to enable sufficient penetration of dyestuff.

Water-soluble dyes suitable for the coloration of organic cellulose derivatives[2] are obtained from many acid dyes by converting their sulfonic acid groups into sulfonamide groups (e.g., by successive treatment with phosphorous pentachloride and ammonia) or alternatively, by synthesis of dyes of the acid type from compounds containing sulfonamide groups. Reddish-orange and orange dyes are obtained by coupling diazotized aniline with 1-naphthol-3.8-disulfonamide or 1.8-naphthasultam.

A method has been evolved for mixing an organic cellulose derivative in solution with 5-20% nitrocellulose and then spinning, the nitrocellulose (along with some acetylcellulose) being denitrated by a saponification treatment. The product, of course, being regenerated cellulose, will dye with the substantive colors[3]. H. Blackshaw[4] has discussed

1. Aust. P. 96996. See Aust. P. 94837, 96997.
2. R. Horsfall, L. Lawrie and J. Henderson, U. S. P. 1759010; abst. C. A. 1930, **24**, 3656; J. S. C. I. 1930, **49**, 657-B. E. P. 257654; abst. C. A. 1927, **21**, 3134; J. S. C. I. 1926, **45**, 976-B; Chem. Zentr. 1927, I, 1217. D. R. P. 479224; abst. C. A. 1929, **23**, 4831; Chem. Zentr. 1929, II, 2506.
3. Soc. Anon. Pour L'Ind Chim. A Bale, E. P. 268363; abst. C. A. 1928, **22**, 1243; J. S. C. I. 1928, **47**, 706-B; Chem. Zentr. 1927, II, 747. Swiss P. 121531.
4. Dyer & Calico Printer, 1926, **55**, 130, 192, 205, 225; abst. C. A. 1926, **20**, 3817.

the methods for dyeing mixed acetylcellulose and viscose filaments.

In dyeing with cotton dyestuffs, it is recommended to start the bath cold and raise the temperature to a maximum of 80° in 0.5 hr. dyeing for a like period, using 10-30% common salt or Glauber's salt in the dye-bath.

Fastness to Washing. Washed with water at 40°, the water-soluble or direct dyes for cellulose ethers or esters are most fugitive, while the dispersed dyes are nearly as fast as the ionamines and developed dyes[1]. When the filaments are washed with 1% soap solution at 40° for 15 min., the direct dyes are then nearly as fast as the developed dyestuffs, the dispersed dyes being more fugacious. The Celliton, Celliton Fast, Cibacet and Duranol series of the dispersoid dyes show a satisfactory resistance.

Basic Dyestuffs. In different cellulose acetates is found a considerable variation in their ability to color with basic dyestuffs. R. Dort[2] has pointed out some of these differences as applied to Celanese acetate silk, especially in connection with the relative fastness. From the information at present available, it appears the cellulose ethers, especially ethylcellulose of high alkylation and benzylcellulose, are much more amenable to dyeing with the basic dyestuffs in general. The cellulose ethers have a lower interfacial tension against neutral or acid aqueous solutions than do the acetylated celluloses, and also are readily swelled and wetted out. The application of basic dyes in conjunction with an intumescing agent is the usual procedure for obtaining heavy shades with basic dyes, whether direct or upon a mordant base. It is essential that any colloiding treatment applied to increase the porosity and dye receptivity of the cellulose ether should be so applied that the swelling of the fibers is uniform, otherwise level dyeings are difficult to obtain. The usual precautions in applying

1. H. Brandenburger, Rayon, 1929, **8**, #8, 16; abst. C. A. 1930, **24**, 242.
2. Amer. Dyestuff Rept. 1926, **15**, 258.

basic dyes hold with the cellulose ethers. In general, if the degree of etherification is such that there is a distinct swelling of the etherized cellulose in water of 16° or higher or lower, there is found to be increased penetrativeness of the basic dye in proportion as the cellulose ether is affected by water, either hot or cold.

Where the dyestuff is difficult to dissolve, it should be made into paste form by means of the addition of formic or acetic acids, glycol or glycerol, or by some liquid which exerts a swelling or solvent action upon the cellulose ether, the nature or proportion of swelling agent used depending upon the cellulose ether employed and the degree of etherification to which it has been subjected. This, in general, is the opposite with the acetylated celluloses, wherein great care must be employed in the selection of a wetting out agent to insure that it has little or no colloiding effect upon the cellulose ester. With etherized cellulose, triacetin is an excellent combined solvent for cellulose ether and dyestuff, and an admirable wetting out agent.

According to P. Rabe[1], Diamond Fuchsine, China Green, Methylene Blue or Rhoduline Heliotrope B may be used for the dyeing of acidyl cellulose as cellulose acetate, if pyridine, methylpyridine or aminopyridine is present in the dyebath. After dyeing the pyridine is removed by formic or acetic acids. It is claimed[2] that the dyeing and printing of acetylcellulose may be effected by coloring agents such as Auramine, Martius Yellow or Malachite Green in the presence of arylcarbolic anions which may be supplied by sodium *o*-cresotinate, benzoic acid or 2-hydroxy*iso*naphthalic acid.

According to I. G. Farbenindustrie[3], clear shades are obtained by the use of phenols (phenol, naphthols, resorcinol, cresolsulfonic acids) in printing or fixing pastes with

1. U. S. P. 1517581. Farbenfabriken v. F. Bayer & Co., E. P. 215373.
2. H. Hoz, W. Bernoulli and A. Link, U. S. P. 1650275. E. P. 231897.
3. E. P. 308780. D. R. P. 441327; abst. J. S. C. I. 1927, **46**, 905-B.

basic colors, addition of tannin with tartar emetic being unnecessary. In the dyeing of basic dyestuffs[1], cellulose acetate in calcium thiocyanate solution has been patented.

Organic cellulose derivatives, as has been demonstrated by R. Clavel[2], are dyed directly in aqueous solution or suspension with non-sulfonated or mono-sulfonated soluble or insoluble dyes containing one or more the following "active" groups: hydroxyl, amino, imino, imide, nitro, nitroso, isonitroso, acylamino or azo groups. When a sulfonic group is present the dye must contain at least two "active" groups. Carboxyl groups may be present or not. Either acid, basic or substantive dyes, or vat dyes of the indigo or anthracene series may be used. Salts which form double salts with dyes as magnesium, stannous or zinc chlorides may be present in the dyebath when basic dyes are employed, or the basic dyes may be used in the form of such double salts.

Dyeing with Volatile Solvents. The major portion of the solvent methods for dyeing are probably now obsolete, having been replaced by processes in which the receptiveness of the cellulose ether or ester is increased either by the addition of swelling or softening agents in order to augment the porosity of the fiber, or else by the use of dispersion and emulsifying agents or emulsions as aids to penetrativeness. And as the use of solvents, colloiding bodies, aids to swelling and porosity-inducing compounds imperceptibly blend one into the other insofar as effect on the fibers is concerned, there is no clear cut line of demarcation between them, many dyeing processes utilizing one or more bodies which assist in the dyeing operation by virtue of the fact that they change the physical structure of the cellulose derivative—usually by temporarily swelling the same —whereby penetration of dyestuff is made easier and more rapid.

1. Farbenfabr. vorm. F. Bayer & Co., D. R. P. 347276; abst. J. S. C. I. 1922, **41**, 325-A.
2. E. P. 182830. U. S. P. 1448432, 1517709. Ital. P. 210113, 210114.

In one process[1] a mixture of alcohol and water is recommended for the dyeing of acetyl silk with methylene blue; in another[2] fuchsin is described as being dyed in a mixture of acetone and water; while glycerol or glycol[3] is the basis of solvent dyeing in another patented method. P. Rabe[4] uses pyridine with water for diamond fuchsine dyeings, methylpyridine or aminopyridine being equally efficient, while the use of ethylene chlorhydrin or epichlorhydrin is the essence of another disclosure[5]. Methyl Violet 6B, China Green base or Alizarin Geronal base are indicated, all being soluble in either of the above solvents.

Ethylene dichloride, dichlorethylene or tri- or perchlorethylene form the subject matter of a British Celanese, Ltd., procedure adapted for working with cellulose ether filaments[6], to which methyl-, ethyl-, propyl-, butyl- or amylalcohols may be added. Recommended are certain dyestuffs of the anthraquinone series, as 1.4-oxyaminoanthraquinone, 1-methylaminoanthraquinone or *p*-nitrobenzeneazodimethylaniline. Glycol acetates, glyceryl acetates or mono-, di- or tri-propionin, or glycerylpropyl ethers[7] have also been brought forward for this purpose. It is said that more satisfactory results are to be obtained by the use of relatively difficultly volatile solvents such as the di-ether of diethylene glycol[8]. The use of *p*-dihydroxybenzene as a cellulose ether solvent in connection with dyeing and printing[9] to increase dyestuff penetration, and cyclohexane, heptane, triethylmethane, nonane, cresols, propylbenzene, *o*-

1. Akt. Ges. fur Anilin Fabrikation, D. R. P. 193135. C. Abel, E. P. 1931, 1906.
2. Knoll & Co., F. P. 383636. D. R. P. 199559. E. P. 24284, 1907. U. S. P. 961241.
3. Furst Guido Donnersmarch'sche Kunstseiden und Acetatwerke, D. R. P. 228867.
4. U. S. P. 1517581.
5. Farbenfabriken vorm. F. Bayer & Co., E. P. 214246; abst. C. A. 1924, **18**, 2610; Chem. Age (London), 1924, **10**, 653.
6. E. P. 282036; abst. C. A. 1928, **22**, 3787; J. S. C. I. 1929, **48**, 169-B. W. Whitehead, U. S. P. 1738978.
7. British Celanese, Ltd., E. P. 313450; abst. C. A. 1930, **24**, 1227. F. P. 653555. Can. P. 305536.
8. *Ibid.* E. P. 313451. Can. P. 312666.
9. British Celanese, Ltd., and G. Ellis, E. P. 346694.

methylethylbenzene, mesitylene, diphenylmethane, hexahydrophenol and 1.4-hydrobenzene[1] have been described specifically for use in conjunction with the cellulose ethers in dyeing, printing and stencilling.

G. Lacroix[2] dissolves benzeneazophenylmethylpyrazolone, hexahydroxyanthraquinone or Algol Brilliant Violet 2B in trichlorethylene, tetra- and penta-chlorethane, chlorbenzene, chlortoluenes, turpentine or tetra- or deca-hydronaphthalin, with addition of soap, the mixture after sieving constituting the dye-bath. L. Levy employs straight acetone[3], or acetone containing a small proportion of water[4].

Dyeing with Volatile Colors. Certain dyes capable of yielding colorations on textiles containing organic derivatives of cellulose[5], and which do not contain sulfonic groups, are more or less volatile under the influence of heat, especially in the presence of a gas or vapor. This property has been utilized by British Celanese, Ltd., to produce colored effects. They apply directly to the filament or fabric colors volatilized by means of heat, as by injection of hot steam at moderate pressure through a solution or colloidal suspension of the dye, using an ordinary air-pressure lacquer spray or analogous mechanism. Suitable colors for this purpose are 4-nitrobenzeneazo-*p*-xylidine (orange), 2-nitro-4-chlor-4'-methyldiphenylamine (golden yellow), 4-nitro-2-methoxybenzeneazodimethylaniline (red), or 4-nitro-2-methoxybenzeneazodiethylaniline (red). The methyl-, ethyl- or benzyl-celluloses are susceptible to this treatment.

Dyeing Cellulose Ethers with Lakes. Cellulose ethers may be dyed by means of mineral colors, from which varnishes, enamels, lacquers and solid masses may be prepared, by means of lakes which are substantially insoluble in water. Thus, a solution of cellulose ether in acetone is

1. H. Dreyfus, U. S. P. 1883351.
2. F. P. 603123; abst. J. S. C. I. 1927, **46**, 964-B.
3. E. P. 227146; abst. C. A. 1925, **19**, 2751.
4. E. P. 251680. Can. P. 279966.
5. British Celanese, Ltd., E. P. 349683; abst. J. S. C. I. 1931, **50**, 923-B; Chem. Zentr. 1931, II, 2936.

first colored with eosine, and to the homogeneous solution there is added with stirring, a slight excess of lead acetate dissolved in water. When the addition has been completed stirring is continued so as to obtain a uniform mass. The red colored cellulose derivative is then precipitated, washed and dried, and may afterwards be dissolved in solvents to a clear, red solution[1].

Dyeing and Printing with Vat Dyes. In the usual process of printing fabrics with vat dyestuffs, the dye is thickened by means of a starch or gum solution and then printed with the addition of an alkali and a sulfoxylate. In order to fix the dyestuff, the material is steamed after printing and then washed and finished. While this process is suitable for material printed on the usual machines, in hand or stencilling printing difficulties arise as it is often not possible to print and steam in one day, and if the material is allowed to remain for a considerable time before being steamed, the sulfoxylate decomposes in the thinly printed layer so that a reduction during the steaming operation cannot take place, the dyestuff being fixed on the fiber only imperfectly.

It is claimed these disadvantages may be obviated by mixing the dye intimately with a water-soluble cellulose ether[2], and treating the godos before steaming, with a solution of a reducing agent as sulfoxylate, whereby the dyestuff does not bleed into the unprinted parts. After printing, the material is treated with the reducing agent and alkali necessary for fixing the dyestuff and then steamed, artistic printing effects being obtainable which cannot be produced in the same style on an ordinary fabric printing machine.

The following examples illustrate the process:

1. Societe Chimique des Usines du Rhone and M. Theumann, E. P. 294137, Addn. to E. P. 275553; abst. C. A. 1929, **23**, 2046; J. S. C. I. 1928, **47**, 783-B. M. Theumann, U. S. P. 1789122; abst. C. A. 1931, **25**, 1101.

2. E. Pfeffer, U. S. P. 1710007. I. G. Farbenindustrie, A.-G., E. P. 279864, 304787, 314904.

1. The printing color is 200 gms. black vat dyestuff[1] in 100 gms. water and 700 gms. "Thickening M," the latter being 1 of methylcellulose dissolved in 9 of cold water. After printing the material is padded with a mixture of 2 gms. Rongalite C, 8 gms. glycerol, 3 gms. "Dissolving Salt B," 12 gms. potassium carbonate and 57 gms. water. The material is then dried and steamed 5 min. with wet steam at 101° in a rapid-ager (Mather-Platt), freed from air, finally washed and soaped at the boil.

2. The material is printed with the black vat dyestuff as before, with acetone and "Thickening A," which is 8 ethylcellulose dissolved in 92 of acetone, and then treated as indicated in Ex. 1.

3. The material is printed with dye in paste form[2] with an equal weight of benzene and alcohol added, and 7 times as much "Thickening B," which is ethylcellulose 8, dissolved in 46 each alcohol and benzene. After printing the material is padded and finished as indicated in Ex. 1.

In printing with a mixture of vat dye and cellulose ether thickening agent[3], the mixture is used in a colloidal state and coagulated by alkali. Thus, goods are printed with a paste made of a vat dye, cellulose ether, sodium benzylanilinesulfonate and water. The print is then slop-padded with an aqueous solution containing sodium formaldehydesulfoxylate, glycerol, *iso*butylnaphthalenesulfonic acid, sodium sulfate and soda. It has been found that vat dyes can be printed next to aniline black when they are applied thickened with cellulose ethers[4], or a reducing agent may be added to the printing color[5].

The process is illustrated as follows:

1. The printing color is composed of yellow vat dye[6],

1. Kalle and Co., D. R. P. 241997.
2. R. Bohn, U. S. P. 753659.
3. E. Pfeffer, E. Fischer and I. G. Farbenindustrie, A.-G., D. R. P. 495712, 525182. Cites D. R. P. 451411.
4. E. Pfeffer and I. G. Farbenindustrie, A.-G., D. R. P. 534641.
5. R. Haller and F. Kurzweil, D. R. P. 408414; abst. Chem. Zentr. 1925, I, 1654.
6. G. Kränzlein, M. Corell and R. Sedlmayr, D. R. P. 412053; abst. Chem. Zentr. 1925, I, 2663.

water and Thickener M (which in this instance is stated to be composed of methylcellulose dry 75, water 925), the printing color for aniline black being 84 gms. aniline salt, 5 gms. aniline oil, 600 gms. thickener M, 25 gms. sodium chlorate, 50 gms. potassium ferrocyanide and 236 gms. water. After the printing the goods are steamed 1 min. at 95°, and then for fixing of the vat dye, is slop-padded in a solution of 100 gms. hydrosulfite conc. powder, 747 gms. cold water, 150 cc. 40° Be. NaOH solution and 3 gms. mordant. Finally, without drying, it is briefly steamed about 15 seconds at 95-98° on rolls, rinsed, weakly acidified, rinsed and soaped while boiling. In order to increase penetration in piece goods dyeing[1] by automatically promoting bleeding or running, emulsions of agents having an emulsifying effect are introduced, especially an alkali salt of carboxymethyl cellulose, obtained by condensing an alkalicellulose with chloracetic acid[2]. Although no wetting properties can be attributed to the carboxyalkylcelluloses, they nevertheless produce good penetration in the dyeing.

In dyeing with vat dyestuffs[3], resist effects may readily be produced by printing upon the material an oxidizing agent as sodium *m*-nitrobenzenesulfonate or sodium bichromate in an aqueous solution of alkylcellulose. Printing colors thus prepared can readily be applied and yield good resist effects because the alkylcelluloses are completely precipitated on the fiber even by a small proportion of alkali, particularly owing to the high temperature of the vat liquor.

The following example illustrates the invention:

A resist paste is prepared with 250 gms. aqueous methylcellulose (15% strength), stirred with 250 gms. cold water, and 250 gms. sodium *m*-nitrobenzenesulfonate in 250 gms. water added. The paste is printed on the goods which are then dried and dyed at 75° with the following mixture: 80 gms. 5.7.5′.7′-tetrabromindigo paste 20% strength, 900

1. I. G. Farbenindustrie, A.-G., E. P. 305230; abst. C. A. 1929, **23**, 4830. F. P. 668638; abst. C. A. 1930, **24**, 1749.
2. *Ibid.* E. P. 317117.
3. *Ibid.* E. P. 290177; abst. C. A. 1929, **23**, 994.

gms. hot water, 40 gms. NaOH solution 40° Be., 16 gms. Turkey red oil 50%, and 16 gms. hydrosulfite conc., the material, after being dyed, is washed, soaped and dried.

R. Clavel[1] dyes materials of cellulose derivatives with vat or sulfur dyes in hyposulfite vats kept weakly alkaline by ammonia, only sufficient alkali being present to form the leuco compound; preferably salts such as barium, calcium or magnesium chlorides and protective colloids as boiled-off liquor, gelatin, glucose or starch being added to the vat. Bromindigo and Pyrogenindigo are suitable colors.

Textiles of or containing cellulose ethers are dyed with vat dyes by applying the leuco compounds by means of a medium of relatively low alkalinity as 2-8 parts alkali for 5 of dye[2], an example being: to treat methylcellulose filaments or tissue for 1 hr. at 75° with 5% Anthrene B (bluish-green) in a bath at 40° containing 1-10 gms. hydrosulfite to 2 gms. sodium carbonate, the tissue being afterwards oxidized in the usual manner. A bluish-green color is obtained very resistant to light and washing.

Vat dyes of the anthraquinone series as Indanthrene, Cibanone, or Algol, may be solubilized and used for dyeing fabrics of either cellulose ethers or acetylcellulose. Example, 1 lb. Algol Pink R is incorporated with 9-10 lbs. 50% aqueous sodium ricinoleate previously heated to 90°, and the heating continued until the requisite degree of solubilization has been attained. The resulting mass is diluted with boiling soap solution (3 lb. neutral soap in 8-10 gals. water), well mixed, and added to a dye-bath containing 300-500 gals. soft water. 100 lbs. cellulose derivative yarn are introduced into the bath and dyed in the usual manner[3]. Solvents or swelling agents for the cellulose compound as

1. E. P. 191553; abst. C. A. 1923, **17**, 3103. F. P. 542940. Can. P. 236696. See also E. P. 182830.
2. C. Dreyfus, F. P. 698269; abst. C. A. 1931, **25**, 3176.
3. British Celanese, Ltd., and G. Ellis, E. P. 227183, Addn. to 219349. G. Ellis, U. S. P. 1618413, 1641965. Can. P. 249159. Ital. P. 254320. Belg. P. 346286.

ethylene dichloride may be incorporated in the paste[1], discharge effects being obtained by subsequent printing of a paste containing formaldehyde-sulfoxylate or other reducing agent and a leucotrope, and thereafter steaming to effect the discharge. If colored discharges are desired, a dyestuff is incorporated in the paste which is unaffected by the discharging agent.

In coloring textiles by vatting methods[2], the vats are maintained at temperatures below the atmosphere (about 0-10°), the process being said to be particularly suitable for coloring materials of cellulose acetate, and to a lesser degree those made of cellulose ethers. In the coloration of textiles made of cellulose ethers, cellulose acetate or cellulose propionate[3], vat dyestuffs are applied containing inorganic alkali and of an alkalinity not exceeding 3 gms. per liter Na_2CO_3, and containing an amount of hydrosulfite not less than 3 times the weight of dyestuff present. The use of Anthrene Jade Green is recommended.

In dyeing or printing acetylcellulose fabrics with vat dyes[4], the alkalis usually employed are replaced by salts of aromatic hydroxy-derivatives such as potassium or sodium phenates, cresolates, xylenolates, catecholates, resorcinolates, guaiacolates, quinolates, *a*- and *b*-naphtholates or sodium *p*-chlorphenate or di-sodium leucoanthraquinonate. For instance, Ciba Scarlet G (acenaphthylene indigo) gives bright scarlet; 44′-dimethyl-55′-dichlor-77′-dimethoxy-22′-bisthionaphthene indigo (thioindigo violet 2B), reddish-violet; Indanthrene Red-violet RRK, bluish-red; Thionol Direct Blue S, dull blue; Indanthrene Pink B, rose; 3.3′-dichlor-*N*-dihydro-1.2.1′.2′-anthraquinoneazine (Duranthene Blue GCD), bright green; Caledon Jade Green, bright green.

1. British Celanese, Ltd., E. P. 295579; abst. C. A. 1929, **23**, 2305.
2. British Celanese, Ltd., and G. Ellis, E. P. 347682. F. P. 708160.
3. British Celanese, Ltd., E. P. 360449.
4. British Celanese, Ltd., and G. Ellis, E. P. 262506. G. Ellis, U. S. P. 1716720.

Cellulose ether or ester silk is dyed with the free leuco-compounds of vat or sulfide dyes or of aminoanthraquinones in aqueous suspension[1], and the color developed by oxidation with air, black liquor, soap and sodium perborate, and especially with soap and hydrogen dioxide. Examples are Ciba Blue G, 1-benzamido-4-hydroxyanthraquinone, indophenol from *p*-aminodimethylaniline and *α*-naphthol. Instead of free alkali[2], the alkali salt of a high molecular weight fatty acid, as sodium stearate may be used. Cellulose ether or ester goods may also be dyed from a hyposulfite vat without hydrolysis by means of quinone arylides of the benzene or naphthalene series or thiazines or oxazines[3]. In dyeing with enolic ethereal salts of vat dyes[4], the material is padded with enolic ethereal salt at a raised temperature and the dyeings developed after drying without requiring steaming. Soledon Jade Green is especially applicable. The addition of a salt is preferable[5], development being with sodium nitrate, ferric chloride or/and HCl[6].

In dyeing and printing cellulose ether and ester fabrics with vat dyes[7], there is applied to the fiber a solution of an ester salt or a leuco vat dye, followed by drying and steaming in order to fix the ester salt on the fiber, and the dyeing then developed by acid oxidation[8]. Details of dyeing and printing cellulose ether and ester filaments and fabrics, together with dyeing directions and formulas, have been

1. British Celanese, Ltd., G. Ellis, H. Olpin and R. Storey, E. P. 341408. G. Ellis, H. Olpin and E. Walker, Can. P. 281192.
2. J. Leitch & Co., Ltd., A. Everest and J. Wallwork, E. P. 274550.
3. British Dyestuffs Corp., Ltd,. J. Baddiley and H. Browning, E. P. 233813. Ital. P. 269803.
4. J. Wilson, J. Thomas and Scottish Dyes, Ltd., E. P. 330253; abst. C. A. 1930, **24**, 6033.
5. *Ibid.* E. P. 330216; abst. C. A. 1930, **24**, 6033. U. S. P. 1448251.
6. Scottish Dyes, Ltd., F. P. 685351; abst. C. A. 1930, **24**, 6033.
7. G. de Niederhäusern, U. S. P. 1816766. Durand & Huguenin, Soc. Anon., E. P. 274094. F. P. Addn. 33853 to F. P. 571264.
8. W. Hentrich, M. Hardtmann and H. Metzl, U. S. P. 1832208.

supplied by A. Schneevoigt[1], H. Franke[2], C. Mullin[3], and H. Burns and J. Wood[4].

Dyestuffs for Cellulose Ethers and Esters. Under this topical heading are arranged under the respective firm names, certain representative dyestuffs and their methods of formation in brief summation, without respect to methods of application, tinctorial properties or dyeing formulas, as indicative of the range of colors found applicable in this field, this topic in nowise overlapping the specific methods of dye application for the various organic cellulose derivatives recorded elsewhere in this Chapter. For facility of classification and reference, they are grouped together in the following order:

1. *I. G. Farbenindustrie.* Anthraquinonylalanines are obtained by condensing aminoanthraquinones or their substitution products with a halogen propionic acid, preferably in the presence of a diluent and absorbent for acid[5]. The alkali salts of the products dye acetate silk. Examples are the condensation of *b*-chlorpropionic acid with 2-, or 1.4-di- or 1.4.5.8-tetra-aminoanthraquinone. Insoluble or difficultly insoluble dyes are preserved in a state of fine subdivision by incorporating methylcellulose with them[6], which may be added during or after the manufacture of the dye. Pastes obtained may be brought to dry, powdered form and used for making lakes or without a substratum as printing colors for paper.

p-Nitrodiazobenzene is coupled with 4-nitro-*m*-phenylenediamine[7], the product dyeing organic cellulose deriva-

1. Melliand's Textilber. 1926, **7**, 354; abst. C. A. 1927, **21**, 2801.
2. Deutsch. Faerber-Ztg., 1932, **68**, 85; abst. Chem. Zentr. 1932, I, 2240.
3. Can. Colorist Textile Processor, 1927, **7**, 190; abst. C. A. 1927, **21**, 4072.
4. J. Soc. Dyers Colourists, 1929, **45**, 12; abst. C. A. 1929, **23**, 2829.
5. E. P. 246840; abst. C. A. 1927, **21**, 500; J. S. C. I. 1927, **46**, 326-B; Chem. Zentr. 1926, II, 2949.
6. I. G. Farbenindustrie, A.-G., E. P. 269918; abst. C. A. 1928, **22**, 1480; J. S. C. I. 1928, **47**, 666-B; Chem. Zentr. 1927, II, 1096. Swiss P. 127223; abst. C. A. 1929, **23**, 1286.
7. *Ibid.* E. P. 270352; abst. J. S. C. I. 1928, **47**, 8-B. F. P. 633812; abst. C. A. 1928, **22**, 3785.

tives non-phototropic fast golden-yellow shades. By treating with a mixture of a diazotizable amine, coupling component and nitrite, and after wringing, developing the dye in an acid bath[1], a direct dye is produced as a color for acetylcellulose and other cellulose derivatives. Twenty-one examples are given. Hydroxyalkylated aminoanthraquinones are prepared by condensing a chlor-, nitro- or methoxy-anthraquinone, or a 1.4-dihydroxyanthraquinone (or its leuco-compound) with hydroxylated alkylamines (*b*-aminoethyl alcohol, 1-*b*-hydroxyethylaminoanthraquinone, 1.4-di-(*b*-hydroxyethylamino)-anthraquinone) and its 5-hydroxy-derivative (blue on acetate silk), and the product from leuco-1.4.5.8-tetrahydroxyanthraquinone (bluish-green on acetate silk)[2].

Naphthazarin is treated at 50-60° in presence of zinc dust or boric acid with an aliphatic amine[3]. Methylamine gives 2.8-di(methylamino)-5-hydroxy-1.4-naphthaquinone, m. pt. 248-252°, and 2.5.8-tri(methylamino)-1.4.-naphthaquinone, m. pt. 224-226°, separable by chlorbenzene. The triamino compound gives blue-green, or with *p*-nitraniline + *b*-hydroxyethyl-*m*-toluidine and 1.4-aminohydroxyanthraquinone, black shades on acetate silk. The diazo compound of a base as *m*-aminobenzenesulfonic acid methyl (or ethyl)phenylamide or 1-methyl-4-aminobenzene-2-sulfonic acid methylphenyltolylamine is coupled with a pyrazolone as 1-(4′-sulfophenyl)-3-methyl-5-pyrazolone[4]. Cellulose acetate dyes result.

Cellulose derivative dyes result when an *o*-phenylenediamine is condensed with an 8-acylamino-1.2-naphthaquinone-4- or -5-sulfonic acid. The acyl groups may be removed by dilute sulfuric acid, the sulfonic group by con-

1. I. G. Farbenindustrie, A.-G., E. P. 287651; abst. C. A. 1929, **23**, 524; J. S. C. I. 1928, **47**, 401-B.
2. *Ibid.* E. P. 289807; abst. J. S. C. I. 1929, **48**, 845-B. D. R. P. 499965; abst. C. A. 1930, **24**, 4639.
3. *Ibid.* E. P. 304804; abst. J. S. C. I. 1929, **48**, 317-B; Chem. Zentr. 1929, I, 2926. F. P. 655167; abst. C. A. 1929, **23**, 4083.
4. *Ibid.* E. P. 325229; abst. C. A. 1930, **24**, 4167. F. P. 660576; Chem. Zentr. 1930, I, 133.

centrated acid[1]; the amino group may be aroylated. From *o*-phenylenediamine and 8-acetamido-1.2-naphthaquinone-5-sulfonic acid are obtained 1-acetamido-*α*-naphthaphenazine-4-sulfonic acid. Desulfonated aminonaphthaphenazine dyes acetate silk. Cyclohexylamine is condensed with an aromatic nitro-derivative as 1-chlor-2.4-dinitrobenzene which contains a reactive halogen atom (HCl is split off and *N*-nitroarylcyclohexylamines result, dyeing acetate silk yellow shades[2].

Aminoanthraquinonecarboxylic amides containing a second auxochromic group and, if desired, a further amido group are synthesized[3], giving deep shades on acetate silk. Examples, 1-aminoanthraquinone-2-carboxylamide, m. pt. 288-289°, condensed with formaldehyde in concentrated sulfuric acid, nitrated, and the NO_2-compound, m. pt. 285-289°, reduced to 1.4-diaminoanthraquinone-2-carboxylamide (blue), also obtainable from 4-nitro-1-aminoanthraquinone-2-carboxyl chloride, m. pt. 238-239°, or from 1-amino-4-*p*-toluenesulfonamideanthraquinone-2-carboxylamide reduced to the 4-aminoamide (violet). 1.4-Diaminoanthraquinone-2-carboxylmethylamide (reddish blue) and -anilide (violet) from 1-amino-4-*p*-toluenesulfonamidoanthraquinonecarboxyl chloride.

Cellulose ether dyes are prepared by coupling aromatic diazo-compounds with aminonaphthols containing at least one sulfonamide group[4], water-soluble dyes for acetate silk being obtained. 5-8-Dihalo-1.2-benzanthraquinones are treated so as to replace the halogen by a group or groups of the formula XR, where X is S, O or NR′, R′ being H or a hydrocarbon radical, and R being H or a hydrocarbon radical[5]. Example, 5.8-di-monomethylamino)-1.2-benzan-

1. I. G. Farbenindustrie, A.-G., E. P. 328291; abst. J. S. C. I. 1930, **49**, 757-B; Chem. Zentr. 1930, II, 2311.
2. *Ibid.* E. P. 340495; abst. C. A. 1931, **25**, 5040. F. P. 684417; Chem. Zentr. 1931, I, 160.
3. *Ibid.* E. P. 350928; abst. J. S. C. I. 1931, **50**, 1004-B.
4. H. Schweitzer, D. R. P. 539114; abst. C. A. 1932, **26**, 1794. I. G. Farbenindustrie, A.-G., D. R. P. 546744.
5. P. Nawiasky and O. Chrzescinski, D. R. P. 533496; abst. C. A. 1932, **26**, 604.

thraquinone dyes acetate silk. Triarylmethane dyes are prepared by condensing an *o*-halogenated aromatic aldehyde with a primary aromatic amine[1], and oxidizing the leuco-base so obtained. With *o*-chlorbenzaldehyde and aniline, on tannin-mordanted acetylcellulose, red-blue to green-blue shades are obtained. Dyes varying from marine blue to black on cellulose ethers or esters result with 4-*p*-amino-arylazo-5.6.7.8-tetrahydronaphthylamines[2], being diazotized on the fiber and coupled with 2.3-hydroxynaphthoic acid to obtain the final color.

2. *Society of Chemical Industry, Basle.* Acetylcellulose dyes (yellow to brown tints) are obtained by coupling non-sulfonated nitrodiazo compounds other than those having an oxy group ortho to the diazo group[3], with monosulfonic acids capable of being coupled, derived from N-aryl, N-alkylaryl-, N-aralkyl- or N-alkylaralkyl-derivatives of aniline. The patent gives detailed tables showing tints produced on cellulose esters. Diazotized aniline[4], coupled with 1-*o*-chlorphenyl-3-methyl-5-pyrazolone, colors acetate silk yellow. 1-Arylamino-4-aminoanthraquinones which contain in the aryl nucleus at least one amino group or group derived therefrom[5], are made by condensing 1-hydroxy- or 1-alkoxy-4-aminoanthraquinone or a 1-4-diaminoanthraquinone with an aromatic diamine as phenylenediamine, naphthalenediamine or benzidine. Dye cellulose ethers blue.

Arylaminoanthraquinones are made by heating with boric acid and a primary aromatic amine the leuco derivative of a hydroxyanthraquinone[6], or of an amino or alkyl-

1. K. Schmidt, D. R. P. 487458; abst. C. A. 1930, **24**, 2302. Ital. P. 251367.
2. I. G. Farbenindustrie, A.-G., F. P. 703118; abst. C. A. 1931, **25**, 4409.
3. Soc. of Chemical Industry, Basle, E. P. 220303; abst. Soc. Dyers and Colourists, 1926, **42**, 64. See E. P. 20313, 1895.
4. *Ibid.* E. P. 256205; abst. J. S. C. I. 1927, **46**, 869-B.
5. O. Bally, P. Grossmann and F. Felix, U. S. P. 1856802; abst. C. A. 1932, **26**, 3677. E. P. 285096; abst. C. A. 1928, **22**, 4832; J. S. C. I. 1929, **48**, 674-B; Chem. Zentr. 1928, I, 3119. Soc. Anon. Pour L'Ind. Chim. A Bale, D. R. P. 501020; abst. C. A. 1930, **24**, 4639.
6. Soc. Anon. Pour L'Ind. Chim. A Bale, E. P. 338412; abst. C. A. 1931, **25**, 2302. F. P. 687039; abst. Chem. Zentr. 1930, II, 3860.

amino derivative, in aqueous solution or suspension. The reaction may be so conducted that any sulfonic groups present in the *b*-position are removed during condensation. The products are acid dyes for cellulose acetate, or if non-sulfonated, dissolve in cellulose acetate lacquers. In another process[1], a non-sulfonated *o*-aminophenol *o*-arylsulfonate, is diazotized and coupled with a non-sulfonated phenol or arylamine of the benzene series or an aniline-formaldehyde-bisulfite compound, the dye is hydrolyzed, then alkylated or acylated, to give products suitable for acetate silk dyeing. Examples are: *o*-aminophenyl toluene-*p*-sulfonate + aniline, hydrolyzed and acetylated, greenish yellow dyeings.

Diazo compounds are coupled in the 3-position with 4-hydroxy-1-naphthoic esters to give[2], according to the first component used, light-fast acid, mordant, lake, or cotton dyes or pigments for acetate silk. Examples of diazo compounds are: aniline (red), *p*-aminoacetanilid (bluish-red), *m*-aminobenzyl alcohol (red-orange), sulfanilic acid (red-orange), 4-chlor-*o*-aminophenol-6-sulfonic acid (chrome red-violet), and *b*-naphthylamine-1-sulfonic acid (red barium lake).

1-Nitroanthraquinones carrying in position-5 or -8 an arylamido or hydrogenated arylamido group[3], and in the other *a*-positions amido- or monoalkylamido- groups, are reduced, and if desired, the products are sulfonated, alkylated or acylated. 4.8-Dinitro-1.5-diaminoanthraquinone gives with aniline at 150-160°, 8-nitro-1.5-diamino-anilinoanthraquinone which on reduction yields 1.5.8-triamino-4-anilinoanthraquinone (blue or acetate silk); the technical mixture of dinitrodiaminoanthraquinones, freed from *b*-derivatives, gives the same final product. The corresponding 8-nitro-1.5-diamino-4-*p*-anisidino-, -4-*o*-anisidino-, -4-*p*-tolui-

1. Soc. Anon. pour L'Ind. Chim. A Bale, E. P. 343006; abst. J. S. C. I. 1931, **50**, 580-B. F. P. 683955; abst. Chem. Zentr. 1930, II, 2835.
2. *Ibid.* E. P. 343016; abst. J. S. C. I. 1931, **50**, 580-B; Chem. Zentr. 1931, II, 2941. F. P. 682841. D. R. P. 534566; abst. C. A. 1932, **26**, 1128.
3. *Ibid.* U. S. P. 1856802. E. P. 344117; abst. J. S. C. I. 1931, **50**, 623-B. F. P. 687299; abst. Chem. Zentr. 1930, II, 3858.

dino-, -4-*p*-chloranilino-, 4-(4'-methoxy-*m*-toluidino)-, and 4-cyclohexylaminoanthraquinone are similarly reduced. 1.5.8-Triamino-4-*p*-anisidino- and -4-*p*-toluidino- anthraquinones, give green blue shades on acetate silk. Acylated 1.5.8-triamino-4-anilinoanthraquinone dyes acetate silk blue.

A leuco-*a*-hydroxyanthraquinone (which may be produced *in situ*) is condensed in aqueous suspension or solution with ammonia or an alkyl- or aralkyl-amine in presence of boric acid[1]. *b*-Sulfonic groups are eliminated during reaction. 4.8-Diaminoanthrarufin-2.6-disulfonic acid with sodium thiosulfate, boric acid and aqueous ammonia gives 4.5.8-triamino-1-hydroxyanthraquinone (blue on acetate silk), 1.8-diamino-5-methylamino-4-hydroxyanthraquinone (green-blue), the corresponding 4.8.5.1-compound (red-blue), and a product from leuco-1.4.5.8-tetrahydroxyanthraquinone and *b*-hydroxyethylamine (blue-green).

Reaction products such as those formed by heating at 150-160°, aromatic amines as aniline or *p*-anisidine[2], with compounds such as (1.5- or 1.8-)diamino-(4.8- or 4.5-)dinitroanthraquinone, are subjected to careful reduction (as with sodium sulfide), thus obtaining dyes suitable for dyeing cellulose ethers blue to blue-green shades. Non-hydroxylated nitrodiazo compounds (e.g. those prepared from *m*-nitroaniline, 2.4-dinitroaniline, or 2.6-dichlor-4-nitroaniline) are combined with ethylbenzylanilinesulfonic acid or other aromatic monamine of the benzene series not derived from metanilic acid and substituted at the N-atom by a residue containing a benzene nucleus, only one of the components containing a sulfonic group. Ethylbenzylanilinesulfonic acid with diazotizing component of *m*-nitraniline (yellow), or with 2-chlor-4-nitraniline (pink), or with 2.4-dinitraniline (bluish-red on cellulose acetate). 2.6-Dichlor-

1. Soc. Anon. pour L'Ind. Chim. A Bale, E. P. 353932; abst. J. S. C. I. 1931, **50**, 1133-B; Chem. Zentr. 1931, II, 3161.

2. F. Ackermann and C. Apotheker, U. S. P. 1792348; abst. C. A. 1931, **25**, 2005; Chem. Zentr. 1931, I, 2808. F. P. 687299; abst. Chem. Zentr. 1930, II, 3859. G. de Montmollin and G. Bonhote, U. S. P. 1534506; abst. C. A. 1926, **20**, 508.

4-nitraniline coupled with diphenylaminesulfonic acid, orange; 4-nitraniline-2-sulfonic acid with methyldiphenylamine, reddish-brown; 2-nitraniline-4-sulfonic acid with diphenylamine, orange-red; 4-nitraniline-4-sulfonic acid with diphenylamine, orange-red; 2.4-dinitraniline with benzylanilinesulfonic acid, reddish-brown; and *m*-nitraniline with the same, yellow.

Azo dyes are prepared by union of diazotized ester salts of unsulfonated *o*-aminophenols with unsulfonated aromatic compounds containing hydroxyl or amido groups[1]. Aminophenol *p*-toluenesulfonate is diazotized in a solution of sodium anilinemethanesulfonate, the product is saponified and the dye obtained colors acetate silk yellow. A chromium-containing dye which colors acetate silk green shades[2] is obtained by chroming the reaction product of 1 mol. diazotized 5-nitro-2-aminophenol, 1 mol. 2-amino-5-hydroxynaphthalene-7-sulfonic acid and 1 mol. *p*-toluenesulfonyl chloride. Coupling diazotized 2-nitro-1-amino-4-methylbenzene with 3-methyl-5-pyrazolone gives an azo dye coloring cellulose esters and ethers yellow[3]. Acetate silk dyes are formed from action of benzaldehyde on 1.4.5.8-tetra-aminoanthraquinone, or 1.4-, 1.5- or 1.8-diaminoanthraquinone, 1-methylamino-4-amino-, 1-phenylamino-4-amino-, 1-amino-4(4′-aminophenylamino)-, 1.5-diamino-4-phenylamino-, 1.4-aminohydroxy-, or 5-chlor-1.4.-diaminoanthraquinone. They form water-soluble powders dyeing orange, red, violet or blue[4].

3. *Scottish Dyes, Ltd.* By nitrating a diphthalimidoanthraquinone as 1.5-diphthalimidoanthraquinone and then treating the product with an alkali sulfide and a hydrolyzing agent as sulfuric acid[5], dyes giving blue shades with

1. Soc. Anon. Pour L'Ind. Chim. A Bale, F. P. 683955; abst. C. A. 1930, **24**, 5164.
2. *Ibid.* Swiss P. 148117; abst. C. A. 1932, **26**, 2324.
3. *Ibid.* E. P. 282782; abst. Chem. Zentr. 1928, I, 2008. Swiss P. 127260; abst. C. A. 1929, **23**, 1281.
4. O. Bally and P. Grossmann, U. S. P. 1777953; abst. C. A. 1930, **24**, 6030.
5. E. Beckett and J. Thomas, U. S. P. 1711873; abst. C. A. 1929, **23**, 3353.

cellulose acetate result. Products dyeing cellulose ethers or esters and usable as vat dyes or pigments are made by reacting with ammonia or a primary amine of the benzene or naphthalene series on phthalic anhydride, phthalimide or the mono- or di-amide of phthalic acid in the presence of iron, nickel or copper[1] or their chloride, sulfate or sulfide.

Monosulfuric esters of anthrahydroquinones are prepared by way of mixed 9.10-diesters in which one ester group is a sulfuric ester and the other an acetyl, benzoyl or other acyl group, by first reducing the corresponding anthraquinone in the presence of a metal or tertiary organic base[2], treating the product with pyridine sulfate and an acylating agent for the formation of the sulfuric and acyl esters. They dye acetate silk with blue fluorescence. Acetylcellulose dyes as Duranol Orange G, Duranol Red 2B, are prepared by mixing aqueous pastes of the dyes with alkali soaps of higher fatty acids[3], and drying at not above 50°.

4. *Chemische Fabrik vorm. Sandoz.* In preparing dyes containing neither carboxyl or sulfonic groups suitable for dyeing cellulose esters[4], diazotized glycol-2-amino-4-nitrophenyl ether is coupled with an azo-component as *m*-toluidine, the dye being developed with *b*-naphthol. Instead of glycol, a glycerol radical may be used, as glyceryl-2-amino-4-nitrophenyl ether[5]. Dyes yellow, brilliant red and brownish shades.

5. *British Alizarine Co.* Anthrapyridone compounds are prepared by cyclisation of an *a*-acetamidoanthraquin-

1. A. Dandridge, H. Drescher, J. Thomas and Scottish Dyes, Ltd., E. P. 322169; abst. C. A. 1930, **24**, 2890.
2. D. Fairweather, J. Thomas and Scottish Dyes, Ltd., E. P. 332907; abst. C. A. 1931, **25**, 604; abst. Chem. Zentr. 1931, I, 3399.
3. J. Wilson, E. Beckett, J. Thomas and Scottish Dyes, Ltd., E. P. 333236; abst. C. A. 1931, **25**, 602; Chem. Zentr. 1930, II, 3338.
4. O. Knecht, U. S. P. 1711390; abst. C. A. 1929, **23**, 3106; Chem. Zentr. 1929, II, 2609; J. S. C. I. 1929, **48**, 512-B. E. P. 245758; abst. C. A. 1927, **21**, 328; J. S. C. I. 1927, **46**, 469-B; Chem. Zentr. 1926, II, 652. Swiss P. 120986, 120987, 120988, 120989, 120990, 120991, 120992, 120995.
5. *Ibid.* U. S. P. 1711391.

one, dye cellulose acetate in aqueous suspension[1]. The cyclisation is effected by boiling the acetyl compound with a large excess of dilute NaOH solution, or with water alone. Boiling 1.4-bisacetamidoanthraquinone 6 hrs. gives a bright red dye, and reddish-yellow, bright orange and blue dyes by cyclisation of diacetylamino-, 1.5-bisacetamido-, and 1.5-diamino-4.8-bisacetamido-anthraquinone.

Suitable cellulose ether or ester dyes are formed either by fusing citric acid with *p*-aminobenzeneazo-*b*-naphthol[2], or other suitable azo dye, containing one or more free primary amino groups but no sulfonic groups, or by fusing *p*-nitraniline with citric acid and converting the product into an azo dye. Yellow and orange-brown shades are produced.

Aminoanthraquinones and aminobenzanthrones are condensed with citric acid[3]. The product of 1.4-diaminoanthraquinone dyes acetylcellulose magenta. When citric acid is fused with unsulfonated indigo or thioindigo[4], dyes containing one or more free primary groups result. Thus, 77′-diaminothioindigo yields a product dyeing cellulose acetate violet-red.

6. *H. Dreyfus and British Celanese, Ltd.* 3.5-Dinitro-derivatives of *o*-toluidines, *o*-anisidines, or *o*-phenetidines are diazotized and coupled with non-sulfonated coupling components[5], particularly *a*-naphthylamines and their hydroxyalkyl-derivatives. The dyeings on acetate silk are readily discharged. Examples: 3.5-dinitro-*o*-anisidine + *N*-chlor-*b*-hydroxypropyl-*a*-naphthylamine (bright blue), or *a*-naphthylamine (yellow).

1. British Alizarine Co., Ltd., W. Dawson and C. Soutar, E. P. 263946; abst. C. A. 1928, **22**, 171; J. S. C. I. 1927, **46**, 211-B.
2. C. Barnard and British Alizarine Co., Ltd., E. P. 281114; abst. C. A. 1928, **22**, 3534; J. S. C. I. 1928, **47**, 83-B. E. P. 281213.
3. *Ibid.* E. P. 258960; abst. J. S. C. I. 1926, **45**, 974-B.
4. *Ibid.* E. P. 281213; abst. C. A. 1928, **22**, 3536; J. S. C. I. 1928, **47**, 83-B.
5. British Celanese, Ltd., D. Mosby, H. Olpin and G. Ellis, E. P. 319308; abst. C. A. 1930, **24**, 2609; J. S. C. I. 1930, **49**, 137-B; Chem. Zentr. 1930, I, 2803. H. Dreyfus, F. P. 675465; abst. C. A. 1930, **24**, 2890; Chem. Zentr. 1930, I, 3728. See F. P. 666626.

1-Phenyl-3-methyl-5-pyrazolone is coupled with a diazotized arylamine, already or subsequently containing a *p*-amido- or *p*-hydroxy-group, dyeing cellulose ethers. Thus, *p*-aminophenol (golden-yellow), *p*-phenylenediamine (orange), *p*-amidodimethylaniline (red), *p*-aminoacetanilide (golden-orange) and 4-dimethylamino-*m*-anisidine (red)[1]. For dyeing cellulose ethers or cellulose acetate[2], stilbene diazobisphenol, stilbene diazo-*m*-bistoluidine, stilbene disazobis-*a*-naphthylamine, aminostilbeneazo-*m*-phenylenediamine or aminostilbeneazo-*m*-toluidine is employed. Gold, red, reddish-brown, plum and black dyes result. Azo dyes are made by coupling diazotized 2.4-dinitro-6-alkoxy-, or alkyl-anilines or their derivatives with coupling components as *a*-naphthylamine and its derivatives[3], colors dyeing violet to blue shades on cellulose ethers and esters resulting.

ar-Tetrahydronaphthylamines are condensed with aromatic nitro-compounds containing reactive halogen, e.g., *ar*-tetrahydro-*a*-naphthylamine with 1-chlor-2.4-dinitrobenzene or its 6-sulfonic acid[4], or the *b*-amine with 1.4-dichlor-2-nitrobenzene, to give yellow dyes for acetate silk. Preferably sulfonic groups are absent. Diazotized amines of the benzene or naphthalene series are coupled with non-sulfonated hydroxyalkylated *a*-naphthylamines[5]; thus, chlor-*b*-hydroxy-*n*-propyl-1-naphthylamine with diazotized *p*-nitraniline (red-violet on acetate silk), 5-nitro-*o*-anisidine (violet), 5-nitro-*o*-phenetidine (violet), 4-amino-4′-dimethylaminoazobenzene (blue-red), and benzeneazo-*b*-naphthylamine (violet-grey).

1. British Celanese, Ltd., and G. Ellis, E. P. 350577; abst. J. S. C. I. 1931, **50**, 966-B; Chem. Zentr. 1932, I, 2390. See E. P. 346751.

2. *Ibid.* E. P. 253978; abst. C. A. 1927, **21**, 2565. H. Dreyfus, Can. P. 276512; abst. C. A. 1928, **22**, 2066.

3. D. Mosby, H. Olpin and G. Ellis, E. P. 319308; abst. C. A. 1930, **24**, 2609. G. Ellis, H. Olpin and E. Kirk, Can. P. 293071.

4. G. Ellis and H. Olpin, U. S. P. 1871673. British Celanese, Ltd., and H. Olpin, E. P. 330602; abst. J. S. C. I. 1930, **49**, 896-B. H. Dreyfus, F. P. 705161; abst. Chem. Zentr. 1931, II, 3274.

5. British Celanese, Ltd., G. Ellis, H. Olpin and D. Mosby, E. P. 343502; abst. J. S. C. I. 1931, **50**, 624-B; Chem. Zentr. 1931, I, 3295.

Basic anthraquinone derivatives are obtained by treating leucohydroxyanthraquinones or anthranols with ammonia or alkylamines in the presence of NaOH or other inorganic alkali, and oxidizing[1]. Thus, 1.2.5.8-tetrahydroanthraquinone is reduced and refluxed with methylamine and the resulting leuco compound oxidized with sodium perborate. Cellulose acetate is dyed greenish-blue. Cellulose ether dyed materials may have the dye extracted therefrom[2], by treatment with a solution of methylene chloride containing 2% acetone, which swells the cellulose ether and dissolves the dye. Dichlorethylene, trichlorethylene and perchlorethylene likewise are suitable.

Dyes are prepared by diazotizing aromatic compounds containing hydroxyl and/or amido groups[3], simple or substituted, and coupling with pyrazolones. Thus, *p*-aminobenzeneazo-1-phenyl-3-methyl-5-pyrazolone gives orange on cellulose acetate. An orange-gold shade on cellulose acetate is obtained from 2.4-dinitro-4′-aminodiphenylamine + phenol[4]. By submitting naphthazarin or its ring substitution derivatives to the action of ammonia[5], acetyl silk dyes result.

7. *Grasselli Dyestuff Corporation.* A monazo dye coloring cellulose esters bright, intense yellow is formed by coupling diazotized *p*-aminoacetanilide with *p*-cresol[6], but by treating hydroxyanthraquinones with ethylene chloride[7], dark crystalline compounds are formed dyeing cel-

1. H. Dreyfus, F. P. 667415; abst. C. A. 1930, **24**, 1226; Chem. Zentr. 1930, I, 596. Can. P. 295007. Belg. P. 356604, 357095, 357662, 360901, 360902.
2. W. Whitehead, U. S. P. 1839819; abst. C. A. 1932, **26**, 1454. U. S. P. 1791990; abst. C. A. 1931, **25**, 2007; Chem. Zentr. 1931, II, 1060.
3. H. Dreyfus, F. P. 709111; abst. C. A. 1932, **26**, 1127.
4. *Ibid.* F. P. 682202; abst. C. A. 1930, **24**, 4405; Chem. Zentr. 1930, II, 2833. Can. P. 295006. G. Ellis, H. Olpin and E. Kirk, Can. P. 324634.
5. *Ibid.* F. P. 679488; abst. C. A. 1930, **24**, 3907; Chem. Zentr. 1931, I, 166. Can. P. 293071.
6. E. Fischer and C. Müller, U. S. P. 1706484; abst. C. A. 1929, **23**, 2301.
7. R. Schmidt and R. Berliner, U. S. P. 1706498; abst. C. A. 1929, **23**, 2304; J. S. C. I. 1929, **48**, 891-B.

lulose acetate red to bluish-red shades. Water-soluble dinitroarylaminodiarylamines which yield fast tints on the cellulose ethers[1], are made by condensing *p*-aminodiphenylamine or its substitution products with an aromatic dinitrohalogen compound as 3.5-dinitro-4-chlorbenzoic acid, 2-chlor-3.5-dinitrobenzoic acid. The condensation may be effected in water, alcohol, pyridine or aniline. Brown dyes upon cellulose ethers with dyes of this type are possible when the sulfonic groups are eliminated, and when they contain at least 2 nitro and 1 carboxylate group[2].

Anthraquinone mercaptans react with alkylene halogenides (ethylene bromide) to form acetate silk dyestuffs[3], thus sodium 1-amino-4-*p*-tolylaminoanthraquinone-2-mercaptan and ethylenechlorhydrin give a dye of bronze-like luster. An alkylcellulose as methylcellulose[4] is incorporated with insoluble or difficultly soluble dyes at the time of their production or shortly thereafter to retain their state of fine dispersion or subdivision.

8. *General Aniline Works.* Dyes producing blue, violet to bluish-black shades on acetate silk are formed by coupling a diazo compound of a 2.4.6-trinitro-1-aminobenzene or substitution products with a sulfonic acid or the *N*-arkyl-, *N*-aryl- or *N*-aralkyl-anilines[5]. Dyeing cellulose ethers direct are compounds as 4-aminobenzylsulfonic acid, ammonium 5-nitro-2-aminobenzylsulfonate, 3.5-dinitro-2-aminobenzylsulfonic acid are diazotized and coupled with

1. H. Wagner, U. S. P. 1709292; abst. C. A. 1929, **23**, 2835; Chem. Zentr. 1929, II, 1852. I. G. Farbenindustrie, A.-G., E. P. 279133; abst. C. A. 1928, **22**, 2847; J. S. C. I. 1928, **47**, 516-B; Chem. Zentr. 1928, I, 756. F. P. 641832; abst. C. A. 1929, **23**, 1277. D. R. P. 504247; abst. C. A. 1930, **24**, 5506.

2. See E. P. 279135.

3. G. Kränzlein and M. Corell, U. S. P. 1710992; abst. J. S. C. I. 1929, **48**, 712-B. E. P. 263178. D. R. P. 472135; abst. Chem. Zentr. 1929, I, 2830. See D. R. P. 204772, 249225, 253507.

4. F. Risse and E. Fischer, U. S. P. 1719944; abst. C. A. 1929, **23**, 4347; J. S. C. I. 1929, **48**, 712-B. See U. S. P. 1730211.

5. W. Hentrich, U. S. P. 1732512; abst. C. A. 1930, **24**, 244; Chem. Zentr. 1930, I, 441. I. G. Farbenindustrie, A.-G., E. P. 295237; abst. C. A. 1929, **23**, 2301. F. P. 634620; abst. Chem.Zentr. 1928, I, 3117. W. Hentrich, D. R. P. 481265; abst. C. A. 1930, **24**, 245; Chem. Zentr. 1929, II, 2509.

diphenylamine, ethylbenzylaniline, ethyl-2-naphthylamine, methylbenzylaniline or hydroxyethyl-2-naphthylamine to form dyes producing yellow, orange, red, bordeaux or reddish violet[1].

Orange to red shades are produced on cellulose acetate by applying an unsulfonated azo dye derived from a diazotized *p*-amino-compound of the benzene series as diazotized *p*-nitroaniline or 3-nitro-4.1-toluidine and a monoethanolamino compound of the benzene series as monoethanolaniline or monoethanol-*m*-toluidine[2]. Orange shades result.

9. *British Dyestuffs Corporation.* By condensing 4.8-dihalogenanthrarufin or 4.8-dinitro-1.5-dichloranthraquinone with an aminobenzoic acid[3], direct dyeing acetyl silk dyes are formed. Thus 4.8-dichloranthrarufin and anthranilic acid dyes greenish-blue. Secondary diazo dyes which color cellulose ethers and esters brown are made by coupling a diazotized unsulfonated nitroamine of the benzene or naphthalene series with an unsulfonated amine[4], rediazotizing and coupling. Carbamides of the anthraquinone series containing 2 or 3 anthraquinonyl groups linked together by the chain -NH.CO.HN°/[5], and having affinity for cellulose acetate silk, are obtained by condensing *a*-anthraquinonyl carbamate or *a*-anthraquinonylcarbamic chloride with equimolecular proportions of *a*-anthraquinones or derivatives, preferably those having 2-amino groups in *a*-positions, such as 1.4-, 1.5-, or 1.8-diaminoanthraquinones, diaminoanthrarufin or diaminochrysazin. Thus, diamino-

1. W. Duisberg, U. S. P. 1757419; abst. C. A. 1930, **24**, 3379; Chem. Zentr. 1930, II, 2191. F. P. 611004; abst. Chem. Zentr. 1927, I, 364.

2. K. Meyer and C. Schuster, U. S. P. 1805919; abst. C. A. 1931, **25**, 3844. F. P. 600106; abst. Chem. Zentr. 1926, I, 2974. K. Schirmacher and K. Stenger, U. S. P. 1865062.

3. British Dyestuffs Corp., Ltd., J. Baddiley and W. Tatum, E. P. 227923; abst. Chem. Zentr. 1925, I, 2664.

4. British Dyestuffs Corp., Ltd., J. Baddiley and J. Hill, D. R. P. 513763; abst. C. A. 1931, **25**, 2003. E. P. 270428; abst. C. A. 1928, **22**, 1692; J. S. C. I. 1927, **46**, 518-B.

5. British Dyestuffs Corp., Ltd., W. Perkin and C. Hollins, E. P. 248858; abst. J. S. C. I. 1926, **45**, 398-B.

anthrarufin heated with *a*-anthraquinonylethyl carbamate forms a dye which colors cellulose acetate brown.

An anthraquinone derivative containing a primary amido group as 1.4-diaminoanthraquinone[1] or 1.5- or 1.8-diaminoanthraquinone is condensed in the presence of calcium chloride or iodine with *a*-aminoanthraquinone, *a*-diaminoanthraquinone, diaminoanthrarufin or diaminochrysazin, orange, brown to red shades are produced on acetylcellulose.

10. *Other Dyestuff Manufacturing Processes.* Cellulose ethers are dyed with anthraquinone-*b*-mercaptopropionic acid dyes, 5-chlor-1-anthraquinonyl-*b*-mercaptopropionic acid dyeing yellow, and 4-amino-1-anthraquinonyl-*b*-mercaptopropionic acid bluish-rose[2]. Diphenylmethane dyestuffs are condensed with phenylmethylpyrazolone, *b*-naphthol or nitromethane in aqueous solution[3], and the leuco-products subsequently oxidized. A dye giving fluorescent shades on acetylcellulose is obtained by condensing thiopyronine with phenylmethylpyrazolone in aqueous NaOH. Under similar conditions, golden-yellow with green fluorescence and red fluorescent dyes for cellulose acetate are obtained from Acridine Orange and phenylmethylpyrazolone and from thiopyronine and nitromethane.

Anthraquinone derivatives which dye cellulose acetate silk are prepared by the reaction of aminohydroxyanthraquinone sulfonic acids such as diaminoanthrarufin or diaminochrysazine or their derivatives with an aldehyde. Thus, sodium diaminoanthrarufin-2.6-disulfonate is dissolved in water and benzaldehyde and sodium tetrathionate added, the product obtained on heating, dyeing cellulose acetate blue[4]. Red and yellow shades on cellulose acetate result when 4-nitro-4′-aminodiphenyl sulfide is diazotized and coupled with sodium 2-naphthylamine-6-sulfonate, *b*-

1. Brit. Dyestuffs Corp., Ltd., W. Perkin and C. Hollins, E. P. 257353; abst. C. A. 1927, **21**, 3133.
2. H. Berthold, U. S. P. 1760806; abst. C. A. 1930, **24**, 3654.
3. G. Hugel, F. P. 589745; abst. J. S. C. I. 1926, **45**, 149-B.
4. Compagnie Nationale de Matieres Colorantes et Manufactures de Produits Chim. du Nord Reunies, F. P. 692927; abst. C. A. 1931, **25**, 1679.

naphthol-7-sulfonic acid, 2-amino-8-naphthol-6-sulfonic acid, 1-phenyl-3-methyl-5-pyrazolone or the like[1].

When the mono-oxamic acid of the monosulfide (4-*p*-aminophenylthiol-phenyloxamic acid) is stirred with *m*-phenylenediamine, a dye results coloring cellulose acetate brown[2]. The diazo-compound of 4-aminodiphenyl-sulfide-4′-oxamic acid with *m*-toluylenediamine, dyes brown. By suspending an insoluble dye as Duranol Violet or Artisil Direct Red 2BL in a state of fine suspension in gelatin or glycerol, cellulose acetate is readily dyed[3]. Monazo dyes are made by coupling the diazo compound from 2.4-dinitro-aniline-6-sulfonic acid or other aromatic amine diazo compound[4], with an aminoalkyl-2-aminonaphthalene. Those containing a single sulfo- or carboxylic-group dye acetyl-cellulose.

Processes have been described for the dyeing of cellulose ethers or esters with alizarin[5], Auramine[6], Bismark Brown[7] and Brilliant Orange G[8].

Azo Colors, as a broad classification including the Monazo, Disazo, Aminoazo, Diaminoazo, Aminoanthraquinone, and "Ice Colors," include an extensive group having valuable dyeing properties for the cellulose ethers and esters, and a wide range of colors after diazotization with a nitrite in acid solution and coupling. Their extent of usefulness and specifically recommended methods of application are perhaps best illustrated, by means of representative processes as evolved and perfected by the various firms at

1. R. Brightman, U. S. P. 1821255; abst. C. A. 1931, **25**, 5997. E. P. 296047; abst. Chem. Zentr. 1929, I, 304.
2. *Ibid.* U. S. P. 1805715. Imperial Chemical Industries, Ltd., and R. Brightman, E. P. 329049; abst. J. S. C. I. 1930, **49**, 756-B; Chem. Zentr. 1930, II, 2836.
3. S. Tootal, E. P. 314149; abst. C. A. 1930, **24**, 1226.
4. Farbenfabriken vorm. F. Bayer & Co., E. P. 253457; abst. C. A. 1927, **21**, 2563.
5. U. S. P. 1448515, 1517709.
6. U. S. P. 1375919, 1421288, 1421289, 1421290, 1430059, 1430060, 1430061, 1443012.
7. U. S. P. 1160979, 1181858, 1242783, 1349265, 1414029, 1414030, 1414031.
8. R. Clavel, U. S. P. 1517709.

home and abroad, as indicated by the products manufactured by the following groups:

1. *I. G. Farbenindustrie.* It is claimed that strong dyeings on cellulose ether and ester filaments and textiles are obtainable by using mono-sulfonated 1.4-diamino- and amino-oxyanthraquinones[1], their alkyl and aryl substitution products, containing the sulfo group not in the side chain, but in 2- or 3-position of the anthraquinone nucleus. With 1.4-diaminoanthraquinone-2-sulfonic acid a deep violet tint is obtained, with 4-oxy-1-aminoanthraquinone-3-sulfonic acid a reddish-violet, with 1-phenylamino-4-aminoanthraquinone-3-sulfonic acid a vivid blue tint, and with 1-phenylamino-4-amino-7-chloranthraquinone-3-sulfonic acid an intense blue with a green hue.

When diethylaniline-*m*-sulfonic acid is coupled with an unsulfonated aromatic diazo-compound of the benzene or naphthalene series containing at least one nitro-group[2], dyestuffs result which on cellulose ethers give deep tints from yellow to violet. Thus, the dyestuff obtained from diazotized 3-nitro-2-methyl-1-aminobenzene with diethylaniline-*m*-sulfonic acid a golden yellow tint results. If 4-chlor-2-nitro-1-aminobenzene be used as base, a deep orange is obtained. With 2.4-dinitro-1-aminobenzene and diethylaniline-*m*-sulfonic acid, reddish-violet dyeings are produced.

The cellulose ethers are colored yellow with 2-chlorbenzene-5-sulfonic acid-1-azo-3-amino-4-cresolmethyl ether; orange with 4-nitrobenzene-3-sulfonic acid -1-azoamino-4-cresolmethyl ether; and golden yellow with 3-nitrobenzene-4-sulfonic acid-1-azo-4-chlor-2-amino-1-phenolmethyl ether. 2-Methylbenzene-5-sulfonic acid-1-azo-3-amino-4-cresolmethyl ether gives pure greenish-yellow[3]. When *p*-cresol in NaOH solution is diazotized with *p*-aminoacetanilide[4],

1. C. Mueller, U. S. P. 1587669. E. P. 228557. F. P. 591708.
2. Farbwerke vorm. Meister Lucius & Brüning, E. P. 243738. D. R. P. 450977.
3. H. Eichwede, E. Fischer and C. Mueller, U. S. P. 1692492, 1692493. E. P. 245790. D. R. P. 501443.
4. E. Fischer and C. Mueller, U. S. P. 1706484. E. P. 270351. Swiss P. 126200, 127714.

yellow dyeings are obtainable on cellulose ethers; brown dyeings from *p*-nitraniline coupled with *p*-acetaminophenol; and orange tints from 3-amino-4-methyl-1-hydroxybenzene with a diazo-solution from *m*-chloraniline.

Cellulose acetate dyestuffs result when amino groups or mono- or di-alkylamine groups are introduced into the 4-position of 1-amino-2-alkylhydroxyanthraquinone[1], either by nitrating or reducing, after protecting the amino-group by acylation, or by introducing halogen in the 4-position for the amido-group. Thus 1.4-diamino-2-methoxyanthraquinone and analogous bodies dye cellulose ethers fast red to blue shades. With 1.4-diamino-2-methoxy(or hydroxy)-anthraquinone, or 2-ethoxy-1.4-diaminoanthraquinone, the cellulose ethers are dyed brilliant red to blue shades[2]. Colors of the 4-nitranilineazodihydroxydiethylaniline type[3], dyed organic cellulose derivatives yellowish red; 3.4.5-trichloraniline, a clear orange; 4-nitranilineazodihydroxydiethyl-3-amino-1-methylbenzene, dark yellowish red; and 2.4-dinitranilineazodihydroxydiethyl-3-amino-1-methylbenzene, a deep bluish bordeaux.

Monoazo dyes are used for acetate silk which are obtained either by coupling a diazotized aminonaphthoic acid with component[4], or by coupling an unsulfonated diazo compound with an aminonaphthoic acid. Thus 2.6-aminonaphthoic acid coupled with *b*-oxynaphthoic acid gives a brick-red shade; using the 2.3-acid instead, a bluish rose results. Cellulose ethers are colored with azo dyes containing more than one sulfonic or carboxyl group[5], made by coupling a diazotized arylamine with fused-ring derivatives of 5-membered ring compounds capable of coupling. Examples are: sulfanilic acid or 2.5-dichloraniline with 2-methylindole, yellow; aniline-*o*-sulfonic acid with 3-hydroxythionenaph-

1. P. Nawiasky, D. R. P. 479225. E. P. 272469.
2. E. P. 272482. F. P. 635054; abst. C. A. 1928, **22**, 3996.
3. G. Reddelien and G. Matzdorf, U. S. P. 1673301. E. P. 274823. D. R. P. 479343. F. P. 634036.
4. E. P. 275307; abst. C. A. 1928, **22**, 2279. D. R. P. 446220.
5. E. P. 284652; abst. C. A. 1928, **22**, 4834. D. R. P. 480904.

thene (S-oxide of thioindoxyl), orange; or the corresponding sulfone, greenish-yellow; 6-chlor-*o*-toluidine with oxindole-6-sulfonic acid, greenish-yellow.

Cellulose ethers and esters are dyed with water-soluble monoazo dyes obtained by coupling a diazotized dinitro-*o*-aminophenol with aminonaphthols containing no sulfonic or carboxylic groups[1], examples being 4.6-dinitro-*o*-aminophenol with 1.6-, 1.8-, 2.8-, or 1.5-aminonaphthol, giving black to brown upon diazotization and development, partially reduced 2.4.6-trinitro-*m*-cresol giving similar dyes. 4.6-Dinitro-*o*-aminophenol with 1.8-aminophenol is especially claimed for fastness. Yellow to orange shades on cellulose ether fabrics and filaments are obtainable in nonphototropic dyeings[2], by coupling diazotized aminomonosulfonic or aminomonocarboxylic acids with *a*-diketohydrindene or its derivatives. Thus, ammonium aniline-4-sulfonic acid-azo-*a*-diketohydrindene gives pure yellow shades; diazo-compounds of 4-chloraniline-2-sulfonic acid, *m*-xylidine-*o*-sulfonic acid, 4-aminoacetanilid-3-sulfonic acid and 5-nitro-2-anisidine-3-sulfonic acid develop yellow to orange shades.

Allylanthraquinones without further substituents in the nucleus or in the alkyl group are suitable dyes for cellulose ethers, and are applied as aqueous dispersions[3]. Thus, 1.4-dimethoxyanthraquinone, golden-yellow; 1.4.5-trimethoxyanthraquinone, greenish-yellow. Suitable dyes are also made by incorporating 1.4-diaminoanthraquinone or Indanthrene Blue RS or Lithol Red 3BN[4], or 1-amino-4-hydroxyanthraquinone with a phenol-aldehyde condensate or an alkali caseinate. Cellulose ethers are colored by azo dyes formed by coupling a diazo-compound of the benzene series free from sulfonic or carboxylic groups with an *N*-alkylated

1. W. Hentrich, U. S. P. 1695654, 1827150. D. R. P. 495620. E. P. 290720. F. P. 629097. Swiss P. 127621. Belg. P. 352614, 354847.
2. W. Hentrich, R. Knoche and M. Hardtmann, U. S. P. 1711890. E. P. 301564. F. P. 640746. D. R. P. 467038.
3. E. P. 307813, 308242. D. R. P. 514952.
4. E. P. 314451; abst. C. A. 1930, **24**, 1521.

4-hydroxy-2-quinoline[1]. *m*-Nitraniline with 4-hydroxy-*N*-methyl-2-quinolone, greenish-yellow; *p*-aminodimethylaniline with 4-hydroxy-*N*-methyl-2-quinolone, red-violet; *p*-chloraniline with 6-chlor-4-hydroxy-*N*-ethyl-2-quinolone, yellow.

Dyes are formed in substance on cellulose ether fibers by coupling a diazo, tetrazo or diazoazo compound free from sulfonic, hydroxy or carboxy groups with 2′.3′-hydroxynaphthoyl-4-amino-1-alkoxymethyl(or ethyl) benzene. Thus 2′.3′-hydroxynaphthoyl-4-amino-3-methyl-1-methoxybenzene and the diazo-compound of *m*-xylidine, a bluish-red shade is obtained. 59 other similar examples are given[2]. In producing insoluble azo dyestuffs on cellulose ethers[3], the fiber is padded at 15-50° with a weakly alkaline 2.3-hydroxynaphthoic arylamide bath to which has been added a water-miscible organic solvent or swelling agent (pyridine, ethyl alcohol or acetone) in which the arylamide or its alkali salt is soluble, the quantity added being only enough to swell the cellulose ether without dissolving it. The color is developed with a diazo solution in the usual manner. Thus, 2.3-hydroxynaphthoxy-2′-toluidine with 4′-methoxydiphenylamine-4-diazonium chloride produces an intense blue, and 2.3-hydroxynaphthoic acid anilid with 3-chloraniline hydrochloride, a brilliant orange.

Green dyeings are obtained on cellulose ethers by 5-hydroxy-1.4-di(*p*-hydroxyphenylamino)-anthraquinone (obtainable from 1.4.5-leuco-trihydroxyanthraquinone and *p*-aminophenol), or 1.2-dihydroxy-5.8-di-(*p*-hydroxyphenylamino)-anthraquinone (obtainable from 1.2.5.8-leuco-tetrahydroxyanthraquinone and *p*-aminophenol)[4]. Cellulose ethers may be dyed with 1.4-diamino-2.3-dialkoxyanthraquinones[5], pink to rose shades resulting from employing

1. K. Holzach and G. v. Rosenberg, D. R. P. 541072. E. P. 327394.
2. E. P. 336938, 339620. F. P. 679280.
3. W. Kirst and P. Sommer, D. R. P. 524350. E. P. 348269.
4. E. P. 362846; abst. J. S. C. I. 1932, **51**, 337-B.
5. P. Nawiasky, B. Stein and A. Krause, D. R. P. 542779, Addn. to D. R. P. 479225. E. P. 362921, Addn. to E. P. 272482. See D. R. P. 446220, 451231. F. P. 603710.

either 1.4-diamino-2.3-diethoxy-, 1.4-diamino-2.3-di-*n*-butoxy- or 1.4-diamino-2.3-dimethoxy-anthraquinone.

Acetate silk may be dyed with carboxylated azo dyes, other than derivatives of salicylic acid[1]. Thus, *p*-aminophenoxyacetic acid with *b*-naphthol, reddish-orange; *p*-aminobenzoic acid with *m*-phenylenediamine, orange; *p*-nitraniline with 4-hydroxy-*a*-naphthoic acid, brown-red. A dye for cellulose ethers is formed by coupling non-sulfonated aromatic diazo compounds with 2.4-diaminophenylmethanesulfonic acid[2]. Thus, aminoazobenzene gives a straw-yellow, 4-nitroso-1-aminobenzene a Corinth, and 1-aminoazonaphthalene an orange. The straw-yellow produced by aminobenzeneazo-2.4-diaminophenylmethanesulfonic acid is turned to yellow-brown by further treatment with 4-nitro-1-diazobenzene[3], and the orange color produced by 1-aminonaphthaleneazo-2.4-diaminophenylmethanesulfonic acid is turned to a reddish-brown.

If cellulose ether filaments are immersed in a bath of 1-amino-4-anilinoanthraquinone, Turkey-red oil and ammonia for an hr. at 70-80°, the filament then has a fast blue color. The anilino-group may be replaced by the *p*-toluidino-, *b*-naphthylamino- or *p*-acetylaminoanilino-groups[4]. Acetate silk may be dyed by treatment in an aqueous medium with non-acidylated aminoanthraquinones[5], or their feebly basic substitution products which do not dye natural fibers. Thus with 1.4-diamino-, a blue-violet; with a mixture of 16.- and 1.7-diamino-, red; 5-nitro-1.4-diamino-, violet; 1.2.4-triamino-, red-violet; and 1.4.5.8-tetra-amino-anthraquinone, blue. Anthraquinone-1-hydrazine dyes acetate silk bluish-red.

The organic cellulose derivatives may be tinted with unsulfonated azo dyes derived from diazotized *b*-hydroxyethyl ethers of aminophenols[6], examples being 4-*b*-ethoxy-

1. R. Metzger, D. R. P. 457957.
2. O. Siebert and M. Raeck, D. R. P. 467036.
3. *Ibid.* D. R. P. 468210; abst. C. A. 1929, **23**, 717.
4. D. R. P. 487941; abst. C. A. 1930, **24**, 1991.
5. K. Meyer, H. Hopff and A. Guenther, D. R. P. 489344.
6. O. Spengler and W. Müller, D. R. P. 495619. F. P. 619329.

hydroxyaniline diazotized and coupled with aniline, acetylated (yellow), with 1.4-aminonaphthol (red), with 2.7-aminonaphthol (orange-red), with salicylic acid (yellow); 3-chlor-4-*b*-hydroxyethoxyaniline with 1-phenyl-3-methyl-5-pyrazolone, yellow; 5-nitro-2-*b*-hydroxyethoxyaniline with resorcinol, yellow.

1.4-Diamino-5.8-dihydroxyanthraquinone when heated with sulfuric acid, methyl alcohol and boric acid gives a product dyeing blue-green shades[1]. 1.4-Diaminoanthraquinone-2-glycol ether, 1-amino-4-hexahydroanilinoanthraquinone-2-glycol ether and 1-amino-4-anilinoanthraquinone-2-glycerol ether dye cellulose ethers fast violet shades[2]. Fast dyes are obtainable on cellulose ethers or cellulose acetate[3] by forming in a neutral bath monoazo dyes which do not contain more than one acid group as sulfonic, carboxylic or oxalic, diazotizing them on the fiber and developing with coupling components as *b*-naphthol, hydroxynaphthoic acids and aminonaphthols. Thus, *p*-aminobenzeneazosalicylic acid with *b*-naphthol gives a red color.

Water-insoluble dyes result by treating alkylsulfonic acids of primary or secondary aminoazo compounds or their salts with alkali agents, and are used for dyeing cellulose ethers[4]. As examples, the azo dye from diazobenzene chloride and sodium methylanilinesulfonate is heated to 90° in sodium carbonate or NaOH solution. The dye which precipitates is brought into suspension with Turkey-red oil and dyes deep, greenish-yellow shades. If diazotized 3.4-dichloraniline is used, an intense golden-yellow shade results; with diazotized *p*-nitraniline, orange shades. If *a*-chloranthraquinone is heated with a 20% solution of hydroxyethylamine and not sulfonated, acetic silk dyes result[5]. Etherized celluloses may also be dyed with monazo dyes prepared by combining diazotized aromatic compounds with

1. P. Nawiasky and A. Krause, D. R. P. 531103.
2. D. R. P. 541637. L. Laska and A. Zitscher, D. R. P. 545846.
3. F. P. 639818; abst. C. A. 1929, **23**, 713.
4. F. P. 646371; abst. C. A. 1929, **23**, 2305.
5. F. P. 653701: abst. C. A. 1929. **23**. 3815.

phenol or its derivatives the positions *p*- to the OH groups of which are free and which contain no other substituents than alkyl radicals, and treating with alkyl halides or acid chlorides[1]. Monoacetyl-*p*-phenylenediamine copulated with *o*-cresol gives a non-phototropic yellow, while *m*-chloraniline and cresol produce a red dyeing.

2. *Dreyfus and Celanese Processes.* Basic anthracene dyes as aminoanthraquinones[2], are used in the form of soluble modifications obtained by pre-treating them with a sulfonated ricinoleic acid compound or other oily solubilizing agents, forming the S. R. A. dyes. The fastness to colors dyed on cellulose acetate is increased by treating with one or more light-fastening compounds[3], as aniline, alkylanilines or alkylphenylenediamines. In those dyeing processes where strong alkalis are normally used[4], the latter is partially replaced by a soluble salt of a hydroxy compound of the cyclic organic series, as sodium or potassium phenolate, xylenolate, cresolate, resorcinolate, quinolate or naphtholate, and thereby diminishes tendering of the fiber.

Dyeing may be effected with acidylaminoanthraquinones derived from monobasic aliphatic acids preferably containing no sulfo-groups, as 1-acetyl (or propionyl-)-aminoanthraquinone or 1.4-diacetyldiaminoanthraquinone, the colors obtained being yellow, greenish-yellow, orange-red and violet[5]. Methyl-, ethyl- or benzyl-cellulose may be dyed scarlet, violet, blue-violet, pure blue and bluish-red shades by means of 1-*b*-hydroxyethylaminoanthraquinone sulfuric ester or other suitable ester of an anthraquinonylamine alcohol[6]. Cellulose ethers may be dyed with compounds in which an aryl dye nucleus (other than an azo dye nucleus) contains either in the nucleus or as a substituent an amino

1. F. P. 700239; abst. C. A. 1931, **25**, 3847.
2. G. H. Ellis, U. S. P. 1719324; abst. C. A. 1929, **23**, 4083. E. P. 219349. F. P. 568655.
3. *Ibid.* U. S. P. 1723230. E. P. 243841. Belg. P. 328736. Can. P. 271279.
4. *Ibid.* U. S. P. 1716720, 1716721. E. P. 262506, 273819.
5. British Celanese, Ltd., and G. Ellis, E. P. 263260.
6. H. Olpin, U. S. P. 1688553. E. P. 285641. Can. P. 285979.

or imino group, one or more H-atoms of which are replaced by an aliphatic side chain containing OH but not carboxyl[1]. Examples are: *a*-chloranthraquinone with *b*-aminoethyl alcohol, scarlet dyeings; 1.4-diaminoanthraquinone with ethylene oxide, blue; 1-amino-4-methoxyanthraquinone with propylene oxide, bluish-red; dibrombenzanthrone with *b*-aminoethyl alcohol, yellow; and anthrapyrimidone with ethylene chlorhydrin, yellow.

Cellulose ethers are colored with hydroxylated alkyl ethers or thioethers obtained from colored phenols or thiophenols (other than azo compounds)[2], by the action of chlorhydrins, alkylene oxides or acetone. Examples: 1-B-hydroxyethylthiol- (yellow), 1-By-dihydropropylthiol- (yellow), 1-methylamino-4-By-dihydroxypropylthiol- (reddish-orange), 1-acetamido-4-B-hydroxyethoxy-anthraquinone (golden-yellow). 1-By-dihydroxypropylthiolanthrapyridone gives yellow shades. Methyl-, ethyl- and benzyl-cellulose are colored with compounds in which an aryl dye nucleus or component is linked to one or more thiourethane or substituted thiourethane residues[3]. Thus, 4-acetamido-1-anthraquinonylthiourethane gives orange shades.

Dyeing of the cellulose ethers may be accomplished by compounds in which an aryl dye nucleus is connected to an amino group or aliphatically-substituted amino group through a side chain comprising a C atom or atoms, with or without N or O toms[4]. Thus, 1-methylamino-4-aminomethylanthraquinone dyes organic cellulose derivatives red. Dyeing may be effected by the application of unsulfonated azo dyes obtained from aminonaphthols or their nuclear substitution products and having the azo groups linked to the naphthalene nucleus in a position ortho or peri to an auxochromic group, such as the dye obtained from aniline

1. H. Dreyfus, E. P. 285968. F. P. 627071. F. P. Addns. 32949, 35560, to F. P. 627071. Can. P. 276556. Belg. P. 343505.
2. *Ibid.* U. S. P. 1783607. E. P. 285969.
3. *Ibid.* U. S. P. 1735963. E. P. 291816. F. P. Addn. 32948 to F. P. 627072. Can. P. 285799.
4. *Ibid.* U. S. P. 1735961. E. P. 292180. See E. P. 292181, 292453. Can. P. 276555, 281190. Belg. P. 348213, 348214.

and 1.8-aminonaphthol, solubilized by sodium ricinoleate[1].

Methylated, ethylated and benzylated cellulose are colcolored by dehydrothiotoluidine either diazotized and coupled in substance or on the fiber[2], with suitable non-sulfonated coupling components, such as phenol (giving yellow), *p*-chlorphenol (yellow), dimethylaniline (orange), *b*-naphthol (orange-red), or 2.3-aminonaphthoic acid or 1-naphthylamine-2-ethyl ether (red). Where a dispersion of a free oxynaphthoic acid arylide is applied to the material and developed with a diazo compound[3] dyeings are obtained. For instance, a fast navy blue shade is obtained from 4-nitro-2-methoxybenzeneazo-*a*-naphthylamine with the *m*-nitranilide of *b*-oxynaphthoic acid. By diazotizing or tetraazotizing a mono- or di-aminoanthraquinone and coupling with a suitable component[4], colors are obtained suitable for dyeing the cellulose ethers. Thus, 1-amino-2-methylanthraquinone with *m*-phenylenediamine gives golden brown shades; with dimethyl-*m*-aminophenol, orange; with *m*-toluidine, golden yellow.

Cellulose ethers are tinted with azo dyes obtained by coupling a diazotized 2.4-dinitro-6-alkoxyaniline or derivatives with coupling components[5], which, for producing readily dischargeable violet to blue shades, may be of the naphthalene series such as naphthylamines, aminonaphthols, alkylnaphthalenes, 1-amino-2-ethoxynaphthalene, hydroxyethyl-*a*-naphthylamine, or chlor-*b*-hydroxy-1-naphthylamine. Cellulose ether silk may be dyed with azo dyes derived from nitroarylamines containing 2 or more linked aryl residues[6]. Examples are 2.4-dinitro-4'-aminodiphenyl-

1. British Celanese, Ltd., G. Ellis, H. Olpin and E. Kirk, E. P. 298993. Can. P. 293058, 293059. Ital. P. 228814. Belg. P. 352382. E. P. 299343. F. P. 656431.
2. British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 306981. Belg. P. 353232. F. P. 662456.
3. British Celanese, Ltd., G. Ellis, H. Olpin and E. Walker, E. P. 310779. F. P. 667167.
4. British Celanese, Ltd., G. Ellis, H. Olpin and D. Mosby, E. P. 310827. Belg. P. 353564. F. P. 661686.
5. British Celanese, Ltd., D. Mosby, H. Olpin and G. Ellis, E. P. 319390.
6. British Celanese, Ltd., and G. Ellis, E. P. 323792.

amine with phenol, yellow; 3-nitro-4-amidodiphenyl ether with *a*-naphthylamine, bluish-red; 2.2′-dinitrobenzidine with 2 mols. *a*-naphthylamine plus 2 mols. 2.3-hydroxynaphthoic acid, black; and 3.3′-dinitro-4.4′-diaminodiphenylmethane with 2 mols. *m*-toluylenediamine, golden brown. In an analogous manner[1], azo dyes are suitable for coloring the cellulose ethers if containing an *ar*-tetrahydronaphthyl group, preferably having no sulfonic group. Examples are, *ar*-tetrahydro-*b*-naphthylamine + phenol, yellow; 2.3-hydroxynaphthoic-*m*-nitranilide, orange; *p*-nitraniline + *ar*-tetrahydro-*a*- or -*b*-naphthylamine, orange to golden yellow; *m*-nitraniline-*ar*-tetrahydro-*a*-naphthylamine, marigold; and *p*-nitraniline-*o*-sulfonic acid + *ar*-tetrahydro-*a*-naphthylamine, orange-red.

The fastness of aminoanthraquinone dyeings to the combined action of light and acids[2] is improved by treating the material, before, during, or after dyeing, with uncolored alkylated aminodiaryls (tetramethyl-4.4′-diaminodiphenylmethane or tetramethylbenzidine), or[3] with alkylated, aralkylated, or arylated carbamides, thiocarbamides or guanidines, as *s*-di*iso*amylthiocarbamide, or tetramethylthiocarbamide, which are retained in the material during any subsequent treatment. With 1.4-dimethylaminoanthraquinone and *sym*-di*iso*amylthiourea, level dyeings are obtained.

When benzylethylaniline is incorporated with cellulose ether materials, before, during or after dyeing[4], marked increase in fastness to light and acid results. Relatively water-insoluble cellulose ether colorants such as 1-amino-4-methylaminoanthraquinone[5], may be used in the form of aqueous dispersions to increase their dyeing capacity, by pre-treating the compounds with a solubilizing agent in

1. British Celanese, Ltd., and H. Olpin, E. P. 330591.
2. British Celanese, Ltd., G. Ellis, T. Ockman and H. Olpin, E. P. 340541. F. P. 694750.
3. *Ibid.* E. P. 340572. F. P. 694749.
4. *Ibid.* E. P. 361362, 361381.
5. G. Ellis, U. S. P. 1716721. E. P. 274841.

the form of a resin soap. To increase the light resistance of the yellow color on cellulose ether or ether fabrics produced by benzeneazo-*a*-naphthylamine chloride, it may be treated with diethylaniline chloride.

If the dyeing is to be made with a water-insoluble dyestuff such as methylaminoanthraquinone[1], it is advocated to use as solvent a mixture of ethylene dichloride and trichlorethylene. Cellulose acetate is dyed blue by means of *p*-aminophenyl-1.4-naphthoquinone monoimide with sodium sulforicinoleate at 100°[2]. Dyeings on cellulose ethers may be effected by *o*-nitro-*b*-phenyl-*b*-phenylamino lactic acid giving yellow shades[3], or by 1-methylamino-4-chloranthraquinone[4] heated with cuprous cyanide and ammonia, the nitrile obtained then being reduced by nascent hydrogen. *p*-Nitraniline diazotized and coupled with hydroxyethyl-*a*-naphthylamine gives a scarlet shade on acetylcellulose[5].

It is claimed that the fastness of cellulose acetate dyeings of anthraquinone derivatives such as 1.4-diaminoanthraquinone or 1-monomethylamino-4-oxyanthraquinone, may be increased by the addition of a small amount of sodium carbonate, borax, disodium hydrogen phosphate, sodium palmitate or potassium oleate[6], to insure the development of no acid reaction.

3. *Methods of R. Clavel.* Cellulose acetate materials are said to be satisfactorily dyed by means of ice colors[7], provided that a relatively large quantity of one or more water-soluble salts, such as zinc, barium, magnesium, sodium, potassium or tin chlorides and a protective colloid as gelatin, albumin, tannates or soaps, are present in the dyebath. For instance, cellulose acetate is dyed black by steep-

1. W. Whitehead, U. S. P. 1738978. E. P. 282036.
2. G. Ellis, U. S. P. 1740890, 1740891.
3. H. Dreyfus, U. S. P. 1829130, 1843417.
4. *Ibid.* U. S. P. 1883350.
5. *Ibid.* F. P. 701372. See F. P. 640013, 651934, 658415, 659026, 688623, 688624. Can. P. 289525. Belg. P. 353563.
6. G. Ellis, Can. P. 271280. H .Dreyfus, Can. P. 281194, 297864. F. P. 603921. G. Ellis and H. Olpin, Can. P. 293063, 293064.
7. E. P. 187964. Can. P. 236949.

ing at 60° with dianisidine chloride, magnesium chloride and sodium bicarbonate, then coupling with *a*-naphthylamine chloride, then afterwards diazotized and copulated with 5-hydroxy-*a*-naphthylamine to develop a full black shade. In the production of azo dyes on cellulose derivative fibers[1], the development is effected at 75-100°, the bases and developers being applied in a separate bath at ordinary temperatures, diazotization being carried on at ordinary temperature.

4. *British Dyestuffs Corporation.* Aminoazo dyestuffs, solubilized by the presence of carboxyl groups and containing no sulfonic groups[2], and preferably in the form of their sodium salts, dye acetylcellulose as indicated in Table XXXII on the following page.

As an emulsifying agent and protective colloid for dyeing cellulose ethers and esters with aminoanthraquinones[3], condensation products of naphthalene with formaldehyde in sulfuric acid solution, or naphthalene sulfo-acids with formaldehyde have been advocated. 1.4-Diaminoanthraquinone condensed with phenylglycidic acid or methylglycidic acid in glacial acetic acid solution in the presence of copper or copper acetate[4], dyes acetyl cellulose bright blue. 1-Aminoanthraquinone and 1-amino-4-hydroxyanthraquinone give red and purple dyes respectively with phenylglycidic acid. If aminoanthraquinones are condensed with sulfochlorides of *o*-oxycarboxylic acids other than salicylic acid, cellulose acetate dyestuffs result[5], bluish-red shades being produced by 1.4-diaminoanthraquinone con-

1. E. P. 204179. U. S. P. 1571320. Can. P. 236697. See E. P. 199754.
2. J. Baddiley, J. Hill and E. Anderson, U. S. P. 1498315.
3. British Dyestuffs Corp., Ltd., J. Baddiley and A. Shepherdson, E. P. 211720. J. Baddiley and W. Tatum, U. S. P. 1574748. British Dyestuffs Corp., Ltd., J. Baddiley, A. Shepherdson, H. Swann, J. Hill and L. Lawrie, E. P. 224077. U. S. P. 1616103. See E. P. 246984. F. P. 587570.
4. J. Baddiley, W. Tatum and British Dyestuffs Corp., Ltd., E. P. 224363.
5. British Dyestuffs Corp., Ltd., J. Baddiley and W. Tatum, E. P. 225678.

Table XXXII. Aminoazo Dyes on Artificial Filaments

Constitution	Shade on acetyl silk			
	Direct	Dev. with β-naphthol	Dev. with β-oxynaphthoic acid	Dev. with *p*-amino diphenylamine
m-Aminobenzoic acid + *o*-anisidine	Yellow	Scarlet	Magenta	Gold
m-Aminobenzoic acid + anthranilic acid	Yellow	Red	Bluish-red	Olive
p-Amino-salicyclic acid + α-naphthylamine	Yellow	Violet	Reddish-blue	Olive
5-Acetyl-amino-2-amino-4-methoxy-toluene + β-oxynaphthoic acid (hydrolized)	Blue-violet	Greenish blue	Blue	Reddish violet
m-Aminobenzoic acid + *p*-xylidine + *m*-phenylene-diamine	Red	Reddish-brown	Reddish-brown	Brown
m-Aminobenzoic acid + *p*-xylidine + α-naphthylamine	Brownish-red	Reddish-violet	Reddish-violet	Brown
m-Aminobenzoic acid + *m*-toluidine	Yellow	Scarlet	Bluish-red	
Anthranilic acid + *o*-anisidine	Orange	Bluish-red	Reddish-blue	
m-Aminobenzoic acid + α-naphthylamine	Reddish-orange	Reddish-violet	Reddish-blue	
p-Aminobenzoic acid + aminohydroquinone-dimethyl-ether	Orange	Reddish-violet	Blue	
m-Aminobenzoic acid + 4-nitro-2-anisidine	Greenish-yellow	Reddish-orange	Red	
m-Aminobenzoic acid + 1.2-aminonaphthol ether	Red	Greenish-blue	Bluish-green	

densed with the sulfochloride of *o*-cresotinic acid. Or[1], the material may be dyed with (a) monosulfonated azo dyes containing no OH-group, in which the sulfo-group is in the *o*-position to the azo groups, or (b) monoazo dyes from unsulfonated diazo-compounds containing no OH-group, and 1-naphthylamine-8-sulfonic acid or methyl, ethyl or phenyl 1-naphthylamine-8-sulfonate.

Cellulose acetate materials may be dyed either in an acid, neutral or alkaline bath by means of "sulfato" compounds of monoazo dyes[2], preferably nitrated monoazo compounds. Or[3], dyeing is effected with aqueous solutions or suspensions of coeramidines (anthraquinoneacridines) which may be produced by heating *a*-arylaminoanthraquinones with sulfuric acid, a full greenish-yellow being dyed with the coeramidine from 1-phenylaminoanthraquinone; golden yellow with 1-anilino-2-methylanthraquinone; and 1-amino-4-*p*-toluidinoanthraquinone, bluish-red. Cellulose ethers are dyed full orange shades by diazotizing *m*-aminobenzenesulfonanilide and coupling with *a*-naphthylamine, and orange red with diazotized *m*-aminobenzenesulfon-*m*-nitranilide and coupling with "cresidine" (*m*-amino-*p*-cresolmethyl ether)[4].

Dry, dispersed dye preparations or dye pastes suitable for the dyeing of cellulose ethers[5] are made with the aid of a product obtained by heating ligninsulfonic acid with NaOH, giving sodium ligninsulfonates. They are said to differ from "oxidized" ligninsulfonic acid in their reaction with ferric chloride.

5. *Gesellschaft fuer Chemische Industrie in Basel.* Cellulose acetate goods are dyed violet, green, blue and

1. G. Frank and British Dyestuffs Corp., Ltd., E. P. 226948.
2. British Dyestuffs Corp., Ltd., W. Perkin and S. Bate, E. P. 237739.
3. British Dyestuffs Corp., Ltd., A. Shepherdson and A. Davidson, E. P. 268933.
4. R. Horsfall, L. Lawrie and J. Hill, U. S. P. 1662514. E. P. 275373. J. Baddiley, U. S. P. 1757501. E. P. 287214. U. S. P. 1757502. E. P. 280320. U. S. P. 1757503. E. P. 287609.
5. British Dyestuffs Corp., Ltd., H. Adams and A. Shepherdson, E. P. 301549.

black shades with monazo dyes containing one or more diazotizable amino groups, the shades being diazotized and developed with alkyl- or aralkyl-*α*-naphthylamines[1]. Fast shades are obtained on the cellulose ethers by the use of tetraminoanthraquinones in which an H-atom of one or both amino groups is substituted by an aryl group[2]. Examples are, 1.5-diamino-4.8-diphenylaminoanthraquinone (greenish blue), 1.8-dianilino-4.5-diaminoanthraquinone (blue), and 1.5-diamino-4.8-(4′.4″-diamino)-dianilinoanthraquinone (bluish green). By the interaction of benzaldehyde, sodium acid sulfite and 1.4.5.8-tetra-aminoanthraquinone, colors result which dye organic cellulose derivatives blue[3].

Acetate silk or a cellulose ether may be dyed or printed with aminoanthraquinonesulfonic acids[4], e.g., sulfonated 4-benzylamino-1-methylaminoanthraquinone (blue), 1-amino-4-*p*-acetamidoanilinoanthraquinone-2-sulfonic acid (blue), 1-amino-4-anilinoanthraquinone-3-sulfonic acid (blue), 1.4-di(2′-sulfo-*p*-toluidino)anthraquinone (green), and 1-aminoanthraquinone-5-sulfonic acid (orange). It is said that these colors do not sublime during the process. Cellulose ethers are dyed with diaminoazo dye (e.g., hydrolyzed *p*-aminoacetanilid + cresidine) in presence of a dispersing agent[5], and then diazotized and developed in weak acid medium with 2.3-hydroxynaphthoic acid (deep black) or *b*-naphthol (deep black). Navy blue shades are obtained by using less diaminoazo compound.

By coupling diazotized 1-amino-4-nitroanthraquinone with resorcinol[6], and treating with a reducing agent as sodium nitrite, violet tones are produced. 2.5-Dimethoxy-1-aminobenzene, soluble in ethyl acetate, dyes acetylcellu-

1. Soc. anon. pour L'Ind. Chim. a Bale, E. P. 231455.
2. Society of Chemical Industry in Basle, E. P. 293006. F. P. 656057. D. R. P. 549241.
3. Soc. anon. pour L'Ind. Chim. a Bale, E. P. 295257. Swiss P. 131100. D. R. P. 546911. F. P. 641675.
4. Society of Chemical Industry in Basle, E. P. 341419.
5. F. Felix and W. Jaeck, U. S. P. 1793390. E. P. 281704.
6. Soc. anon. pour L'Ind Chim. a Bale, Swiss P. 134943, 136257. E. P. 309087.

lose silk a fast red[1], while cellulose ethers may be printed by first impressing the material with sulfonic derivatives of anthraquinone and vaporizing[2].

6. *Grasselli Dyestuff Corporation.* Aminoanthraquinone-N-methylsulfonic acid compounds have been recommended for the dyeing of the cellulose ethers[3], the sodium salt of 1.4-diaminoanthraquinone-N-methylsulfonic acid giving a clear, bright violet; sodium 1.5-dihydroxy-4.8-diaminoanthraquinone-N-methylsulfonate, producing blue shades, and sodium 1.4.5.8-tetra-aminoanthraquinone-N-methylsulfonate dyeing greenish-blue. Ethyl- or propylcellulose[4] are cellulose ethers which may be dyed with *o*-aminoanthraquinone sulfonic acids, 1-aminoanthraquinone-2- (orange shade), 2-aminoanthraquinone-1- (yellow), 2-aminoanthraquinone-3- (yellow), 1-amino-4-bromanthraquinone-2- (yellowish-red), 1-amino-5-toluidoanthraquinone-2- (dark red), 1-amino-4-thioanthraquinone-2- (red-violet), and 1-amino-4-dihydroglyoxalylanthraquinone-2-sulfonic acid (violet).

Dyes suitable for acetate silk contain as one constituent a naphthylaminecarboxylic acid (suitably 2.3-naphthylaminecarboxylic acid)[5], toether with another component such as resorcinol, *b*-naphthol, *b*-naphthylamine, ethyl-*b*-naphthylamine, 2.3-aminonaphthoic acid, dimethyl-*m*-toluidine, phenylmethylpyrazolone, *m*-toluylenediamine, 1.5-naphthylenediamine, *a*-naphthylamine, dimethylaniline, *o*-anisidine, aminoquinonedimethyl ether or 2.5-dichloraniline, yellow to red to blue-violet shades being produced.

A method applied solely to the cellulose ethers[6] comprises coupling diethylanilinesulfonic acid with unsulfonated aromatic diazo compounds of the benzene or naph-

1. F. P. 709779; abst. Chem. Zentr. 1931, II, 3400.
2. Soc. Pour L'Industrie Chim. a Bale, F. P. 683118. E. P. 282853. D. R. P. 489863.
3. W. Duisberg, W. Hentrich and L. Zeh, U. S. P. 1609702.
4. W. Duisberg, W. Hentrich, C. Weinand and L. Zeh, U. S. P. 1587708. D. R. P. 433236.
5. L. Laska and F. Weber, U. S. P. 1702832.
6. H. Eichwede and E. Fischer, U. S. P. 1599748.

thalene series; 3-nitro-2-methyl-1-aminobenzene with diethylaniline-*m*-sulfonic acid producing a golden yellow tint. When 2-chlor-2-nitro-1-aminoazobenzene or 2-nitro-2-aminobenzene-1-carboxylic acid ester is employed, orange colors are produced. Cellulose ether material is dyeable with ammonium 2.6-dinitroaniline-4-sulfonate or other acid-substituted dinitroanilines when diazotized, and the diazo compounds thus formed are coupled with *b*-naphthylamine or other aromatic amine having no acid group in the molecule[1].

Ethylcellulose threads are dyed with disazo compounds of amines or substituted amines coupled with alkylaralkylaniline sulfonic acids or their substituents, the dye, for instance, from 6-nitro-2-toluidine and N-methyl-N-benzylaniline sulfonic acid or sodium N-methyl-N-benzylanilinesulfonate, dyeing yellow; *a*-naphthylamine and sodium ethylbenzylanilinesulfonate dyeing orange red; while 2.4-dinitroaniline with sodium methylbenzylanilinesulfonate dyes bluish-red[2].

7. *Badische Anilin & Soda Fabrik.* The dyeing of cellulose ethers and esters may be carried out by the use of water-soluble sulfamic acids of the dye[3], the colors obtained being diazotized and developed with chromogens or coupled with diazo-compounds. Thus, the azo dye from *p*-aminophenylsulfamic acid and *b*-naphthol, used in acid solution, gives brownish-red shades, while further diazotization and treatment with *b*-naphthol produces a red-violet color. Cellulose esters may be dyed by employing insoluble or difficultly soluble azo dyestuffs in the form of their water-soluble bisulfite derivatives[4].

Or[5], unsulfonated azo dyes may be used containing at least 1 monoethanolamino group either in aqueous solution

1. W. Duisberg, W. Hentrich and L. Zeh, U. S. P. 1595178.
2. W. Duisberg and W. Hentrich, U. S. P. 1575324. D. R. P. 418940, 423601.
3. Badische Anilin & Soda Fabrik, E. P. 204280; abst. C. A. 1924, **18**, 909. D. R. P. 420017. Belg. P. 309771.
4. F. Guenther, U. S. P. 1526142.
5. E. P. 251155; abst. C. A. 1927, **21**, 1361. F. P. 600106.

or suspension, with or without the addition of Turkey-red oil or other dispersing agent. Cellulose acetate is dyed orange or scarlet shades with dyes obtained (1) by diazotizing *p*-nitraniline and coupling with monoethanol-*m*-toluidine, or (2) by diazotizing 3-nitro-4-toluidine and coupling with monoethanolaniline. Or the cellulose carboxylates may be dyed with isatoic anhydride derivatives[1]; thus, the azo dyestuff from diazotized sulfanilic acid or 1-amino-2-chlorbenzene-5-sulfanilic acid and anthranilic acid is converted into the corresponding isatoic derivatives by means of phosgene.

8. *General Aniline Works, Inc.* Products suitable for the dyeing of cellulose ethers and esters are formed when a 1.4-diamino-2-hydroxyanthraquinone compound is treated with formaldehyde in the presence of sulfuric acid, a nitro-group is introduced into the resulting product which is then treated with water, and the nitro-group reduced. Fast red to blue shades are obtained[2]. Non-phototropic yellow dyeings on cellulose ethers or esters are obtainable by using monoazo dyes derived from a *p*-substituted phenol as coupling component[3], and containing not more than one sulfonic group. Examples are: *p*-phenylenediamine, *p*-aminoacetanilide, *p*-phenylenediaminesulfonic acid or *m*-chloraniline, coupled with 1 mol. *p*-cresol.

Acetate silk may be dyed with unsulfonated azo dyes derived from diazotized *b*-hydroxyethyl ethers of aminophenols[4]. Examples are: 4-*b*-hydroxyethoxyaniline, diazotized and coupled with aniline and acetylated (yellow shade); with 1.7-aminonaphthol, red; with 2.7-aminonaphthol, orange-red; with 2-*b*-hydroxyethoxyaniline and *b*-naphthol, red, and with salicylic acid, yellow; 3-chlor-4-*b*-

1. E. P. 259634. D. R. P. 433147; abst. Chem. Zentr. 1926, II, 2232.
2. P. Nawiasky, U. S. P. 1736088. E. P. 272469. D. R. P. 479225.
3. E. Fischer and C. Mueller, U. S. P. 1765142. E. P. 269934. D. R. P. 469514. F. P. 632887.
4. O. Spengler and W. Mueller, U. S. P. 1770714. F. P. 619329. D. R. P. 495619.

hydroxyethoxyaniline with 1-phenyl-3-methyl-5-pyrazolone, yellow; and with 5-nitro-2-*b*-hydroxyethoxyaniline, yellow with resorcinol.

Fast dyeings on cellulose ethers of golden yellow to orange and reddish orange are produced by use of suitable basic monoazo dyes such as produced from diazotized 4-aminobenzene-1-sulfamide and aminocresol ether, the dye from diazotized 2-nitro-1-aminobenzene-4-sulfamide and *m*-toluidine, or the dye from diazotized 4-aminobenzene-1-sulfamide and naphthylamine. Golden yellow to reddish orange shades are formed[1]. Material from cellulose ethers or esters is dyed navy blue to black shades by treatment with a monoazo dye derived from an aromatic *p*-nitramine and *a*-aminotetrahydronaphthalene, tetrazotizing the dye on the fiber and further coupling with 2.3-hydroxynaphthoic acid[2].

9. *Imperial Chemical Industries.* Anthraquinone dyes are made by condensing *p*-phenylenediamine with an anthraquinone derivative containing in the 1-position, an amino or alkylamino-group, and in the 4-, 5- or 8-positions a halogen atom; a halogen atom may also occupy the 2-position and may be replaced by a sulfonic group by treating the products with a soluble sulfite. The unsulfonated products dye cellulose ethers in green and other shades[3]. It has been reported that the printing strength of aminoanthraquinone may be improved by the addition up to 5% of a hydroxyethylamine, as triethanolamine.

Fabrics of cellulose ethers or esters are printed with water-insoluble aminoanthraquinones or their derivatives other than vat dyes[4], and commercial triethanolamine added to the printing paste.

10. *British Alizarine Co.* In the dyeing of organic cellulose derivatives the following or similar dyes may be

1. H. Eichwede and E. Fischer, U. S. P. 1802204. E. P. 243737.
2. K. Schirmacher and K. Stenger, U. S. P. 1865062.
3. Imperial Chemical Industries, Ltd., A. Shepherdson and W. Tatum, E. P. 315905. F. P. 673117.
4. Imperial Chemical Industries, Ltd., A. Shepherdson and L. Smith, E. P. 330652. F. P. 686428.

used[1]: dyes formed from *m*-nitraniline and *a*-naphthylamine or from *m*-aminophenyloxamic acid and *b*-naphthol; or indigodiacetic acid obtained by fusing *o*-carboxyphenyliminodiacetic acid with KOH and oxidizing. Or[2], cellulose esters may be dyed with compounds made by condensing *p*-nitrophenol with chloracetic acid, reducing the nitro group, diazotizing and coupling with *b*-naphthol. A bright bluish-red anthraquinone dye is prepared by boiling 2.4-dibrom-1-aminoanthraquinone with sodium sulfide, and condensing the product with chloracetic acid.

11. *Other Processes.* C. Gränacher[3] prepares diazotizable fibers by treatment of alkalicellulose with nitroxylyl chloride, *o*- or *p*-nitrochlorbenzene, 1-chlor-2.4-dinitrobenzene or their homologues. For instance, mercerized yarn is swollen by treatment with 10% aqueous NaOH for several hrs., the alkali carefully removed, and the fibers in moist condition treated at 90-95° for several hrs. in presence of lithium chloride, with fused 1-chlor-2.4-dinitrobenzene. The cotton is then washed and treated with a reducing agent. Or the diazotizable fibers may be produced by treatment with an aromatic *o*-dinitro compound in presence of an inorganic agent which binds acid, other than a caustic alkali[4].

Azo dyes are prepared according to a process of the Farbenfabriken vorm. F. Bayer & Co.[5] by coupling a diazotized dinitroanilinesulfonic or dinitroanilinecarboxylic acid with an aromatic amine which does not contain a sulfo-group but which may be substituted in the amino group. The products dye acetylcellulose deep red, bordeaux, blue, violet and bluish violet shades. Or[6], the fibers may be dyed in an alkaline hyposulfite vat with 2-amino-, 1.5-dinitro-, 1.5-diamino-, 1-amino-2-methyl-, 1-methylamino-,

1. C. Barnard and British Alizarine Co., Ltd., E. P. 252240.
2. *Ibid.* E. P. 252646; abst. C. A. 1927, **21**, 2388.
3. E. P. 347117; abst. Chem. Zentr. 1931, II, 3397.
4. C. Gränacher, E. P. 347263; abst. Chem. Zentr. 1931, II, 3397.
5. E. P. 225862; abst. C. A. 1925, **19**, 1632.
6. W. Kilby and Morton Sundour Fabrics, Ltd., E. P. 214112; abst. C. A. 1924, **18**, 2610.

1-amino-2.4-dibrom-, 1-amino-5-chlor-, or 1-nitro-4-chlor-anthraquinone, giving orange, yellow, red violet and pink shades. These dyeings may be diazotized and developed with *b*-naphthol.

An aminoazo compound is condensed with a phthalic acid or anhydride to give a phthalamic acid. The products from phthalic acid and aminobenzeneazodiphenylamine dye acetate silk orange; or aminoazobenzene, yellow; and from tetrachlorphthalic acid and *p*-nitrobenzeneazo-*b*-naphthylamine, yellow to orange[1]. Artificial silk from cellulose ethers or esters may be dyed with azo dyes prepared from nitrated hydroxydiazo-compounds[2], and aromatic amines or phenols or their substitution products. Diazotized picramic acid and *b*-naphthylamine, *a*-naphthylamine, *m*-phenylenediamine and *a*-naphthol, produce colored dyeing yellow, violet, orange, and brown shades respectively.

Cellulose acetate fibers or fabrics may be colored by impregnation with a compound capable of coupling with a diazo compound and a nitrite, afterwards developing with a diazotizable amine. *b*-Hydroxynaphthoic acid coupled with 2.5-dichloraniline chloride gives reddish-orange shades[3]. Acetylcellulose goods may be dyed by means of alkylaminoazo compounds containing no sulfonic or carboxylic acid groups[4], suitable dyes being those prepared by coupling methylaniline or dimethylaniline with the diazo compounds of aniline, chloranilines, nitroanilines, nitroanisidines, aminomethylanilines or aminoazobenzenes.

A di- or poly-aminoanthraquinone hydrohalide is heated with dicyanodiamide, or the mixed bases are treated with hydrogen halide and heated at 150-200°. Cellulose acetate dyes result, and from 1.4-diaminoanthraquinone,

1. L. Holliday & Co., Ltd., and C. Shaw, E. P. 298098.
2. B. Helmert, D. R. P. 469513; abst. C. A. 1929, **23**, 1288.
3. Akt. Ges. fur Anilin-Fabrik., E. P. 262537; abst. C. A. 1927, **21**, 3751.
4. Burgess, Ledward & Co., Ltd., and W. Harrison, E. P. 190313; abst. C. A. 1923, **17**, 2964. E. P. 193646.

dyeing yellow; 1-amino-4-hydroxyanthraquinone red[1]. Cellulose ester products are dyed in shades fast to light by means of aqueous suspensions or colloidal solutions of derivatives other than amino-derivatives, of *a*-hydroxyanthraquinone which contain at least one other hydroxyl or halogen substituent in the molecule, but not those polyhydroxyanthraquinones which contain 2 OH in *o*-position to one another. Yellow dyes result from the use of 1.5-dihydroxy-, 1-hydroxy-4-chlor-, and 1.6-dihydroxy- and 1.6-dihydroxy-4-chlor-; orange from 1.4-dihydroxy-; reddish-yellow from leuco-1.4-dihydroxy-, 1.4.6-trihydroxy- or 1.4.6-trihydroxy-2-chlor-anthraquinone[2].

Details of dyeing the cellulose ethers and esters with these dyestuffs have been published by A. Hall[3], and by J. Sisley[4].

Anthrarufins. A part or all of the halogen in halogenated anthrarufins may be replaced by OH by heating with sulfuric acid[5], with or without boric acid. The halogenated products may be aminated or alkylaminated, preferably as leuco-compounds, and OH groups may be alkylated. 6-Chlor-1.4.5-trihydroxyanthraquinone, from 4.6-dichloranthrarufin, is converted into the 6-methylamino-compound giving greenish-blue on cellulose ethers or esters, or into a methyl ether, dyeing yellow.

Partially alkylated products of *pp'*-diaminoanthrarufin are used for dyeing cellulose acetate and other organic cellulose derivatives[6], the products being prepared by blocking one amido group by an acyl or other group, of *pp'*-diaminoanthrarufin, and submitting to the moderated action

1. E. Beckett, P. Baugham, J. Thomas and Scottish Dyes, Ltd., E. P. 348661. R. Petitdidier and F. Feynier, U. S. P. 1847697.
2. E. Beckett, J. Thomas and Scottish Dyes, Ltd., E. P. 238936. U. S. P. 1838523; abst. C. A. 1932, **26**, 1452.
3. Textile Colorist, 1924, **46**, 153; abst. C. A. 1924, **18**, 1202.
4. Tiba, 1931, **9**, 17; abst. C. A. 1931, **25**, 1677.
5. British Celanese, Ltd., G. Ellis, H. Olpin and E. Kirk, E. P. 343444; abst. J. S. C. I. 1930, **50**, 623-B; Chem. Zentr. 1931, I, 3296.
6. Compagnie Nationale de Matieres Colorantes et Manufactures de Produits Chimiques du Nord, Reunies Etablissements Kuhlmann, F. P. 700004; abst. C. A. 1931, **25**, 3490. See F. P. 695981.

of alkylating agents and then eliminating the blocking group. One can also condense 4.8-dihalogen anthrarufin with an aminobenzoic acid or 4.8-dinitro-1.5-dichloranthraquinone with an aminobenzoic acid, with reduction of the nitro-group. The dye, for instance, from 4.6-dichloranthrarufin and anthranilic acid in nitrobenzene dyes acetylcellulose greenish-blue tones[1].

Dianisidine Group. In the R. Clavel process[2], acetylcellulose is dyed with dianisidine hydrochloride and sodium acetate, diazotized and developed with sodium *b*-oxynaphthoate, a black being formed. Or dianisidine hydrochloride with NaOH solution is diazotized and coupled as before, a navy blue color being obtained. In another process[3], 5-nitro-2-anisidine is combined with diethylaniline in the presence of ligninsulfonic acid, and the product ground to a powder. The E. Knoevenagel process for acetylcellulose coloring employs dianisidine[4].

Indophenols. When cellulose acetate threads are treated with one of the indophenol dyes such as the reduced compound of dimethyl-*p*-aminophenyl-1.4-naphthoquinoneimide[5], deep blue shades are obtained. Organic cellulose derivatives may also be dyed with the aryl- or substituted aryl-benzo or -naphthoquinone monoimide series[6], generally comprised within the term indophenols, blue and violet shades resistant to light and soap being obtained.

Fast green or blue shades are produced on cellulose ethers and esters with indophenols prepared by joint oxidation of a halogenated *p*-aminophenol and an aromatic

1. British Dyestuffs Corp., J. Baddiley and W. Tatum, E. P. 227923; abst. Chem. Zentr. 1925, I, 2664.
2. U. S. P. 1811576; abst. C. A. 1931, **25**, 5042; Chem. Zentr. 1932, I, 2515.
3. British Dyestuffs Corp., Ltd., J. Baddiley, J. Hill and A. Shepherdson, F. P. 33009, Addn. to F. P. 623761; abst. C. A. 1929, **23**, 1281.
4. U. S. P. 1002408; abst. J. S. C. I. 1911, **30**, 1157. F. P. 383636; abst. J. S. C. I. 1908, **27**, 332.
5. G. Ellis, U. S. P. 1545819; abst. C. A. 1925, **19**, 2880; J. S. C. I. 1925, **44**, 709-B. See E. P. 220505.
6. G. Ellis and British Celanese, Ltd., E. P. 220505; abst. C. A. 1925, **19**, 736; J. S. C. I. 1924, **43**, 865-B. Belg. P. 311611.

amine having the *p*-position free[1], or by condensing a halogenated *p*-nitrosophenol with an aromatic amine having the *p*-position free, or by joint oxidation of a suitable *p*-diamine and a halogenated phenol having the *p*-position free. In general, bluer shades are obtained generally with indophenols carrying the phenolic nucleus only one chlorine atom, such as the indophenols from 2-chlor-4-amino-1-phenol and dimethylaniline or *o*-toluidine. Greener shades result with the indophenols from 2.6-dichlor-4-amino-1-phenol or 2.6-dibrom-4-amino-1-phenol and dimethylaniline or diethylaniline.

Where the substituted benzoquinone remains through the acylamino group[2], a purer blue color results.

Naphthalic Acid Types. Cellulose ethers may be dyed by the sulfamic acid of a 4-amino-1-naphthalic imide or substituted imide, as the ethylimide, phenylimide or 4-*m*-xylylimide[3]. Thus ethylcellulose when treated with 4-sulfamino-1.8-naphthalic acid or derivatives of 4-sulfamino-1.8-naphthalic anhydride, dye deep yellow tints which show a beautiful green fluorescence. If the 4-amino-1.8-naphthalimide carries as substituent in the imide group a hydroaromatic residue as a cyclohexyl derivative[4], yellow colors fluorescing green are likewise obtained.

Deep greenish yellow tints result by interaction of 4-amino-1.8-naphthalic anhydride with hydrazine, as phenylhydrazine[5].

1. A. Goeschke, U. S. P. 1691517; abst. C. A. 1929, **23**, 528; J. S. C. I. 1929, **48**, 15-B; Chem. Zentr. 1929, I, 2588. Soc. Anon. Pour L'Ind. Chim. a Bale, E. P. 261423; abst. C. A. 1927, **21**, 3469; J. S. C. I. 1928, **47**, 121-B; Chem. Zentr. 1927, I, 2358. E. P. 300299; abst. C. A. 1929, **23**, 4083; J. S. C. I. 1929, **48**, 317-B. D. R. P. 478476; abst. C. A. 1929, **23**, 4350; Chem. Zentr. 1929, II, 1351. Swiss P. 122569; abst. J. S. C. I. 1929, **48**, 716-B.

2. F. Munz, D. R. P. 453455; abst. Chem. Zentr. 1928, I, 755. P. Castan, Mon. Sci. 1925, **15**, 145; abst. C. A. 1925, **19**, 3377.

3. I. G. Farbenindustrie, A.-G., E. P. 352099; abst. J. S. C. I. 1931, **50**, 1046-B; Chem. Zentr. 1932, I, 292. See E. P. 304739, 328308.

4. *Ibid.* E. P. 328308; Addn. to E. P. 304739; abst. C. A. 1930, **24**, 5510; J. S. C. I. 1930, **49**, 709-B; Chem. Zentr. 1930, II, 2701. F. P. 667983; abst. C. A. 1930, **24**, 1522. F. P. 38447, Addn. to F. P. 667983; abst. C. A. 1932, **26**, 1132.

5. *Ibid.* E. P. 338095, Addn. to E. P. 304739; abst. C. A. 1931,

Phenylamine Dyes. In dyeing or printing cellulose acetate[1], sodium diphenylaminesulfonate or sodium carbazosulfonate or their alkyl-, chlor- or nitro-derivatives, are added to the dye bath or printing paste and then colored in the usual manner at 50° or lower. Cellulose derivatives are dyed in yellow to red shades of excellent fastness to washing, light and chlorine[2], by means of diphenylamine derivatives produced by condensing 2.4-dinitrochlorbenzene with aromatic amines which contain no sulfonic acid groups. Suitable dyestuffs are 2.4-dinitro-, 2.4-dinitro-2′-hydroxy-, 2.4-dinitro-4′-hydroxy-, 2.4-dinitro-2′-carboxy-, 2.4-dinitro-4′-amino-, 2.4-dinitro-4′-carboxy-, 2.4-dinitro-4′-acetylamino-, and 2.4-dinitro-*N*-methyl-diphenylamine, all used in aqueous suspension or colloidal solution.

The dyeing of cellulose ethers may also be effected by means of oxidizable amines with the aid of chloramides or acidylchloramides, *p*-toluenesulfonchloramide being a typical example[3]. The following amines are suitable: *p*-aminodiphenylamine, 2.4-diaminodiphenylamine, *p*-aminophenol, *p*-phenylenediamine, aminonaphthols and *α*-naphthylamine. They may be applied by mechanical impregnation in presence of acid or an oxidation catalyst as vanadium chloride. The following diphenylamines have been advocated as suitable for the dyeing of cellulose ethers and organic esters[4]: 4-chlor-2-nitro-3′-methyl-, 4-chlor-2-nitro-4′-ethoxy-, 4-chlor-2-nitro-4′-acetamido-, 4-brom-2-nitro-, 2-nitro-, 4-brom-2-nitro-4′-methoxy-, 2-nitro-4-methyl-, 2-nitro-4′-

25, 2303; J. S. C. I. 1931, **50**, 243-B; Chem. Zentr. 1931, I, 2681. W. Eckert, C. Müller and W. Gmelin and I. G. Farbenindustrie, A.-G., D. R. P. 516982, Addn. to D. R. P. 515029; abst. C. A. 1931, **25**, 2007.

1. Soc. Anon., J. Geigy, E. P. 213593; abst. C. A. 1924, **18**, 2433; J. S. C. I. 1925, **44**, 708-B; Rayon, 1926, **1**, #1, 55.

2. A. Hall and Silver Springs Bleaching and Dyeing Co., Ltd., E. P. 222001; abst. C. A. 1925, **19**, 1059; J. S. C. I. 1924, **43**, 939-B.

3. British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 298699; abst. C. A. 1929, **23**, 3110; J. S. C. I. 1928, **47**, 926-B; Chem. Zentr. 1929, I, 1153. H. Dreyfus, F. P. 656931; abst. C. A. 1929, **23**, 4351. Can. P. 293060. See E. P. 219349, 224925, 242393, 242711, 269960, 273819, 273820.

4. *Ibid.* E. P. 305560, 305566; abst. J. S. C. I. 1929, **48**, 281-B; Chem. Zentr. 1929, II, 356. See E. P. 219349, 224925, 237943, 239470.

ethoxy-4-methyl-, 4-chlor-2-nitro-, 4-brom-2′-nitro-, and 2-nitro-4′-acetamido-diphenylamine.

Cellulose derivatives are dyed golden yellow by 4-chlor-2-nitro-4′-methoxydiphenylamine[1], and a medium shade of blue by *o*-ethoxybenzeneazo-*α*-naphthylamine and then diazotizing and developing with *b*-oxynaphthoic acid. Cellulose acetate is treated in the presence of ammonia and an oxidizing agent with arylamines or their derivatives, or mixtures of amines and phenols suitable for production of indamines or indophenols[2]; treatment with *pp*′-dihydroxydiphenylamine and Turkey-red oil at 40° gives a brownish red; 3.5-dichlor-4-amino-4′-hydroxydiphenylamine, bluish red; 4-dimethylamino-4′-hydroxydiphenylamine, a blue; and 4-amino-4′-hydroxydiphenylamine, a violet.

Pyrazolones. Cellulose acetate material may be dyed and printed with pyrazolone dyes containing no sulfo-groups[3], e.g., azo dyes prepared by coupling diazo compounds with 1-phenyl-3-methyl-5-pyrazolone or 1.3-dimethyl-5-pyrazolone, the dyes being used in solution with alkali or dissolved in an organic solvent miscible with water, or dispersed in a solubilizing agent. Thus, benzeneazo-1-phenyl-3-methyl-5-pyrazolone dyes greenish yellow, *p*-methoxybenzeneazo-1-phenyl-3-methyl-5-pyrazolone a golden yellow and dimethyl-*p*-aminobenzeneazobenzeneazo-1-phenyl-3-methyl-5-pyrazolone, orange shades.

Quinones. In the dyeing of cellulose ethers with quin-

1. British Celanese, Ltd., and G. Ellis, E. P. 346694; abst. C. A. 1932, **26**, 2065; Chem. Zentr. 1932, I, 292.

2. G. Ellis, U. S. P. 1618415; abst. J. S. C. I. 1927, **46**, 249-B. H. Dreyfus, F. P. 36013, Addn. to F. P. 595759; abst. C. A. 1930, **24**, 4171. A.-G. für Anilin-Fabr., F. P. 605127; abst. J. S. C. I. 1927, **46**, 964-B; Caout. et Gutta. 1927, **24**, 13425; Chem. Zentr. 1929, I, 1619. I. G. Farbenindustrie, A.-G., D. R. P. 470849; abst. C. A. 1929, **23**, 2045; Chem. Zentr. 1927, I, 1218. G. Ellis, Can. P. 265238; abst. C. A. 1927, **21**, 1018. H. Dreyfus, Can. P. 307039. See E. P. 237943.

3. G. Ellis, F. Stevenson and C. Croft, U. S. P. 1600277; abst. C. A. 1926, **20**, 3578; J. S. C. I. 1926, **45**, 977-B. E. P. 224681; abst. C. A. 1925, **19**, 1352; J. S. C. I. 1925, **44**, 39-B. Can. P. 260530; abst. C. A. 1926, **20**, 3578. See E. P. 219349.

one residues as of the benzoquinones[1], there are used in the un-reduced state, *N*-arylated *N*-containing derivatives of benzo- and naphtho-quinones such as 2.5-di-(phenylamino)-benzoquinone, 2.5-di(*p*-aminophenylamine)-benzoquinone or 2.5-di(*p*-dimethylaminophenylamino)-benzoquinone, and 1-imino-2-hydroxy-4-(4'-aminophenylimino)-naphthalene, reddish-gray, brown, purplish-brown and puce shades respectively.

Thiazoles. According to G. Ellis and H. Olpin[2], methyl-, ethyl- or benzyl-cellulose may be dyed with unsulfonated thiazoles, the dyestuffs being either applied in substance or dyed on the fiber. Those containing diazotizable amino groups may be diazotized on the fiber and suitably coupled, while those containing groups capable of effecting a coupling, may be similarly developed by means of diazo bodies. On account of their low solubility they are usually applied in a suspension or dispersion. Yellow shades are obtained by diazotizing dehydrothio-*p*-toluidine with either phenol, *m*-toluylenediamine, *m*-toluidine, 2.4-dinitrochlorbenzene or 2.5-dichlornitrobenzene. Dimethylaniline gives orange; *b*-naphthylamine, reddish orange; *b*-naphthol, orange red; 1-naphthylamine-2-ethyl ether, red, and 2.3-hydroxynaphthoic acid, bluish red.

Urea Colors. Methyl-, ethyl-, or benzyl-cellulose may be dyed by means of compounds containing one or more urea or thiourea residues, or by coupling diazotized amino-substituted diarylureas or diarylthioureas. Thus, 2.4-dinitrophenylurea gives a yellow shade; 2.4-2'.4'-tetranitrodiphenylurea, yellow[3]; dinitrodiaminodiphenylurea, golden

1. British Celanese, Ltd., G. Ellis, H. Olpin and E. Kirk, E. P. 321401; abst. C. A. 1930, **24**, 2897; J. S. C. I. 1930, **49**, 320-B; Chem. Zentr. 1930, I, 3244. H. Dreyfus, F. P. 679489; abst. C. A. 1930, **24**, 3910; Chem. Zentr. 1930, II, 311. See E. P. 219349, 224925, 242393, 242711, 269960, 273819, 273820.

2. U. S. P. 1871673. H. Dreyfus, Can. P. 293066.

3. British Celanese, Ltd., H. Dreyfus, G. Ellis, T. Ockman and H. Olpin, E. P. 316526, Addn. to E. P. 291118; abst. C. A. 1930, **24**, 1991; J. S. C. I. 1929, **48**, 894-B; Chem. Zentr. 1930, I, 745. H. Dreyfus, Can. P. 285799; abst. Chem. Zentr. 1932, I, 2242. See E. P. 283253. D. R. P. 268658.

yellow[1]; disazo dye from tetrazotized 4.4'-diaminodiphenylurea and 2 mols. phenol, pure yellow.

Urethanes. Methyl-, ethyl- and benzyl-cellulose may be dyed by use of a compound containing at least one urethane residue[2], as 4.4'-dinitrodiphenylurethane, dyeing yellow. If there is used an azo coloring matter which comprises at least one amino group substituted by an aliphatic grouping containing not less than two OH-groups, as an azo dye from picramic acid and dihydroxypropylaniline, yellow shades also result[3]. Likewise the cellulose ether or ester may be dyed with a coloring compound containing at least one thiourethane residue, as the product obtained by heating 1-acetylaminoanthraquinone 4-isothiocyanate with ethyl alcohol or alcoholic potash[4].

Xanthenes. Xanthene dyes are formed by condensing 3.7-tetra-alkyldiaminoxanthones with secondary or tertiary aromatic amines having a free *p*-position to the amino group[5], with the use of phosphoryl chloride, phosphorous chlorides, carbonyl chloride or other reagent capable of replacing the ketonic group by halogen, as tetramethyldiaminoxanthone is condensed with *a*-ethylnaphthylamine in the presence of phosphoryl chloride, to form a color dyeing acetylcellulose bright magenta shades from a tannin mordant. Tetraethyldiaminoxanthone dyes cellulose derivatives a brighter and bluer shade.

1. H. Dreyfus, G. Ellis, T. Ockman and H. Olpin, U. S. P. 1883352. Can. P. 321714. See U. S. P. 1618413, 1618414, 1690481. E. P. 269960.

2. H. Dreyfus, U. S. P. 1735960; abst. C. A. 1930, **24**, 972; J. S. C. I. 1930, **49**, 54-B. E. P. 273819, 273820. E. P. 292452, 292453; abst. C. A. 1929, **23**, 1513; Silk J. 1928, **5**, #52, 80; Chem. Zentr. 1929, II, 1944. Can. P. 281190. See U. S. P. 1618413, 1618414, 1690481.

3. *Ibid.* U. S. P. 1735901; abst. C. A. 1930, **24**, 972; J. S. C. I. 1930, **49**, 54-B.

4. *Ibid.* U. S. P. 1735963; abst. C. A. 1930, **24**, 972; J. S. C. I. 1930, **49**, 54-B. E. P. 291816; abst. C. A. 1929, **23**, 1287; J. S. C. I. 1928, **47**, 639-B. F. P. 32948, Addn. to F. P. 627072; abst. C. A. 1929, **23**, 1287; Chem. Zentr. 1928, II, 392. Can. P. 285799. See E. P. 291118, 285968, 285969.

5. Imperial Chemical Industries, Ltd., A. Coulthard and E. Rodd, E. P. 320345; abst. C. A. 1930, **24**, 2608; Chem. Zentr. 1930, I, 2803.

Methyl- and benzyl-cellulose specifically, and the cellulose ethers in general[1], are dyed reddish- or greenish-blue shades with azo dyes made by coupling a diazotized aminoxanthene, particularly Rhodamine 3G extra, with such components as phenol, *m*-toluidine or dimethylaniline.

Altex dyes, developed by Imperial Chemical Industries, Ltd.,[2] and suitable for coloring acetylcellulose and the cellulose ethers, their "all purpose" union dyes including (Altex prefix) Yellow G, Red B, Brown G, Dark Green B, Light Green G, Saxe Blue R, Navy B, Black DB, Orange G, Bordeaux B, Nigger Brown G, and Helio R. In general, the dyestuffs are dissolved by pouring on boiling water and stirring, the material being dyed in the presence of 10-40% Glauber's salt. Salt is given as an alternative, but it is advisable to omit this when real silk is present on account of danger of spotting and tendering. Maintenance of the dye-bath at 180-185° is recommended.

Azonines are a class of direct colors and developed for acetate silk, products of Leopold Cassella Co.[3] and in mixed goods dyeings, as a rule do not stain cotton in combination with acetylcellulose, and therefore are indicated for two-color effects. Azonine G dissolves directly in hot water, other members of the group requiring either the addition of HCl or the aid of solubilizers as tetrahydronaphthalene to cause them to dissolve. Azonine R, 2R and S are freely miscible with each other and produce yellow to orange shades without development. Azonine 2R is said to be aminoazotoluene. Azonine B, R, 2R and S are best applied with the aid of HCl, but may be made into paste form with tetra- or deca-hydronaphthalin or other analogously acting body, and the paste thus formed then dissolved in boiling water. The Azonines may be diazotized

1. British Celanese, Ltd., and G. Ellis, E. P. 311433; abst. C. A. 1930, **24**, 973; J. S. C. I. 1929, **48**, 678-B; Chem. Zentr. 1929, II, 2506. See E. P. 219349, 224925, 242393, 242711, 269960, 273819, 273820.

2. F. Grove-Palmer, Silk J. 1931, **8**, #85, 38; abst. C. A. 1931, **25**, 5994.

3. Textile Colorist, 1925, **47**, 231; abst. C. A. 1925, **19**, 1950.

and developed with phenol, resorcinol, the naphthols and specific developers.

Cibacet dyestuffs, manufactured by Gesellschaft fuer Chemische Industrie in Basel, include a comprehensive line of colors for the dyeing of methyl-, ethyl-, benzyl- and acetyl-cellulose, embracing (Cibacet) Yellow 3G and GN, Orange 2R, 3R, Red 3B and GR, Violet B and 2R, Scarlet G, Blue B and 2R, Sapphire Blue G, Marine Blue BN and Diazo Black B, BN and J. These are dyed in the usual soap bath containing a small amount of ammonia, Glauber's salt or ammonium chloride, the acid dyes requiring 2% acetic acid or sulfuric acid as additions to the dye-bath. Upon diazotization and coupling in the usual manner, the Cibacet dyestuffs give brilliant and fast colors which withstand washing and light well. For instance, diazotization of Cibacet Yellow R and development with *b*-oxynaphthoic acid gives violet brown, with acetanilid yellow-orange, and with *b*-naphthol a bluish-red. Orange 2R, Scarlet G and the Diazo Blacks are diazotizable.

Ionamine dyes, which are sulfonic acids of acid dyestuffs, have been described by A. Green and K. Saunders as being readily soluble in water, hydrolyzed without difficulty in a slightly acidified dye-bath to the amine and formaldehyde sulfurous acid. Acetate takes up the former progressively as hydrolysis progresses, and contains the dyestuff as the free aminoazo base. The color thus produced may be developed by diazotizing the base on the fiber and coupling with phenols or amines[1].

The suitability of compounds of the ionamine type to act as cellulose acetate dyestuffs appears to be limited by two factors: the sulfonic acid must be sufficiently soluble in water, and the hydrolyzed base must be sufficiently soluble in cellulose acetate. Too high a degree of molecular complexity may render the base too insoluble in the fiber substance. Ionamines having the greatest affinity for ace-

1. A. Green and K. Saunders, J. Soc. Dyers & Col. 1923, **39**, 10; abst. C. A. 1923, **17**, 3920; J. S. C. I. 1923, **42**, 138-A.

tate silk have none for cotton, and differential effects can therefore be obtained on mixed materials. Ionamines having only one salt-forming group in the molecule (Ionamine B) have the maximum stability towards hydrolysis, and when dyed are little affected by organic acids. Those having two salt-forming groups (Ionamine A) are easily hydrolyzed, and can be dyed with a formic or oxalic acid bath. They are readily changed in shade, even by dilute organic acids, and are therefore unsuitable as self shades, although when diazotized and developed give deep and fast colors. Ionamine A is a direct yellow, the B an orange, the H, orange yellow, and the L, dull yellow. They are not primarily intended for cellulose ether dyeing[1].

Cellit, Celliton and *Cellitazol* line of colors suitable for dyeing acetylcellulose and the cellulose ethers as distributed by General Dyestuff Corporation, represent a series of both direct and developed colors said to have excellent fastness properties. The Celliton range is usually pastes dissolvable in hot water and then sieved into the dyebath, the powder brands being stirred with water at 105-120° F. to a uniform paste and then treated like ordinary paste dyes. The goods are dyed 0.5-1 hr. at 140-170° F. in a frothing olive oil soap containing 2.3 lbs. soap per 100 gals. soft water. Being unaffected by metals, it is not necessary to dye exclusively in wooden vats. The paste products must be protected from frost and from drying.

The Cellit dyestuffs are powder products soluble in water, the yellow and orange brands being prone to show prototropic effects, Cellit Fast Yellow GGN being the least susceptible. They cannot be used for mixed fabrics containing animal fibers, as the latter are severely stained. They do not leave vegetable fibers entirely unstained. In dyeing, they are dissolved in water and dyed at 170° F., in a proportion of goods to liquor of 1-30, pale shades being best in 0.5-1 hr. at an initial temperature of 70-80°. Glau-

1. A. Green and K. Saunders, J. Soc. Dyers & Col. 1924, **40**, 138; abst. J. S. C. I. 1924, **43**, 504-B.

ber's salt or ammonium chloride is added to the dye-bath, but Cellit Fast Yellow GGN requires an addition of 3-5% acetic acid.

Cellitazols are developed dyestuffs of the brands (Cellitazol) AZ, B, ORB, R, RB, SR, STN conc., STN and STA. According to the developer used, they withstand cross-dyeing in most instances. They are dyed with HCl in the bath of Tetrapol or Tetralin, or dissolved in formic acid, as Cellitazol R. The goods are diazotized in the usual manner with nitrite and HCl, followed by the usual developers. Metal vessels should not be used[1].

Celliton Yellow 5G (powder) is said to be the purest greenish-yellow shade obtainable[2], Celliton Orange R and GR being used for beautifying and shading scarlet shades after yellow.

Duranol dyes are products of the British Dyestuffs Corporation, the principal brands being (Duranol) Orange G, Red G, Red 2B, Blue G, Black and Violet 2R, sold as 10% pastes, requiring but dilution with water to the strength desired just prior to application. They may be printed on acetate silk or acetate and cotton, having no affinity for the latter, but do stain animal fibers as wool and real silk. Duranol Blue G exhausts slowly, therefore requiring a longer dyeing period for the development of full shades. They are said to have excellent fastness to washing, alkalis, acids, perspiration, rubbing and to light, and suitable fastness to the usual fulling and to cross-dyeing.

Celatene group, said to be the first direct-dyeing colors for acetylcellulose to be produced in bulk[3] is manufactured by Scottish Dyes, Ltd., and dyes acetate silk "under almost any condition which does not destroy the fiber." In order to insure best results from a level-dyeing viewpoint, the initial temperature of dyeing should be lowered to as low

1. Anon., Rayon J. 1927, **2**, #3, 17.
2. G. Rudolph, Kunstseide, 1930, **12**, 198; Jentgen's Rayon Review, 1930, **2**, #5, 216; abst. C. A. 1931, **25**, 208. Kunstseide, 1929, **11**, 261; abst. C. A. 1929, **23**, 4823. Rayon, 1929, **9**, #9, 14, 41; abst. C. A. 1930, **24**, 502.
3. W. Todd, Rayon, 1926, **2**, #8, 12.

as 30°. The amount of liquor used is 20-40 times the weight of material, depending upon the type of dyeing machine and material to be colored. The necessary amount of dye paste is sieved into the bath and the temperature raised to 60°, then in a half hour to 70-85°, being continued 0.75-1 hr. The material is then taken out, well rinsed in water to clear the shade from any dissolved dyestuff, and dried in the usual way. The Celatenes are not recommended for dyeing wool or silk unions with acetate silk, as the shades, althought fast to light, are not fast to washing[1].

Nacelan dyes are products of National Aniline Co., comprising an extended range suitable for dyeing cellulose ethers or acetylcellulose products. In the use of these colors it is recommended to dissolve them separately even if other colors are to be used in conjunction. A dispersing agent is of assistance in solubilizing refractory colors. It is advised to enter the material in a luke-warm bath[2], the temperature being raised to 80° during working of the goods, and the dyeing continued for 45-60 min. Black may require 1.5 hrs. Medium and heavy shades are assisted by the presence of 20-40% Glauber salt crystals[3]. A scouring before dyeing is usually advisable.

For light yellow dyeings, for instance[4], a bath of 1% each Niagara Blue DB and Diazine Black OB with 0.1% Nacelan Yellow G, in 15% solution of Glauber's salt and 0.05% Diazine Red 5BL is said to give full, bright shades.

Setacyl and Setacyl Direct Dyes, representing an older and a newer series of dyestuffs for the cellulose ethers and esters, are products of J. R. Geigy, Basle, the Cetacyl Direct dyes being suspension colorants showing excellent fastness to light and washing[5]. Some of the Setacyl dyes appear to be basic products, but there appears little in the literature

1. L. Hooley, Color Trade J. 1925, **16**, 93; abst. C. A. 1925, **19**, 2415.
2. W. Holst, Dyestuffs, 1931, **32**, 25; Textile Colorist, 1931, **53**, 481; abst. C. A. 1932, **26**, 309.
3. *Ibid.* Rayon and Synthetic Yarn J. 1932, **13**, #2 ,35.
4. *Ibid.* Rayon and Synthetic Yarn J. 1932, **13**, #3, 16.
5. H. Brandenburger, Melliand Textber. 1929, **10**, 869.

as to their chemical classification, and considerable confusion in the literature with respect to the older and newer series of dyestuffs. The "Brilliant" dye series appear entirely distinct from the "Direct" class.

S. R. A. Dyes (*S*ulfonated *R*icinoleic *A*cid), of British Celanese, Ltd., and Celanese Corporation of America, are colors suitable for the dyeing of cellulose acetate and the cellulose ethers[1], and in general are 10% pastes or powders of azo, anthraquinone and other dyestuffs in a fatty solvent as Turkey-red oil or oleic acid, yielding clear, stable solutions suitable for dyeing when diluted with water. Most of the S. R. A. colors have no affinity for vegetable colors, but slightly stain animal fibers. Although a dye liquor containing the S. R. A. colors is essentially a colloidal solution, the usual addition of assistants as sodium chloride and sulfate is desirable, it being generally true that the substantive affinity of a dyestuff for acetylcellulose is roughly proportional to its basicity and molecular simplicity[2].

The S. R. A. colors comprise: Yellow I, of lemon shade; Yellow II, greenish lemon; Yellow VIII, daffodil; Yellow IX, gold; Golden Orange I, reddish gold; Golden Orange III, similar to I; Orange I, bright tangerine; Orange II, yellower than Orange I; Red I, scarlet; Red III, blue scarlet; Red V, bluish crimson; Red VII, brilliant bluish red; Heliotrope I, bright red violet; Violet II, brilliant bluish violet; Blue III, reddish blue; Blue IV, pure blue; Blue VII, greenish blue; and Black IV, developed with *b*-oxynaphthoic acid.

Yellow. Organic cellulose derivatives are dyed fast, greenish-yellow shades free from phototropy by means of

1. G. Ellis, J. Soc. Dyers & Col. 1924, **40**, 285; abst. J. S. C. I. 1924, **43**, 864-B; J. Soc. Dyers & Co. 1925, **41**, 98; abst. C. A. 1925, **19**, 1780; Chem. Zentr. 1925, II, 987. J. Soc. Dyers & Col. 1926, **42**, 184; abst. C. A. 1926, **20**, 2752; Chem. Zentr. 1926, II, 1198. Color Trade J. 1925, **16**, 82; abst. C. A. 1925, **19**, 2415.

2. C. Mullin, Can. Colorist Textile Processor, 1926, **6**, 329, 339, 365, 374; **7**, 6, 14; abst. C. A. 1927, **21**, 177, 1014, 1358. R. Dort, Chemicals, 1925, **24**, #19, 19; #23, 19; #1, 22; #5, 21; abst. C. A. 1926, **20**, 1325; Chem. Zentr. 1926, I, 3102. Melliand, 1929, **1**, 102; abst. C. A. 1929, **23**, 3347. F. Stevenson, Dyer & Calico Printer, 1926, **55**, 86; Chemicals, 1926, **25**, #17, 19; abst. C. A. 1926, **20**, 2076.

monoazo dyestuffs obtained by coupling 1.3-dihydroxyquinoline with diazotized aniline or its homologues[1], particularly with halogenated aniline and toluidines[2]. 1.3-Dihydroxyquinoline is also applicable. The cellulose derivatives may also be colored with monoazo dyes from diphenylaminemonosulfonic acid coupled with unsulfonated diazo compounds of the benzene or naphthalene series[3]; thus, *m*-nitraniline + diphenylaminesulfonic acid gives a golden yellow. Azo dyes may also be formed by coupling a non-sulfonated diazo compound with *b*-naphthylamine- or *b*-naphthol-8-sulfonic acid; e.g., 2.5-dimethoxyaniline + crocein (yellow), 5-nitro-*o*-anisidine + phenyl-*b*-naphthylamine-8-sulfonic acid (seal-red), *o*-chloraniline + phenyl acid (reddish yellow), and 2.5-dimethoxyaniline + crocein acid (pink)[4].

Fast yellow shades on cellulose ethers[5], which do not exhibit phototropy, are obtained by applying thereto 5-nitro-4-amino-*m*-xylene or 5-chlor-3-nitro-*o*-toluidine with a small quantity of Turkey-red oil. By condensing *ar*-tetrahydro-*a*-(or -*b*-)naphthylamine (2.4-dinitrophenyl-*ar*-tetrahydro-*a*-(or -*b*-)naphthylamine, 2-nitro-4-chlorphenyl-*ar*-tetrahydro-*b*-naphthylamine, or 2.4-dinitro-6-sulfophenyl-*ar*-tetrahydro-*a*-naphthylamine) with nitroaromatic compounds containing one or more labile halogen atoms[6], as 2-nitro- or 2.4-dinitro-chlor(or brom-)benzene or 2.5-dichlornitrobenzene, greenish-yellow to brownish yellow shades are obtained.

1. J. Baddiley and J. Hill, U. S. P. 1611986; abst. C. A. 1927. **21**, 655. E. P. 236037; abst. C. A. 1926, **20**, 993; J. S. C. I. 1925, **44**, 708-B.
2. Badische Anilin und Soda Fabrik, E. P. 11205, 1905; abst. J. S. C. I. 1905, **24**, 840. See D. R. P. 117167.
3. H. Eichwede, E. Fischer and C. Müller, D. R. P. 441325; abst. J. S. C. I. 1927, **46**, 905-B.
4. F. Weber, D. R. P. 452213; abst. J. S. C. I. 1929, **48**, 15-B; Chem. Zentr. 1928, I, 259.
5. Imperial Chemical Industries, Ltd., S. Thornley and A. Twemlow, E. P. 353878; abst. J. S. C. I. 1931, **50**, 1137-B; Chem. Zentr. 1932, I, 2515.
6. British Celanese, Ltd., and H. Olpin, E. P. 330602; abst. C. A. 1930, **24**, 6032; Chem. Zentr. 1931, I, 1366. F. P. 688624; abst. Chem. Zentr. 1930, I, 165. See E. P. 219349, 224925, 242393, 242711, 269960, 273819, 273820.

The cellulose ethers may be dyed fast tints by compounds in which an aryl dye nucleus[1] is linked to one or more thiocyanate, cyanate, isothiocyanate, isocyanate or simpler or aliphatically substituted urea or thiourea residues, lemon to golden yellow tones being produced. Cellulose ethers are also dyed yellow with monosulfoarylazodiarylamines containing at least 1 nitro-group in the diarylamine complex, as with 4-benzeneazo-2.6-dinitro-4′-sulfo- or 4-benzeneazo-4′-nitro-2′-sulfo-diphenylamine[2].

In dyeing cellulose ethers and esters yellow[3], use is made of derivatives, non-sulfonated in the nuclei, of 4-amino-1.8-naphthalimide substituted or not on the imide N by alkyl or an isocyclic hydrocarbon residue. The dyeings partly show a beautiful green fluorescence. Cellulose ethers are dyed in the usual manner in a colloidal solution or aqueous suspension, with or without the addition of a protective colloid or a salt. The 4-amino-1.8-naphthalic acid derivatives are obtainable by causing 4-amino-1.8-naphthalic acid anhydride to react with ammonia, or an amine of the aliphatic or isocyclic series.

Yellow to orange shades are produced on cellulose ether or ester materials by nitroacridine compounds[4] such as *a*- or *b*-nitroacridine, dinitroacridine or tetranitroacridine,

1. H. Dreyfus, U. S. P. 1854460, 1854461, 1854462, 1855131. E. P. 291118; abst. C. A. 1929, **23**, 1287; J. S. C. I. 1928, **47**, 601-B; Chem. Zentr. 1928, II, 1943. F. P. 627072; abst. Chem. Zentr. 1928, I, 2007. F. P. 32948, Addn. to F. P. 627072; abst. C. A. 1929, **23**, 1287. Can. P. 276553; abst. C. A. 1928, **22**, 2067. Can. P. 285799. Ital. P. 228813. Belg. P. 350777; abst. Chem. Zentr. 1929, II, 355. See E. P. 285968, 285969.

2. E. Fischer and C. Müller, U. S. P. 1674168; abst. C. A. 1928, **22**, 2847; J. S. C. I. 1928, **47**, 744-B; Chem. Zentr. 1928, II, 1944. I. G. Farbenindustrie, A.-G., E. P. 275230; abst. C. A. 1928, **22**, 2279; J. S. C. I. 1928, **47**, 783-B; Chem. Zentr. 1927, II, 2715. F. P. 638138; abst. C. A. 1929, **23**, 285. D. R. P. 468981; abst. C. A. 1929, **23**, 994.

3. W. Eckert and C. Müller, U. S. P. 1836529; abst. C. A. 1932, **26**, 1454. I. G. Farbenindustrie, A.-G., E. P. 304739; abst. C. A. 1929, **23**, 4831; J. S. C. I. 1930, **49**, 506-B; Chem. Zentr. 1929, I, 2924. F. P. 646371; abst. C. A. 1929, **23**, 2305. W. Eckert and C. Müller, D. R. P. 515029; abst. C. A. 1931, **25**, 1685; Kunst. 1931, **21**, 94.

4. British Alizarine Co., Ltd., W. Dawson, C. Soutar and R. Wood, E. P. 276542; abst. C. A. 1928, **22**, 2471.

with or without the addition of an acid or salt. Yellow shades also result by the use of unsulfonated nitro-derivatives of compounds containing two or more aryl radicals or aromatic residues[1], two of which are united by a single linkage other than N alone. Examples are the use of 3-nitrobenzidine, 3.3′-dinitrobenzidine, 3.3′-dinitro-*o*-tolidine, 3-nitro-4-aminodiphenyl ether, and 3.3′-dinitro-4.4′-di(dimethylamino)diphenyl ketone.

Green. Green or blue-green shades on cellulose ethers are producible with a dihydroxymercaptoanthraquinone compound[2], the compound having both the hydroxyl and mercapto groups in *a*-positions and containing less than two sulfonic groups in the anthraquinone nucleus. The dyestuff is formed by eliminating both sulfonic groups from Solway Emerald. Green dyeings are also obtained by using certain compounds of the Malachite Green and Brilliant Green types, as by oxalates of unsulfonated triarylmethane derivatives such as the 2.4-dimethyl-derivatives of Malachite green obtained by oxidizing the product of condensation of 4.4′-tetramethyldiaminobenzohydrol with *m*-xylene[3].

Threads and fabrics of cellulose acetate are colored with nitro-derivatives of carbazoles[4], with or without other substituents such as halogen, hydroxy or amino groups, being dyed bright yellowish green by use of 1-nitrocarbazole solubilized with sodium sulforicinoleate.

Red. Dyestuffs of the Rhodamine type, distinguished by their brightness and good solubility[5] are obtained by

1. British Celanese, Ltd., G. Ellis, H. Olpin and W. Miller, E. P. 283253; abst. C. A. 1928, **22**, 3996. U. S. P. 1679935; abst. C. A. 1928, **22**, 3787. Can. P. 293054. F. P. 639825.
2. W. Tatum and W. Todd, L. Hooley and J. Thomas, U. S. P. 1869286. E. P. 358033; abst. J. S. C. I. 1932, **51**, 179-B.
3. L. Lawrie, F. Linch and E. Rodd, U. S. P. 1772515; abst. J. S. C. I. 1930, **49**, 944-B. E. P. 297897; abst. C. A. 1929, **23**, 2836; J. S. C. I. 1928, **47**, 891-B; Chem. Zentr. 1929, I, 1274. F. P. 655948; abst. C. A. 1929, **23**, 4084. D. R. P. 529692.
4. British Celanese, Ltd., G. Ellis, H. Olpin and W. Miller, E. P. 283081; abst. C. A. 1928, **22**, 3996.
5. Imperial Chemical Industries, Ltd., and M. Wyler, E. P. 333016; abst. C. A. 1931, **25**, 602; J. S. C. I. 1930, **49**, 983-B; Chem. Zentr. 1931, I, 3726. E. P. 331687.

heating diethylamino-oxybenzoylbenzoic acid (m. pt. 203°) with sulfuric acid, diluted, allowed to crystallize and esterified with ethyl alcohols and HCl gas, cellulose ethers being dyed bluish red.

Rose. As a colorant for the etherized celluloses[1], the ethers of 1.4-diamino-2.3-dioxyanthraquinone are used, suitable compounds being 2.3-dimethoxy-, 2.3-diethoxy-, or di-*n*-butoxy-1.4-diaminoanthraquinone.

Violet. By diazotizing 4-amino-6-acylaminoresorcin-dialkyl- or diaryl-ether and coupling with 2.3-oxynaphthoic acid or its arylamino-derivatives, violet dyes for the cellulose ethers result[2], which are said to be particularly fast to washing, over-dyeing and chlorine, and show a good fastness to light. 4-Amino-6-benzoylaminoresorcindimethyl ether with Turkey-red oil or the corresponding diethyl ether or 2.3-oxynaphthoic anilide are specified. Also clear violet or blue tones are obtained on cellulose ethers or esters by the use of 2-amino-5-benzoylaminohydroquinonedimethyl (or diethyl) ether or 2-amino-5-*p'*-chlorbenzoylaminohydroquinonedimethyl (or diethyl) ether upon diazotization and development with 2.3-oxynaphthoic acid or 2.3-oxynaphthoic acid anilide[3].

Blue. Greenish to deep blue shades are obtained on cellulose acetate or cellulose ethers by immersion in a hot, aqueous suspension containing hexa-aminodianthraquinonyl thioether[4], or a dyestuff obtained by nitrating 1.5- or 1.8-diphthaliminoanthraquinone[5] and subsequent partial

1. P. Nawiasky, A. Krause and B. Stein, D. R. P. 542779, Addn. to D. R. P. 479225; abst. Chem. Zentr. 1932, I, 2098. D. R. P. 479225; abst. Chem. Zentr. 1929, II, 2506.
2. H. Wagner, A. Kuchenbecker, R. Huss and C. Mueller, D. R. P. 509401; abst. C. A. 1931, **25**, 421; Chem. Zentr. 1931, I, 1019.
3. *Ibid.* D. R. P. 511205, Addn. to D. R. P. 509401; abst. C. A. 1931, **25**, 1685; Chim. et Ind. 1931, **25**, 1218; Chem. Zentr. 1931, I, 1526. See D. R. P. 509304.
4. Scottish Dyes, Ltd., E. Beckett, J. Thomas and R. Tonkin, E. P. 231206; abst. C. A. 1925, **19**, 3598; J. S. C. I. 1925, **44**, 393-B.
5. H. Drescher, J. Thomas and Scottish Dyes, Ltd., E. P. 214765; abst. C. A. 1924, **18**, 2715; J. S. C. I. 1924, **43**, 590-B.

hydrolysis with alkali sulfide. Thus, a blue dyestuff is obtained when 1.5-diphthaliminoanthraquinone dissolved in sulfuric acid is nitrated, washed and treated with sodium sulfide. 1-Methylamino-4-anilinoanthraquinone gives a light, greenish blue shade on cellulose ethers or organic cellulose esters[1].

Dyeing with Logwood Colors. In the C. Bedford process[2], an aqueous solution of logwood or hematine is applied, followed by treatment with a bichromate bath, the temperature of which varies depending upon the nature of the artificial fiber and the depth of color desired. In the fixation of iron salts on fabrics composed of cellulose organic esters[3], the fiber is first mordanted with a 40-55% solution of a ferric salt at 40-60°, and then dyed with logwood or other vegetable dyes, the process being especially applicable to ethylcellulose fabrics. Ferric chloride is preferred.

Black Dyeings on Cellulose Ethers and Esters. The cellulose ethers and esters can be dyed black by the following methods: 1, by means of an amine, diazotize and couple with a suitable naphthol; 2, dye with a direct dyeing black; 3, color with an oxidation black; 4, dye with a direct dyeing blue, yellow and red mixture; or 5, with cellulose acetate filaments only, hydrolyze and dye with direct colors. According to A. Hall[4], coupling with amines is unsatisfactory because of the affinity of the cellulose derivative for the amine, which reduces the amount supplied for coupling and gives an unstable shade. The temperature of coupling

1. Soc. Anon. Pour L'Ind. Chim. a Bale, F. P. 697541; abst. C. A. 1931, **25**, 3176; Chem. Zentr. 1931, II, 637. See F. P. 568655.
2. E. P. 263222; abst. C. A. 1928, **22**, 171; Chem. Zentr. 1927, I, 2360; Silk J. 1927, **3**, #35, 75.
3. G. Rivat, E. Cadgene and C. Dreyfus, U. S. P. 1779494; abst. C. A. 1931, **25**, 217; J. S. C. I. 1930, **49**, 1149-B. E. P. 273692; abst. C. A. 1928, **22**, 2067; J. S. C. I. 1928, **47**, 744-B; Chem. Zentr. 1927, II, 2573. F. P. 636057; abst. C. A. 1928, **22**, 4835.
4. Am. Dyestuff Reptr. 1929, **18**, 671; abst. C. A. 1930, **24**, 1221. Am. Dyestuff Reptr. 1929, **18**, 545; abst. C. A. 1929, **23**, 5323. Am. Dyestuff Reptr. 1923, **12**, 33; abst. C. A. 1923, **17**, 1150.

should be raised and length of time increased above normal for a complete reaction[1].

According to the R. Clavel process[2], organic cellulose derivative fibers are dyed with diphenyl black base in presence of an aliphatic carboxylic acid, as shown by the following details:

1. For one kilo of filaments a stock solution is prepared with 200 gms. diphenyl black base, 250 cc. lactic acid, 550 cc. acetic acid 50%, and the whole diluted to 1250 cc. with water. The diphenyl black base is dissolved in the acids by warming and diluting. A second stock solution is prepared with 125 gms. aluminum chloride 30° Be., 125 gms. chromium chloride 30° Be., 20 gms. cupric chloride 40° Be., 150 gms. sodium chlorate in 60 cc. water and the whole made up to 1250 cc. The dyebath is prepared so that the weight of the diphenyl black base corresponds to 12% of the weight of the goods, and is made up of 750 cc. each stock solution I and II, the whole diluted with water to about 4.5-6.5 liters. The dyeing is performed in the cold, the goods being turned 2 or 3 times in the bath and soaked for 0.5 hr. They are then removed from the bath and whizzed. Oxidation or development is effected by placing the goods in a drying room at 80°, preferably turning the goods on a rod every half hour. After development to the point desired, the goods are washed twice, soaped at 50-60°, rinsed with two soft waters and one hard water and scoured.

Or[3], cellulose acetate may be colored with the developing dyes or "ice colors" by employing in the base baths or developer baths a relatively large quantity of water-soluble

1. Silver Springs Bleaching & Dyeing Co., Ltd., and A. Hall, E. P. 258699; abst. C. A. 1927, **21**, 3134. See U. S. P. 1657255. E. P. 311435.

2. U. S. P. 1547789; abst. C. A. 1925, **19**, 3024. E. P. 194840; abst. C. A. 1923, **17**, 3611; J. S. C. I. 1923, **42**, 448-A; Chem. Tech. Uebers. 1923, **47**, 159; Chem. Zentr. 1923, IV, 208.

3. R. Clavel, U. S. P. 1549906; abst. C. A. 1925, **19**, 3599; J. S. C. I. 1925, **44**, 801-B; Caout. et Gutta. 1926, **23**, 13315. E. P. 187964; abst. Chem. Zentr. 1923, II, 576. See U. S. P. 979966, 1378443.

chloride as magnesium or calcium chlorides. As is known, many bases and developers cannot be employed either neutral or alkaline, because precipitation occurs. By the use of protective colloids, precipitations and separations are avoided, and the dyestuffs can be held in suspension. Thus, 1 kgm. cellulose acetate fiber is dyed black by treating 30-45 min. with 20-25 liters of a bath containing 20 gms. dianisidine hydrochloride, 40 gms. magnesium chloride and 40 gms. sodium carbonate. The goods are washed once each with soft and hard water and then brought into a diazotizing bath containing 50 gms. sodium nitrite and 200 cc. concentrated hydrochloric acid and vigorously stirred in the same for 0.5 hr. at 15°. The succeeding developing bath consists of 20 gms. naphthylamine chloride and 8 gms. sodium bicarbonate in which bath the goods are treated 1 hr., then washed, introduced into a second diazotizing bath of the same composition as the former. The goods are then washed, followed by a second weakly alkaline developing bath consisting of 5 liters boiled-off liquor, 30 gms. aminonaphthol, 5% magnesium chloride and 20 liters of water as calculated on the weight of the goods, a full black development taking place in about an hour. Then follows the final washing in water, one in hot soap solution at 60° and finally one brightening bath.

E. Speight[1] obtains full black shades on cellulose ether or ester silk by direct dyeing with secondary disazo dyes obtained by diazotizing aniline, toluidine, xylidine, chloraniline or chlortoluidine and coupling with *α*-naphthylamine or *α*-naphthylamine-6 (or 7)-sulfonic acid, the amino compound thus formed being diazotized and coupled with 1.5-naphthyldiamine or 1.5-aminonaphthol to form the disazo dye. In dyeing mixed goods containing cellulose ether or

1. U. S. P. 1780320; abst. C. A. 1931, **25**, 1101; J. S. C. I. 1930, **49**, 1149-B. E. P. 314651; abst. C. A. 1930, **24**, 1522; J. S. C. I. 1929, **48**, 716-B; Chem. Zentr. 1930, I, 439. F. P. 674526; abst. C. A. 1930, **24**, 2897. Can. P. 316335. See L. Cassella & Co., E. P. 7067, 1889; abst. J. S. C. I. 1890, **9**, 385. M. Hoffmann and A. Weinberg, E. P. 9214, 1885; abst. J. S. C. I. 1889, **8**, 700. L. Cassella and Co., E. P. 2718, 1892; abst. J. S. C. I. 1892, **11**, 516.

ester fibers with those of wool[1] the process is carried out with the aid of a suitable substantive black and also a wool color of the same shade, the dye bath containing ammonium acetate. The dyeing is started at 40-50° and gradually raised to the boiling point. While the cellulose derivative portion is dyed more deeply at the beginning, the woollen portion becomes more deeply dyed at the close of the process due to the acid reaction of the liquor. When deeper shades are desired, it is necessary to add a little acetic acid to the dye bath, about 1%, in order to attain greater depth of shade on the wool.

Black dyeings with white or colored effects are produced by printing the white or previously dyed goods with a fat, wax or chemically inert resist[2], treating with *p*-aminodiphenylamine or 4-hydroxy-4′-amino-5′-methyldiphenylamine, and developing the black by oxidation. Although it is possible to dye the cellulose ethers black by means of logwood with after-chroming, with SRA Black IV, Celatene Black and Acetosilk Black, all of the methods leave much to be desired[3].

In preparing black dyeings on cellulose ether or ester filaments or fabrics[4], the Silver Springs Bleaching & Dyeing Co. and A. Hall impregnate the materials with a solution or dispersion of *α*-naphthylamine and then treat with an aqueous solution of nitrous acid at 35-40°, containing 1% sod-

1. Anon., Rayon, 1930, **10**, #6, 12. P. Virck (U. S. P. 1774621. E. P. 306637. F. P. 644436 and Addn. 34611) use 2-(4-aminophenylamino)--6-hydroxynaphthalene chloride or 2-(4-aminophenylamino)-7-(4-aminophenylamino)naphthalene chloride with sodium acetate followed by bichromate for a fast blue-black, or 2-(4-aminophenylamino)-6-(4-aminophenylamino)-naphthalene chloride for green-black. H. Dreyfus (F. P. 710323) impregnates the cellulose derivative fabric with *p*-aminodiphenylamine, then with aniline, followed by an oxidizing agent.

2. I. G. Farbenindustrie, A.-G., E. P. 311467; abst. C. A. 1930, **24**, 973; J. S. C. I. 1929, **48**, 678-B. F. P. 666463; abst. C. A. 1930, **24**, 1522. F. P. 36398, Addn. to F. P. 666507; abst. C. A. 1930, **24**, 1522, 4171. D. R. P. 508562; abst. C. A. 1931, **25**, 826.

3. Anon., Rayon, 1927, **4**, #3, 7. See E. P. 246879, 255962, 258699, 260312.

4. E. P. 321034; abst. C. A. 1930, **24**, 2615; J. S. C. I. 1930, **49**, 54-B; Chem. Zentr. 1930, II, 142.

ium nitrite and 5% sulfuric acid. Or[1], 2.4-dinitrodiphenylamine is applied in a dye liquor or printing paste, and is reduced simultaneously with or subsequent to the corresponding diamino compound which is then subjected to oxidation. For instance, 5 parts organic cellulose derivatives are immersed for 1 hr. in 200 parts of an aqueous liquor at 75° and containing 1.25 parts of 2.4-dinitrodiphenylamine, 0.4 part soap, 0.4 part ammonia, sp. gr. 0.88, and 0.5 part sodium hydrosulfite, whereby the fiber becomes dyed with 2.4-diaminodiphenylamine. The fibers, which are almost colorless, are then rinsed and immersed in 200 parts of water containing 0.2 copper sulfate, 1 concentrated hydrochloric acid and 10 parts of a 40-volume solution of hydrogen dioxide, further quantities of H_2O_2 being added until the fibers assume a deep black shade. The dyed goods are then well soaped and washed.

The advantages claimed for this method are that it avoids the use of 2.4-diaminodiphenylamine and utilizes the cheaper nitro-compound. In common with oxidation pigments, the resulting black shade is said to be very fast to all agencies, and if properly dyed is fast to rubbing. Also[2], when fibers are treated with a mixture of aniline and at least one organic amine serving as an oxidation catalyst such as *p*-aminodiphenylamine, *p*-phenylenediamine, *p*-aminophenol or nitrosodimethylaniline, followed by oxidation in a hot acidified solution of a bichromate at least nearly saturated with sodium chloride, aniline-black dyeings on cellulose ether or ester fibers result of excellent fastness. Other amines may be used with the aniline, such as *o*- and *p*-toluidines, *b*-phenylenediamine or *a*-naphthylamine.

On account of the fact that cellulose acetate filaments show an absorbent selectivity for basic compounds[3] and do

1. Silver Springs Bleaching & Dyeing Co., Ltd., and A. Hall, E. P. 322893; abst. C. A. 1930, **24**, 2897; Chem. Zentr. 1930, II, 818; Rayon, 1931, **12**, #3, 58.

2. *Ibid.* E. P. 337746; abst. C. A. 1931, **25**, 2302; J. S. C. I. 1931, **50**, 197-B; Chem. Zentr. 1931, II, 1766.

3. Silk J. 1930, **7**, #76, 39; #77, 37; #78, 33; abst. C. A. 1931, **25**, 1677.

not absorb salts, A. Hall suggests that the fibers be treated with aniline first, and then oxidized in a fresh bath.

The I. G. Farbenindustrie[1] have detailed a method of reserving dyestuffs obtainable by oxidation on the fiber which is applicable to the cellulose ethers, aniline black being reserved by means of vat dyestuffs by mixing the latter with the cellulose ether or other precipitating agent capable of precipitating by alkali, adding reserving agents as sodium bisulfite, sodium acetate or zinc oxide, and printing the material with the colors thus obtained. The non-reserved aniline black is first developed in the usual manner by steaming the material for a short time, and the vat dyestuffs fixed by subsequently treating in an alkaline hydrosulfite bath and finally steaming.

The following example illustrates the method:

The reserve is either printed on the white material which is subsequently prepared with a solution of aniline black, or other color is printed on the material previously prepared with aniline black. For colored reserves, the formula comprises 100 gms. yellow dyestuff[2], 600 gms. thickening M (methylcellulose solution), 100 gms. 50% acetic acid and 200 gms. sodium acetate. The "thickening M" is prepared by dissolving 75 gms. methylcellulose in 925 gms. hot water, dissolution taking place on cooling. The solution of aniline black comprises 84 aniline salt, 5 aniline oil, 50 tragacanth 60:100, 30 sodium chlorate and 54 (gms.) potassium ferrocyanide in 777 gms. water. After the material has been printed, it is steamed for 1 min. in the Mather-Platt apparatus at 95-100°, padded in the hydrosulfite bath prescribed below, directly steamed in a roller box for 15 sec. at 98°, rinsed cold, acidified, chromed with a solution of 2 gms. potassium bichromate per liter and finally rinsed. The hydrosulfite bath consists of 100 gms.

1. E. P. 311740; abst. C. A. 1930, **24**, 974; J. S. C. I. 1930, **49**, 815-B; Chem. Zentr. 1929, II, 2831. F. P. 675045; abst. C. A. 1930, **24**, 2897.

2. For instance, as prepared according to Example 1 of E. P. 205502, issued to Farbwerke vorm. Meister, Lucius u. Brüning.

concentrated hydrosulfite powder, 150 cc. NaOH solution of 40° Be., and 3 gms. of a wetting agent.

In printing and fixing vat dyes by aniline black or other dyes which are oxidized on the fiber[1], the vat dye is mixed with cellulose ethers as a thickening agent and printed on the fabric with aniline black. The latter is developed and the goods submitted to an alkaline bath and reducing and wetting-out agents, the dye being fixed by steam. In an example, the printing dye contains a vat dye, sodium chlorate, potassium ferrocyanide and water, the thickening agent comprising methylcellulose. After printing and developing, the goods are treated with a solution of hyposulfite and NaOH. They are finally dried and steamed.

Contrary to the established practice in the dyeing of cotton in which padding liquors as basic as possible are used in order to preserve the strength of the cotton, it has been found[2] that the formation of oxidation aniline black on cellulose ether and ester filaments proceeds satisfactorily when excess of acid is present in the liquor. It is generally preferable to add organic acids to aniline hydrochloride in preparing the padding liquor, acetic acid being the most useful. Under such conditions the padded fabric can be fully aged within 5 min. at about 100°, and the final shade developed by a short after-chroming with a solution containing 1.25% sodium bichromate and 1% acetic acid.

Mixed fabrics containing a cellulose ether and cotton are dyed black by first treating it with an aqueous suspension of *p*-aminodiphenylamine or 2.4-diaminodiphenylamine which is absorbed by the cellulose derivative but not the cotton; then padding with an aniline black liquor containing aniline hydrochloride, hydrochloric acid, potassium chlorate and copper sulfate, drying, ageing at 40-50° for development of black on both fibers, and finally after-chroming at room temperature for 1 hr. with aqueous sodium

1. E. Pfeffer, D. R. P. 534641; abst. C. A. 1932, **26**, 1133.
2. British Celanese, Ltd., G. Ellis and W. Miller, E. P. 332624; abst. C. A. 1931, **25**, 420; J. S. C. I. 1930, **49**, 1024-B.

bichromate (sp. gr. 1.005-1.015)[1]. H. Dreyfus[2] dyes cellulose ethers by means of aniline in the presence of HCl and acetic acid and oxidizes with a chlorate to give a deep black.

In a mixed fabric containing methyl-, ethyl- or benzylcellulose in association with cotton or wool[3], level black shades are obtained by applying a mixture of *p*-aminodiphenylamine and aniline in equal parts, and oxidizing in the usual manner. Black shades are also obtainable by dyeing with oxidation aniline black in the presence of a considerably greater proportion of acid than commonly used in the dyeing of cotton materials, the excess acid being in the form of an acid salt or mineral acid, but preferably as an organic acid. A satisfactory solution for dyeing by the padding or ageing method is prepared by mixing a solution containing aniline hydrochloride 127 gms., glacial acetic acid 25 gms., water 248 gms., alcohol 100 gms., and 50% acacia solution 200 gms. with a solution containing sodium chlorate 80 gms., cupric chloride 3 gms. and water 217 gms. immediately before use.

Cellulose ether and ester filaments are dyed in very fast black shades by application of 2.4-diaminodiphenylamine[4], from aqueous solutions or suspensions and subsequent immersion in hot aqueous oxidizing solutions[5], or by impregnation with a paste containing an oxidizing agent, a catalyst, an acid and 2.4-diaminodiphenylamine, followed by exposure in a warm, moist atmosphere to develop the

1. British Celanese, Ltd., A. Mellor and D. McLellan, E. P. 351577; abst. J. S. C. I. 1931, **50**, 838-B. British Celanese, Ltd., and G. Ellis, E. P. 351457; abst. Chem. Zentr. 1932, I, 1302. H. Dreyfus, F. P. 712209; abst. C. A. 1932, **26**, 2064.

2. F. P. 688755; abst. C. A. 1931, **25**, 1101; Chem. Zentr. 1931, I, 365.

3. British Celanese, Ltd., and G. Ellis, E. P. 311435; abst. C. A. 1930, **24**, 973; J. S. C. I. 1929, **48**, 678-B. H. Dreyfus, F. P. 666626; abst. Chem. Zentr. 1930, I, 2168. Can. P. 293069.

4. A. Hall, U. S. P. 1657255; abst. C. A. 1928, **22**, 1050; J. S. C. I. 1928, **47**, 189-B. Silver Springs Bleaching and Dyeing Co., Ltd., and A. Hall, E. P. 258699; abst. J. S. C. I. 1926, **45**, 976-B.

5. See Silver Springs Bleaching & Dyeing Co., Ltd., and A. Hall, E. P. 246879.

black shade. Aniline, *o*-toluidine, *p*-phenylenediamine and *p*-aminodiphenylamine may be added.

A deep black shade is also produced by immersion in a hot colloidal solution of *α*-naphthylamine, benzidine, toluidine or *pp'*-diaminodiphenylamine, diazotizing, and developing in a slightly acid solution containing *b*-hydroxynaphthoic acid or resorcinol[1]. In a bath containing sodium carbonate and sulfate[2], artificial silk is dyed black with black polyazo dyes, the goods being entered at 50°, raised to 70° and withdrawn after cooling down to 40°.

Dyeing Processes Involving Saponification. These are applied primarily to cellulose acetate fibers and textiles, and involve the superficial or peripheral removal of a portion of the acid radical by means of a saponifying treatment, the dyeing process then being applicable as to regenerated or reconstituted cellulose similar to that obtained from the viscose and copper-ammonia processes and from the denitration of nitrocellulose filaments. The methods of the Badische Anilin & Soda Fabrik[3], Clayton Aniline Co.[4], I. G. Farbenindustrie[5], Lyons Piece Dye Works[6], Societe Chimique des Usines du Rhone[7], British Cellulose &

1. L. Lawrie, H. Blackshaw and British Dyestuffs Corp., E. P. 224359; abst. C. A. 1925, **19**, 1352; J. S. C. I. 1925, **44**, 39-B.
2. R. Lavaud, E. P. 227854; abst. J. S. C. I. 1925, **44**, 754-B.
3. E. P. 209849; abst. C. A. 1924, **18**, 1757; J. S. C. I. 1924, **43**, 251-B. F. P. 558900; abst. Rayon, 1927, **2**, #5, 50; J. Soc. Dyers & Col. 1923, **39**, 327; Chem. Zentr. 1923, IV, 987. F. P. 29098, Addn. to F. P. 558900; abst. Chem. Zentr. 1928, I, 2758. Belg. P. 317800.
4. E. P. 214330; abst. C. A. 1924, **18**, 2609; J. S. C. I. 1924, **43**, 508-B.
5. U. S. P. 1602695; abst. C. A. 1926, **20**, 3822; J. S. C. I. 1927, **46**, 9-B. U. S. P. 1610961; abst. J. S. C. I. 1927, **46**, 249-B; Chem. Zentr. 1927, I, 1217. U. S. P. 1615242; abst. C. A. 1927, **21**, 826; J. S. C. I. 1927, **46**, 249-B. E. P. 267695; abst. C. A. 1928, **22**, 1243. F. P. 383636; abst. J. S. C. I. 1908, **27**, 332. F. P. 605127; abst. Chem. Zentr. 1927, I, 1218. F. P. 610539; abst. J. S. C. I. 1927, **46**, 407-B.
6. E. P. 310844; abst. J. S. C. I. 1930, **49**, 1024-B; Rayon Record, 1930, **4**, #22, 1158.
7. U. S. P. 1366023; abst. C. A. 1921, **15**, 946; J. S. C. I. 1921, **40**, 145-A; Paper, 1921, **27**, #25, 34; Chem. Tech. Uebers. 1921, **45**, 131; Mon. Sci. 1923, (5), 13, 14; Textilber. 1921, **2**, 456. U. S. P. 1440501; abst. C. A. 1923, **17**, 1154; J. S. C. I. 1923, **42**, 180-A; Chem. & Met. Eng. 1923, **28**, 225. E. P. 150989; abst. J. S. C. I.

Chemical Manufacturing Co.[1], British Celanese, Ltd.[2], H. Dreyfus[3], C. Dreyfus[4] and co-workers[5], and the disclosures of A. Hall[6], J. Preston[7] and others[8], all belong in this category. The cellulose ethers are not dyed by these methods.

Package Dyeing. The British Celanese, Ltd., method dyes methyl-, ethyl- or benzyl-cellulose in the package or wound form of yarns or piece goods, as in the form of cops, pirns or cheeses, or as rolls of knitted or woven fabric[9], by means of aqueous dispersions of relatively in-

1921, **40**, 692-A; Textilber. 1921, **3**, 20. E. P. 183806; abst. C. A. 1923, **17**, 213; J. S. C. I. 1923, **42**, 652-A; Chem. Ztg. 1923, **47**, 578. E. P. 192994; abst. C. A. 1923, **17**, 3612; J. S. C. I. 1923, **42**, 926-A. F. P. 512649; abst. Chim. et Ind. 1921, **6**, 650. D. R. P. 505610; abst. C. A. 1931, **25**, 591. Swiss P. 90096, 100109. Belg. P. 291902, 291921. Ital. P. 211190. See U. S. P. 1061771. F. P. 416752.

1. E. P. 175485, 175486; abst. J. S. C. I. 1922, **41**, 202-A; Caout. et Gutta. 1922, **19**, 11496; Chem. Tech. Uebers. 1922, **46**, 259. E. P. 176034; abst. J. S. C. I. 1922, **41**, 289-A. E. P. 193912, 194244, 195920. India P. 5688, 5689, 5690. See E. P. 169741.

2. E. P. 306611; abst. J. S. C. I. 1929, **48**, 354-B. E. P. 313404. E. P. 313971; abst. C. A. 1930, **24**, 1229; Silk J. 1929, **6**, #65, 78. E. P. 316521; abst. C. A. 1930, **24**, 1991; Silk J. 1929, **6**, #66, 70. E. P. 339429; abst. C. A. 1931, **25**, 2576; J. S. C. I. 1931, **50**, 390-B; Chem. Zentr. 1931, II, 1355; Silk J. 1931, **7**, #82, 54; Chim. et Ind. 1931, **25**, 956. E. P. 339997; abst. C. A. 1931, **25**, 2059; J. S. C. I. 1931, **50**, 534-B; Silk J. 1930, **7**, #83, 52; Chem. Zentr. 1931, I, 2270. E. P. 340982; abst. C. A. 1931, **25**, 5042; Chem. Zentr. 1931, II, 3046. E. P. 343953; abst. C. A. 1932, **26**, 306; J. S. C. I. 1931, **50**, 486-B; Chem. Zentr. 1932, I, 2405. See E. P. 302775, 304596, 309377, 314447, 318468.

3. F. P. 713184; abst. C. A. 1932, **26**, 1784.

4. F. P. 694879; abst. C. A. 1931, **25**, 1993; Chem. Zentr. 1931, I, 1385. Can. P. 296540. Can. P. 298341; abst. C. A. 1930, **24**, 2898. Can. P. 302878; abst. C. A. 1930, **24**, 4631.

5. C. Dreyfus and H. Platt, U. S. P. 1884621. C. Dreyfus and G. Schneider, E. P. 316521; abst. C. A. 1930, **24**, 1991. F. P. 679429; abst. C. A. 1930, **24**, 3911; Chem. Zentr. 1930, II, 2833. R. Dort, Can. P. 317115.

6. Am. Dyestuff Reptr. 1931, **20**, 583; abst. C. A. 1931, **25**, 5995.

7. Rayon Record, 1930, **4**, #12, 651.

8. W. Coltof, H. Waterman and I. Wolf, Zts. ang. Chem. 1931, **44**, 163; abst. J. S. C. I. 1931, **50**, 1007-B; C. A. 1932, **26**, 1446.

9. British Celanese, Ltd., G. Ellis and T. Ellison, E. P. 311675; abst. C. A. 1930, **24**, 973; J. S. C. I. 1929, **48**, 678-B; Chem. Zentr. 1929, II, 2506. H. Dreyfus, F. P. 668864; abst. C. A. 1930, **24**, 1749. F. P. 667167; abst. C. A. 1930, **24**, 1227. See E. P. 220505, 224681, 227943, 239470, 253978, 263260, 283081, 283253, 299343, 300929, 305560, 306981, 310827.

soluble dyes, in which the whole of the coloring matter is in the colloid state, and preferably of perfectly homogeneous dispersion. In the case of dyeing by the azoic or development process, either the base or the developer may be insoluble. The base may be applied first and then diazotized and developed, or conversely, the formed color being treated with a suitable diazo-solution and then developed. The use of α-methylaminoanthraquinone, anhydrous 1.4-di-(monomethylamino)-5.6-dioxyanthraquinone or benzeneazo-1-phenyl-3-methyl-5-pyrazolone are specified as being particularly applicable.

Or the cop, spool or bobbin of cellulose ether yarn may be immersed in an organic liquid containing dye and removing before the color change has taken place throughout the winding[1]. Multiple color effects result when several dyes of varying penetrative power are present in the liquid, or when successive immersions are made in different dye solutions.

Dyeing Composite Fabrics. In compound of mixed fabrics in which a portion is of the cellulose ethers or organic esters[2], a multitude of processes and a myriad of variants have been proposed, depending upon whether the fiber other than the organic cellulose derivative was an animal fiber as wool or natural silk, or a vegetable fiber as cotton or linen, or a rayon (regenerated or reconstituted cellulose) or permutations and combinations of these various fibers. Only a few of the representative methods can be touched upon herein. The Aceta Ges.[3] mix wool with nitroacetylcellulose fibers containing 1-2% N and acid equivalent to about 54% acetic acid. It is claimed such a mixture may be subjected to the ordinary hot vat treatment as used in wool

1. W. Whitehead, U. S. P. 1871486. British Celanese, Ltd., E. P. 269195; abst. J. S. C. I. 1928, **47**, 745-B.

2. J. Chittick, Textile World, 1927, 1716. J. Calladine, Russa, 1931, **6**, 1543; abst. C. A. 1932, **26**, 1791. Enco, Russa, 1931, **6**, 489; abst. C. A. 1931, **25**, 3173. R. Dort, Rayon, 1928, **7**, #9, 28. C. Mullin, Can. Colorist Textile Processor, 1927, **7**, 114; abst. C. A. 1927, **21**, 3131.

3. E. P. 319354; abst. C. A. 1930, **24**, 2616; J. S. C. I. 1930, **49**, 943-B.

dyeing, and to carbonization as with aluminum chloride without damage. In the treatment of materials comprising natural silk with alkaline liquors[1], the silk may be protected against the alkali by having acetylcellulose filaments present upon which the alkali may exert a saponifying effect.

Natural silk which is to be woven with cellulose ether or ester filaments[2] is best degummed in the yarn and then sized with sizing agents which are readily removed by hot water or other reagent which does not deleteriously affect the organic cellulose derivative, such sizes containing gelatin, starch, soaps, drying oils or potassium, sodium, ammonium, calcium, magnesium or zinc oleates, stearates, naphthenates or resinates. Waterproof and gasproof compound fabrics or sheet materials may be formed by uniting under appropriate conditions of temperature and pressure, woven or knitted fabrics of methyl-, ethyl- or benzylcellulose with non-thermoplastic fibers[3], and then applying sufficient to nearly melt the plastic cellulose derivative.

Methods for producing designs on mixed fabrics have been described[4] in which cellulose ethers or esters form a portion of the fibers, by selecting dyestuffs and methods of application, suitable to one class of fibers and unsuited to the other[5]. A. Hunter obtains two-color effects on lace and other fabrics composed of cellulose acetate and rayon[6] by dyeing the acetate portion with a basic dye containing amino or alkyl- or aryl-amino groups which have been liberated by treatment of the dye salt with sodium carbonate or other suitable alkali, and then dyeing the cellulose por-

1. H. Dreyfus, Can. P. 307525. F. P. 677262; abst. C. A. 1930, **24**, 3118. See also F. P. 661936, 669247.
2. British Celanese, Ltd., E. P. 339896; abst. J. S. C. I. 1931, **50**, 341-B.
3. C. Dreyfus, E. P. 248147; abst. Chem. Zentr. 1926, II, 2855.
4. Soc. Anon. Des Etablissements Petitdidier (Ancienne Maison Jolly-Belin), D. R. P. 536068; abst. C. A. 1932, **26**, 1134.
5. C. Dreyfus and C. Palmer, Can. P. 313341.
6. E. P. 191120; abst. C. A. 1923, **17**, 3103; J. S. C. I. 1923, **42**, 180-A.

tion another shade by means of a direct dye. Liberation of the dye base is said to increase the affinity of the dye for the acetate silk while diminishing its affinity for the regenerated cellulose.

In the J. Briggs and L. Richardson process[1], the cellulose fibers are first dyed in the usual manner with substantive dyes and then subjected to partly alkaline soaping and the dyeing then continued in the same bath at a higher temperature where the dye first absorbed by the cellulose bleeds off and goes over to the cellulose acetate portion, dyeing being continued until both classes of fibers assume the shade desired. Or the cotton-acetylcellulose fabric may be colored with a sulfur dye in a bath containing an alkali metal sulfide[2], and a faintly alkaline salt as sodium bicarbonate or borax, then the acetate silk dyed with a dyestuff having no affinity for cotton[3]. Mixtures of natural silk and cellulose acetate are degummed by heating with an alkaline liquor containing alkaline hydroxides, borates, phosphates, phenolates, cresolates or a sulfonated oil[4], but if the temperature is raised above 80°, the cellulose acetate may be wholly or partially delustered.

Instead of extruding filaments from a cellulose ether solution, W. Sachs[5] has described a method of making textiles from filaments by cutting ethylcellulose sheets or thin films into tiny strips, and turning these strips into simple or multiple-twisted yarns. It is claimed these ethylcellulose yarns may be mixed in any proportion with vegetable, animal or mineral fibers in a manner so as to closely simulate natural wool or silk. It is also alleged that these ethylcellulose yarns may be woven, stretched, plaited,

1. E. P. 178946; abst. Chem. Tech. Uebers, 1922, **46**, 318.
2. I. G. Farbenind. A.-G., E. P. 320027; abst. C. A. 1930, **24**, 2616; J. S. C. I. 1930, **49**, 280-B; Chem. Zentr. 1930, II, 143.
3. A. Möhring, G. Schultze and P. Schlack, U. S. P. 1860473; abst. C. A. 1932, **26**, 3937.
4. British Celanese, Ltd., and G. Ellis, E. P. 306067; abst. C. A. 1929, **23**, 5049; J. S. C. I. 1929, **48**, 353-B. See E. P. 264936.
5. D. R. P. 342097; abst. Chem. Zentr. 1922, II, 48; Chem. Tech. Uebers, 1923, **47**, 132; Textilber. 1921, **2**, 377.

kneaded, beaten or sewn with other yarns to obtain both useful and pleasing effects[1].

According to British Celanese, Ltd.[2], filamentous material having a basis of methyl-, ethyl- or benzyl-cellulose is brought into contact with a textile fabric also having a basis of organic derivatives of cellulose, and the assembly is pressed under such conditions that the filamentous material is caused to dissolve or melt and coalesce to the textile fabric, thus producing a material one or both faces of which has the normal appearance of a textile fabric[3]. In dyeing mixed fabrics containing acetate silk with vat or sulfur dyes[4], a sulfurized phenol is added to the bath whereby the acetate silk is reserved. Or ammonium sulfate or other ammonium salt may be added to the sulfur bath to prevent saponification and consequent dyeing of the acetate silk[5].

In a method evolved by the I. G. Farbenindustrie[6], mixed acetate silk fabrics are dyed with a preparation containing a dye for the wool or cotton and a diazotizable amine having affinity for acetate silk, together with a wetting agent of the alkylnaphthalenesulfonic acid type. The mixture dissolves in hot water without residue. Examples are: Zambesi Black, α-naphthylamine and sodium butylnaphthalenesulfonate on wool-acetate silk fabric, diazotized and developed with 2.3-hydroxynaphthoic acid for deep black; Diamine Black BH, dianisidine and the wetting agent on cotton-acetate fabric, diazotized and developed as before for

1. H. Dreyfus, W. Dickie and W. Taylor, Can. P. 324225.
2. E. P. 355860; abst. J. S. C. I. 1931, **50**, 1005-B.
3. British Celanese, Ltd., and W. Taylor, E. P. 375356; abst. J. S. C. I. 1932, **51**, 720-B.
4. I. G. Farbenind., A.-G., and A. Peters, D. R. P. 526277; abst. C. A. 1931, **25**, 4413; Chem. Zentr. 1931, II, 1933.
5. British Dyestuffs Corp., Ltd., and H. Mudford, E. P. 238721; abst. C. A. 1926, **20**, 2079; J. S. C. I. 1925, **44**, 845-B; Chem. Zentr. 1926, I, 1044.
6. E. P. 299787; abst. C. A. 1929, **23**, 3584; J. S. C. I. 1930, **49**, 416-B; Chem. Zentr. 1929, I, 1747. F. P. 663207; abst. C. A. 1930, **24**, 729.

dark blue[1]. W. Chase[2] has described the application and properties of the Duranol, Dispersol, Ionamine, Azonine direct, Setacyl direct, Cellit and Celatene and S. R. A. dyes on Celanese, and direct, developed, sulfur and vat dyes on cotton of these unions, for solid or contrasting colors, and W. Bennett[3] for the dyeing of wool with acetylcellulose.

In dyeing fabrics composed of wool or silk associated with acetylcellulose[4], the wool or silk is reserved during the dyeing of the cellulose acetate by adding to the dyebath an acid sulfuric ester or ester salt of a higher aliphatic alcohol as cetyl alcohol. As a fixative in the dyeing of organic cellulose derivatives[5], ethylenethiodiglycol has been proposed. A method of applying gallocyanine dyes to cellulose ester fibers[6] has been modified to include also cotton in mixed fabrics[7], the union fabric being printed or padded with a paste containing the leuco-form of the dye and an oxidizing agent as sodium chlorate, then dried, steamed, and after-chromed with sodium bichromate[8].

G. Rudolph[9] has described blue, red and white effects in cotton-wool-acetylcellulose silk union fabrics by dyeing the wool with a blue (acid) dye from an acid bath, the cotton with a red cotton dye at 50° in the presence of 3% Katanol W (for retarding absorption of the cotton dye by

1. R. Clavel, Color Trade J. 1925, **16**, 129; abst. C. A. 1925, **19**, 1950.
2. Textile World, 1927, **71**, 1424; abst. C. A. 1927, **21**, 1551.
3. Rayon, 1928, **7**, #2, 28; #3, 18; abst. C. A. 1929, **23**, 519. See also Silk J. 1928, **4**, #44, 60; #45, 51; abst. C. A. 1929, **23**, 281.
4. H. Schütte, C. Schöller, F. Günther, J. Nüsslein and H. Haussmann, D. R. P. 552005; abst. C. A. 1932, **26**, 4481. I. G. Farbenind., A.-G., E. P. 333554; abst. C. A. 1931, **25**, 604.
5. H. Müller, U. S. P. 1717242. Cites U. S. P. 1485790. D. R. P. 339690, 340552.
6. Durand & Huguenin, A.-G., E. P. 352808; abst. J. S. C. I. 1931, **50**, 923-B. D. R. P. 526193; abst. C. A. 1931, **25**, 4413; Chem. Zentr. 1931, II, 1497.
7. *Ibid.* E. P. 359861; abst. J. S. C. I. 1932, **51**, 99-B. D. R. P. 534466; abst. C. A. 1932, **26**, 855; Chem. Zentr. 1931, II, 3549.
8. G. Choisy, Russa, 1931, **6**, 979; abst. C. A. 1931, **25**, 5568. W. Bennett, Dyer, Calico Printer, 1928, **59**, 204; abst. C. A. 1928, **22**, 3533.
9. Kunstseide, 1926, **8**, 13; abst. J. S. C. I. 1926, **45**, 484-B.

the wool), and leaving the acetylcellulose white[1]. T. Meisenheimer[2] has emphasized that in the cross dyeing of cotton, wool or silk with acetylcellulose, the presence of oil or grease on the fibers accompanying the acetate silk causes a staining of the cellulose and animal fibers due to the mordanting action of the oils for the acetate filaments.

Immunizing. One of the methods available for rendering cellulose and reconstituted cellulose resistant to direct dyes is by partial or superficial treatment of the cellulose with an allyl halide, producing an allylcellulose[3]. Allyl bromide either in its liquid form or when dissolved in an organic solvent is used, or alternatively, allyl chloride may be employed. For immunizing purposes, cotton yarn or regenerated cellulose is treated with 15% NaOH solution, the major portion of the alkali removed, and the alkalicellulose thus formed allylated with allyl bromide, being suspended in a tube through which allyl bromide vapor is circulated. After 2-3 hrs. sufficient allylcellulose is formed so that it is resistant to direct dyes, this change being accompanied by a gain in weight of 18-25%. The etherification may also be carried out by heating the alkalicellulose in a 7% solution of allyl bromide in carbon tetrachloride. It is claimed that cellulose immunized in this manner has a high tensile strength and is very durable, and the process is preferable to esterifying the cellulose with an aromatic carboxylic or sulfonic chloride, resulting in the formation of cellulose *p*-toluenesulfonate.

In the immunization of cellulose threads according to the process of R. Boehringer and H. Wolf[4], the yarn is treated successively, while in the form of cops mounted on perforated tubes, with an alkali (12% aqueous NaOH) and an esterifying agent as a 20% solution of *p*-toluenesulfochloride or benzyl chloride in carbon tetrachloride, result-

1. C. Dreyfus, Can. P. 276367; abst. C. A. 1928, **22**, 2067. F. P. 613647; abst. Chem. Zentr. 1927, I, 1218.
2. Textile World, 1928, **73**, 2007; abst. C. A. 1928, **22**, 1855.
3. Soc. Chem. Ind. in Basle, E. P. 342689; abst. J. S. C. I. 1931, **50**, 485-B.
4. U. S. P. 1829735; abst. J. S. C. I. 1932, **51**, 722-B.

ing in the esterification to cellulose *p*-toluenesulfonate, or etherification to benzylcellulose.

Immune cotton yarn may be subjected to processes of singeing, de-sizing, scouring, bleaching and mercerizing as employed for cotton. It has dyeing properties similar to cellulose acetate silk and a special range of Imacol dyes capable of dyeing immune yarn in shades fast to light and washing but having no affinity for cotton, are now available. Imacol dyes (Sandoz) may be used with direct cotton dyes in the same dye-bath[1] (see pp. 642, n. 2; 725, n. 4; 941, n. 7; 1009, n. 2).

It has also been found possible to change vegetable fibers into those having no affinity for substantive dyestuffs by the method of A. Landolt[2], which consists in partially esterifying the fiber in the presence of tertiary amines. Thus cellulose may be treated with phthalic, maleic, succinic or benzoic anhydrides, benzoyl or phthalyl chloride, or nitrobenzoic or methylbenzoic acids, in the presence of pyridine, quinoline or triethylamine, to form cellulose phthalate, succinate, benzoate, maleate, nitrobenzoate or methylbenzoate, depending upon the reactants employed. The immunization process of O. Jaeck[3] is quite similar, reading upon the transformation superficially of cellulose into cellulose maleate or acetomaleate by means of maleic anhydride and glacial acetic acid. Sulfuric acid or ammonium sulfate is used as catalyst. It is said that if cotton is impregnated with crude copper sulfate solution, then dried, and acetylated with acetic anhydride at 100°, immunization is complete in less than an hour[4].

Producing Resists. According to J. Höpker[5] resists in dyeing with vat dyestuffs may be easily produced upon the material by printing an oxidizing agent, as sodium *m*-nitro-

1. E. P. 246609; abst. J. S. C. I. 1926, **45**, 270-B. See M. Fahrländer, Textilber. 1926, **7**, 463; abst. J. S. C. I. 1926, **45**, 703-B.
2. U. S. P. 1878783.
3. U. S. P. 1812790. Soc. Chem. Ind. in Basle, E. P. 315434.
4. Soc. Chem. Ind. in Basle, E. P. 315435; abst. J. S. C. I. 1930, **49**, 986-B. F. P. 677494; abst. C. A. 1930, **24**, 3112.
5. U. S. P. 1730211; abst. C. A. 1929, **23**, 5597.

benzenesulfonate or sodium bichromate, or a mixture of both of these salts with an aqueous solution of alkylcellulose, drying the material, and then dyeing it in the usual manner in the hot dye liquid of a vat dyestuff. Printing colors thus prepared may be easily applied and yield good resist effects because the alkylcelluloses are completely precipitated on the fiber, even by a small quantity of the alkali, particularly owing to the elevated temperature of the vat dye liquor.

The following examples are illustrative of the process:

1. A resist printing paste is prepared from 250 gms. 15% aqueous solution methylcellulose, and stirred with 250 gms. cold water. There are then introduced 250 gms. sodium *m*-nitrobenzenesulfonate into 250 gms. water, the paste thus prepared being printed on the material which is then dried and dyed at 79° in a vat liquid prepared with 30 gms. 5.7.5′.7′-tetrabromindigo paste 20%, 40 gms. NaOH solution of 40° Be., and 16 gms. hydrosulfite concentrated powder, the whole being made up to 1 liter. The material after dyeing is washed, soaped and dried.

2. 250 gms. each 15% solution of methylcellulose and water are added to a solution of 200 gms. sodium bichromate in 300 gms. water, and this paste printed on the material which is then dried and dyed at 78° in a vat-liquor prepared with 30 gms. N-dihydro-1.2-1′.2′-anthraquinoneazine, 100 gms. NaOH solution of 30° Be., 70 gms. glycose (1:1), and 12 gms. hydrosulfite concentrated powder, the whole being made up to 1 liter. The material, after being dyed, is washed, soaped at the boil, rinsed and dried.

Fabrics formed either from acetylcellulose or viscose, alone or with other fibers not deleteriously affected by mercerizing agents[1], are treated in selected areas only with sulfuric, phosphoric, hydrochloric or nitric acids, zinc chloride or calcium thiocyanate, the solutions being applied by a printing operation on the fabric with a resist, and then immersing in the solution.

1. Calico Printers' Assoc., Ltd., and F. Roberts, E. P. 215860; abst. C. A. 1924, **18**, 3481.

Discharge Effects. White resist or discharge effects are obtained by overall-printing cellulose acetate materials, before or after the printing with zinc acetate or zinc oxide[1], with dyes which have an affinity for the cellulose ester and are capable of forming insoluble complexes with the metal compound, then steaming and heating with a dilute acid to remove the insoluble complex. Colored effects are obtained by adding to the zinc acetate, printing paste dyes which have an affinity for the cellulose derivative, but form no insoluble complex with metal compounds. The action of discharge effects, particularly reducing pastes, and especially when used on acetate silk, is facilitated by first padding the dyed material with a non-volatile acidic substance as oxalic, citric or benzenesulfonic acids[2]. Potassium or sodium chlorate[3], or other discharge oxidants as 30% hydrogen dioxide, silver peroxide, nitric acid, acid permanganate or sodium peroxide, but preferably bleaching powder[4], followed by treatment with citric acid may be used in place of the chlorate.

Clear white and colored discharge effects on filaments of cellulose derivatives dyed with those colors commonly used for this type of filament are obtained in the usual manner by means of reducing agents containing sodium formaldehyde-sulfoxylate, provided that thiocyanates such as calcium, barium or ammonium thiocyanate are present. A satisfactory discharge paste contains 15 gms. formusol (sodium formaldehyde-sulfoxylate), 70 gms. of 3% tragacanth solution and 10 gms. of a solution of calcium thiocyanate(sp. gr. 1.44)[5]. The R. Clavel process for producing

1. Calico Printers' Assoc., Ltd., and J. Whinfield, E. P. 348715; abst. J. S. C. I. 1931, **50**, 755-B; Chem. Zentr. 1931, II, 2936; Silk J. 1931, **8**, #89, 56; Textile Mfr. 1931, **57**, #682, 380.
2. British Celanese, Ltd., and G. Ellis, E. P. 334518; abst. J. S. C. I. 1930, **49**, 1147-B.
3. *Ibid.* E. P. 312655; abst. C. A. 1930, **24**, 973; J. S. C. I. 1929, **48**, 678-B.
4. British Celanese, Ltd., E. P. 315005; abst. C. A. 1930, **24**, 1522; J. S. C. I. 1931, **50**, 292-B.
5. L. Smith, U. S. P. 1651639; abst. C. A. 1928, **22**, 875; J. S. C. I. 1928, **47**, 50-B. E. P. 262254; abst. C. A. 1927, **21**, 3752; J. S. C. I. 1927, **46**, 71-B.

discharge effects in dyeing cellulose ethers and esters[1] is facilitated by preliminary treatment of the materials with metallic salts capable of forming compounds with the dyes, such as salts of tin, zinc, aluminum, iron or chromium, which are preferably applied in the form of printing pastes in the presence of acids or acid salts, after which the materials are dyed and subjected to discharge printing. Zinc oxide and zinc phosphate are specified.

In the C. Alabouvette process[2], the artificial filaments are dyed with a dischargeable dye which is discharged with hyposulfite, and for printing a mordant is used composed of glycerol, zinc nitrate and phenol, resorcinol, cyclohexanol, *p*-toluenesulfon-amide or -anilide. R. Clavel[3] has outlined a process in which the artificial silk that has been weighted with compounds of tin, zinc or aluminum, and dyed with a dischargeable dye, are treated with a paste containing a discharging agent and a non-dischargeable dye. Or[4], substances such as gelatin and casein may be used as resists, and in the case of mixed fabrics, different effects may be produced by selective dyeing of the different fibers composing the fabrics. Or the entire surface of the fabric may be printed with a design and then locally discharging the same[5], as in the procedure advanced by C. Dreyfus.

The discharge printing of fabrics containing organic derivatives of cellulose to produce light figures on dark backgrounds[6] may be accomplished by superficial saponification if cellulose acetate is present, then applying dischargeable

1. E. P. 308757; abst. C. A. 1930, **24**, 510; J. S. C. I. 1930, **49**, 238-B; Silk J. 1929, **6**, #62, 72; Chem. Zentr. 1929, II, 656. F. P. 657003; abst. C. A. 1929, **23**, 4350. See E. P. 270987, 277602, 280094, 300894, 303129.
2. F. P. 662243; abst. C. A. 1930, **24**, 510; Chem. Zentr. 1923, I, 288.
3. D. R. P. 535144; abst. C. A. 1932, **26**, 1133.
4. British Celanese, Ltd., E. P. 316983, Addn. to E. P. 295582; abst. C. A. 1930, **24**, 1991; J. S. C. I. 1930, **49**, 506-B. See E. P. 182830, 194840, 219349, 224925, 295582, 314208.
5. Can. P. 289906.
6. C. Dreyfus and H. Platt, U. S. P. 1884620. E. P. 314446; abst. C. A. 1930, **24**, 1521. British Celanese, Ltd., E. P. 334543, Addn. to E. P. 312655; abst. C. A. 1931, **25**, 1102; J. S. C. I. 1930, **49**, 1147-B. See E. P. 270987, 304596, 306611, 309377, 314447, 315005.

dyes and finally locally treating with discharges, or by the local application of a chromate and then applying an acid to the fabric[1]. Or by the incorporation of a pyrazolone dye with the discharge agent which may be a formaldehyde-sulfoxylate, a hyposulfite or stannous chloride, facilitating the discharge by the application of anthraquinone or a swelling agent as a thiocyanate[2]. Suitable dyes are those obtained by coupling 1-phenyl-3-methyl-5-pyrazolone with a diazotized amidobenzene. Dyed spun or woven threads may also be totally discharged, if made of cellulose derivatives[3], by treating the threads with a composition containing charcoal, or of potassium or sodium zincates[4], the latter treatment being applicable to methylcellulose as well as ethyl- or benzylcellulose. If increased penetration is desired[5], *p*-dihydroxy-compounds as hydroquinone, or toluquinol or their mono-ethers or halogen derivatives may be added to the printing pastes.

British Celanese, Ltd., and G. Ellis[6] have found that anthraquinone compounds having affinity for cellulose ethers, are not appreciably reduced or otherwise affected by stannous compounds which, on the other hand, are capable of discharging many colorations on cellulose ethers, for example, those attained by difficultly insoluble azo or nitrodiarylamine series. As the anthraquinone coloring matters remain in the unreduced state in the presence of stannous compounds they yield their true shades when utilized for the coloration of stannous discharges. Suitable compounds are 1-acetylamino-, 1-propionylamino-, 1-chlor-

1. C. Dreyfus and G. Schneider, Can. P. 324415.
2. H. Dreyfus, F. P. 706670; abst. C. A. 1932, **26**, 317. British Celanese, Ltd., and G. Ellis, E. P. 346751; abst. J. S. C. I. 1931, **50**, 716-B; Silk J. 1931, **8**, #88, 54; Chem. Zentr. 1932, I, 1301.
3. Soc. Pour La Fabrikation de la Soie Rhodiaseta, E. P. 297186; abst. C. A. 1929, **23**, 2580; J. S. C. I. 1928, **47**, 855-B; Chem. Zentr. 1929, I, 597. F. P. 647865; abst. C. A. 1929, **23**, 2582; Chem. Zentr. 1929, I, 1636. Du Pont Rayon Co., Can. P. 303000.
4. G. Ellis, U. S. P. 1874177.
5. British Celanese, Ltd., and G. Ellis, E. P. 346694; abst. J. S. C. I. 1931, **50**, 716-B; Textile Mfr. 1931, **57**, 306.
6. E. P. 351457; abst. J. S. C. I. 1931, **50**, 838-B; Textile Mfr. 1931, **57**, #684, 458; Silk J. 1932, **8**, #92, 54. See E. P. 316989.

4-oxy-, 1-amino-2-methyl-, 1-acetamino-4-oxy-, 1-ethanolamino-, 1-amino-4-oxy-, 1-methylamino-4-amino, 1.4-diamino-2-methoxy-, 1.4-diamino-, 1.4-diethanolamino-, 1.4-diethanolamino-5.8-dioxy-, and 1.5-di(monomethylamino)-4.8-dioxy-anthraquinone. As discharges[1], sodium, potassium or aluminum chlorate may be employed in conjunction with accelerators or catalysts as prussiates or salts of vanadium, aided by assistants as tartaric or citric acid or their sodium salts. As an efficient discharging agent for organic cellulose derivatives, A. Fischesser[2] advocates zinc formaldehyde-sulfoxylate (Hydraldite Z or Decroline).

As communicated by the Society of Chemical Industry in Basle[3], white or colored discharges on acetate silk are produced by printing the material with a paste composition of zinc formaldehyde-sulfoxylate, which may be used with an acid or alkali as required. The discharge and resist printing on Celanese dyed with S. R. A. colors[4] has been elaborated upon by J. Bert.

Stripping Dyestuffs. In the removal of dyes from colored cellulose ethers or acetylcellulose[5], it is claimed the addition of calcium thiocyanate as recommended by the British Dyestuffs Corporation does not give perfectly satisfactory whites, better results being obtained by printing with sodium sulfoxylate to which is added a benzene derivative containing one or more OH-groups as resorcinol, or lactic or glycollic acids, which do not react with the re-

1. I. G. Farbenindustrie, A.-G., E. P. 317333; abst. C. A. 1930, **24**, 2309; Chem. Zentr. 1930, I, 2168. F. P. 666463; abst. C. A. 1930, **24**, 1522. F. P. 678901; abst. C. A. 1930, **24**, 3656. G. Ellis, Can. P. 293070.

2. U. S. P. 1747540; abst. C. A. 1930, **24**, 1750; J. S. C. I. 1930, **49**, 987-B; Chem. Zentr. 1930, I, 3613. D. R. P. 461753; abst. J. S. C. I. 1930, **49**, 762-B; Chem. Zentr. 1928, II, 714.

3. E. P. 285973; abst. C. A. 1929, **23**, 289; J. S. C. I. 1928, **47**, 331-B.

4. Dyer, Calico Printer, 1929, **61**, 75; abst. C. A. 1929, **23**, 2829.

5. Scheuer, Lauth & Co. and L. Diserens, Bull. Soc. ind. Mulhouse, 1929, **95**, 349; abst. C. A. 1929, **23**, 4817; J. S. C. I. 1929, **48**, 751-B. A. Wolff, Bull. soc. ind. Mulhouse, 1929, **95**, 352; abst. C. A. 1929, **23**, 4818. See E. P. 262254; abst. J. S. C. I. 1927, **46**, 71-B. A. Schneevoigt, Textilber. 1926, **7**, 354; abst. J. S. C. I. 1926, **45**, 662-B.

ducing agent. Phenol is contraindicated because it exerts a too powerful solvent action on the fiber. Dyes which are destroyed by reduction are unaffected by hyposulfite NF alone when fixed on acetate silk, but are deeply degraded by the action of colored removing pastes consisting of basic dyes dissolved in resorcinol, hyposulfite F and tannin. Addition of anthraquinone or its derivatives is practically without effect, showing that the effect is not due to a catalytic action of the basic dye similar to that produced by Setopaline, Patent Blue or nitroalizarin in the removal of naphthylamine bordeaux. A large number of Duranol, Ionamine, Acetonine and Setacyl dyes may be removed by addition of 5-10% of resorcinol. Care should be exercised to reduce the resorcinol to 2% based on the color, or the fiber may be seriously impaired.

British Celanese, Ltd.[1], have described a method of stripping dyestuffs by a physical process which consists in treating the colored textile material or film with both a solvent for the dyestuff and a swelling agent for the cellulose ether or ester. Mixtures of water and acetone, acetone and diacetone alcohol, acetone and ammonium thiocyanate or benzene and acetone are specified.

Printing on Cellulose Derivatives. The types of dyestuffs used in textile printing are sharply classified into two classes, (1) those which dye cellulose or regenerated cellulose as obtained from the decomposition of viscose, reduction of copperammonia cellulose or denitration of nitrocellulose, all processes in which we are not interested herein, and those processes which color the cellulose esters and cellulose ethers, that is, which dye the cellulose derivative in the form in which filaments were prepared therefrom, without chemical change in original composition. In general, the dyestuffs found applicable are all basic, a number belonging to the acidic dyes among which may be mentioned Acid Violet, Woolgreen, Supramin Yellow R, Alizarine Ru-

1. W. Whitehead, E. P. 260289; abst. C. A. 1927, **21**, 3470; J. S. C. I. 1928, **47**, 284-B; Chem. Zentr. 1927, I, 1220.

binole R, Alizarine Blue SAP, Alizarine Yellow, Metanil Yellow and Cloth Red. Certain water-insoluble or emulsion dyes have also been found suitable as the SRA dyes, Celliton Fast dyes and Duranols. These latter dyes may be used either in an aqueous bath or in the powder form with appropriate solvents as glycol monomethyl ether, methyl or ethyl lactate, methyl or ethyl oxybutyrate or methylethyl ketone.

The dyestuffs used must be free from salt or other adulteration which is insoluble in the organic solvents used. In addition to coloration by dyestuffs, printing by pigments is also employed, the latter being ground more than once in the solvents in order to assure maximum covering power and uniformity of tone. By selecting dyes very fast to light as of the anthraquinone type, Indanthrene and vat colors, Lithol Reds, Helio Fast colors and inorganic pigments, action by light is practically *nil*. A solution containing 7.5-10% of the cellulose compound is the usual concentration, usually associated with plasticizers and in conjunction with those solvents of lowest vapor pressure and highest boiling point, the diluent or transitory solvents being of lower boiling point. For spraying, a concentration of 3.5-6% concentration of cellulose is usually sufficient, it being necessary to select a cellulose compound of minimum viscosity in order to assure maximum covering power with the minimum of solvent used.

It is of importance that the printing pastes be anhydrous and that the vessels, printing rolls and dye-troughs be dry. If water is used instead of solvents, the cellulose compound may be precipitated in the indentations of the engraving, and is removable with difficulty if at all. With properly executed printings on cellulose derivative fabrics, the fastness to water is very good and fastness to rubbing surprisingly so. The solvents are readily recoverable with modern solvent recovery systems, usually a regain of 89-90% being obtained depending upon the efficiency of the apparatus and the nature of the solvent. Considering the

fact that all handling as well as refinishing is entirely omitted and that every particle of dyestuff, lake or pigment used in printing remains on the fabric and is not removed by repeated washing, this method of transfixation of color on artificial textile is comparatively a very economical one[1].

The British Celanese, Ltd., method of printing is intended to obviate the frequency with which the prints are marred because the edges of the design are not sharply defined, this advantage being avoided and sharply defined local colorations being obtained by the use of non-mordant colors with basic aluminum acetate. The materials treated with the basic acetate are preferably dried before being printed or stencilled. The following examples indicate the *modus operandi* of the process:

1. A fabric containing ethylcellulose and cotton is impregnated with a solution of 15 gms. per liter of basic aluminum acetate at 75° for 0.75 hr. The fabric is then dried and printed in any desired manner, when the colors applied will be found to be sharply defined[2].

2. A fabric consisting wholly of ethylcellulose is treated for 2 hrs. at 40° in a solution containing 4% basic aluminum acetate, then dried and printed.

In the usual methods of intaglio printing of textile materials[3], engraved rollers are employed, the engraving being carried to a substantially uniform depth, which means that the design will be reproduced in uniform shade. A method of printing has been described in which designs are implanted on cellulose ether or ester textiles and showing gradations of color by means of printing plates or roll-

1. W. Kemmerich, Cellulose, 1930, **1**, #10, 263; abst. C. A. 1931, **25**, 4711.

2. H. Platt, U. S. P. 1822453; abst. C. A. 1931, **25**, 5998. E. P. 299849; abst. C. A. 1929, **23**, 3584; J. S. C. I. 1930, **49**, 237-B; Chem. Zentr. 1929, I, 1514. Imperial Chemical Industries, Ltd., A. Shepherdson and L. Smith, E. P. 351056; abst. J. S. C. I. 1931, **50**, 801-B. In this connection see Ital. P. 271214, 271382, 273863, 277486. H. Dreyfus, F. P. 651934; abst. C. A. 1929, **23**, 3584. C. Dreyfus, Can. P. 297376.

3. British Celanese, Ltd., and J. Wainwright, E. P. 335206; abst. C. A. 1931, **25**, 1391; J. S. C. I. 1931, **50**, 17-B.

ers engraved to varying depths. The dispersed, water-insoluble coloring matters are applied in aqueous pastes preferably containing swelling agents, or in solution in organic solvents. The addition of alkyl or alkylene chlorides as tetrachlorethane or trichlorethylene markedly enhances the penetrativeness of the colors[1]. For a blue design, 1.4-di-(monomethylamino)anthraquinone, and for a navy blue, *p*-aminobenzeneazonaphthylamine is employed, while other suitable colors include 2.4-dinitrodiphenylamine, benzeneazo-1-naphthalene-4-azophenol, 1-amino-4-methylaminoanthraquinone or 1.4-di(monomethylamine)anthraquinone.

Printed colored effects fast to rubbing are obtainable on organic cellulose derivatives[2] by means of printing pastes containing specially solubilized dyes[3] or other dyestuffs capable of exerting a swelling or solvent action on the cellulose compound, as salts of benzene-, naphthalene- and anthracene-sulfonic acids and substituted derivatives as phenol, naphthol, aminonaphtholsulfonic acids and particularly, sodium, ammonium or potassium thiocyanates. A bluish-red effect, for instance, may be obtained by means of a printing paste containing 40 gms. (prepared by heating 4 gms. 2.4-dinitrobenzene-1-azodimethylaniline, 12 cc. water and 24 gms. of 70% sodium ricinoleate until dispersion of the dyestuff is complete), 5 gms. soda ash, 20 gms. ammonium thiocyanate, 40 gms. water and 295 gms. thickening agent. After printing the fabric is dried by hot air, steamed 15-20 min. in dry steam, soaped lightly at 60° and washed and dried. As assistants to dye penetration, water-soluble formic acid esters with a polyhydroxylic alcohol to-

1. British Celanese, Ltd., E. P. 297848; abst. C. A. 1929, **23**, 2836; J. S. C. I. 1930, **49**, 237-B; Chem. Zentr. 1929, I, 1153. See E. P. 284376; abst. C. A. 1928, **22**, 4834.

2. British Celanese, Ltd., G. Ellis and E. Greenhalgh, E. P. 244143; abst. C. A. 1927, **21**, 331; J. S. C. I. 1926, **45**, 124-B. See E. P. 224681, 224925, 227183, 237943.

3. British Celanese, Ltd., and G. Ellis, E. P. 219349; abst. C. A. 1925, **19**, 579; J. S. C. I. 1924, **43**, 906-B.

gether with water are used with the cellulose derivative[1]. Commercial triethanolamine is said to improve the printing strength of water-insoluble azo and substituted diphenylamine compounds when used on fabric containing cellulose ethers or esters[2]. The amount of hydroxylamine used is up to 5% of the printing paste. Suitable dyes are Dispersol Fast Orange A and BS, and Dispersol Yellow A.

In comparison with the regenerated cellulose artificial filaments as obtained from the viscose, nitrocellulose and copperammonia processes, the cellulose ethers and esters are relatively less porous and hence less water-absorptive, and it is usual, therefore, in the printing or stencilling of fabrics comprised of them to include a body or bodies exerting a softening, swelling or solvent action in order to increase dye receptivity. The G. Ellis and E. Greenhalgh process for producing colored patterns on this class of textile depends for its efficiency upon the selection and utilization of such swelling agents[3]. The H. Arzt process produces fast tints by suspending a pigment in an organic solvent containing cellulose ethers, adapting the solvent and the quantity used to the degree of swelling or porosity effect required[4].

In the coloring of cellulose ether or ester fabrics by means of a transfer sheet, having a coloring matter deposited thereon[5], the transference may be effected by bringing the fabric into pressure contact with the transfer sheet or medium, preferably with the aid of heat. Fabrics made of ethylcellulose are uniformly colorable by subjecting the

1. I. G. Farbenindustrie, A.-G., E. P. 311795; abst. C. A. 1930, **24**, 981; J. S. C. I. 1929, **48**, 609-B; Brit. Plastics, 1929, **1**, #3, 114.

2. Imperial Chemical Industries, Ltd., A. Shepherdson and L. Smith, E. P. 351056; abst. Silk J. 1932, **8**, #92, 53. F. P. 713635; abst. C. A. 1932, **26**, 1802.

3. U. S. P. 1792152; abst. C. A. 1931, **25**, 2008. E. P. 244143; abst. Chem. Zentr. 1926, I, 2970. C. Dreyfus, Can. P. 290464.

4. D. R. P. 540997; abst. C. A. 1932, **26**, 2328; Chem. Zentr. 1932, I, 1862.

5. British Celanese, Ltd., E. P. 293022; abst. C. A. 1929, **23**, 1514; J. S. C. I. 1929, **48**, 811-B; Silk J. 1928, **5**, #52, 80; Chem. Zentr. 1928, II, 1944. F. P. 656466; abst. C. A. 1929, **23**, 4351. C. Dreyfus, Can. P. 288363.

fabric to pressure in contact with a transfer sheet having the coloring matter deposited thereon, the pressure being local only at points or areas and may be combined with an embossing operation. Such fabrics may be colored by leuco-compounds of gallocyanine dyes[1], since these have a greater affinity for the cellulose derivatives than when in the fully oxidized form.

Composite fabrics containing cellulose derivatives together with other material as cotton[2] are printed with anthraquinone base colors adapted to produce dyeing reactions upon the fabric, the printed colors being fixed, and are then rinsed in a reducing bath of sodium bichromate solution to remove all color from the fibers other than that of the cellulose compound. An ink suitable for marking such fabrics contains lead chromate, a drying oil, a cellulose ester and a solvent therefor[3]. In producing differential colors on a textile material comprising cellulose ester or ether yarns[4], there may be locally applied a diazotizable amine in the presence of a swelling agent, and then developed. A modification of the general method of transfer printing upon cellulose derivatives has been mentioned by C. Dreyfus[5] and consists in wetting the fabric with a weak solvent, placing on the fabric a transfer sheet coated with a substance containing a wax having a dye dispersed therein which is at least partially soluble in the liquid used to wet the fabric, then impressing the design surface on the softened fabric.

1. Durand & Huguenin, A.-G., E. P. 352808; abst. J. S. C. I. 1931, **50**, 923-B; Textile Mfr. 1931, **57**, #684, 461; Silk J. 1932, **8**, #93, 54. F. P. 701852. D. R. P. 526193; abst. C. A. 1931, **25**, 4413; Chem. Zentr. 1931, II, 1497.

2. R. Petitdidier and F. Feynier, U. S. P. 1847697; abst. C. A. 1932, **26**, 2605.

3. H. Platt, Can. P. 317112. J. R. Geigy (E. P. 231897) adds aromatic sulfonic or carboxylic acids to the printing paste, or the cellulose ether or ester goods are impregnated with these compounds before being printed. A printing paste recommended comprises Setoglausine, 2-naphthol-7-sulfonic acid, acetic acid and a gum thickening. Salicylic acid or benzene-, naphthalene- or anthraquinone-sulfonic acids may be used. See L. Lilienfeld, E. P. 231804. Aust. P. 105040.

4. *Ibid.* Can. P. 317114; abst. C. A. 1932, **26**, 1454.

5. Can. P. 290861.

H. Hager[1] divides printing with the Naphthol AS colors into three groups, the discharge and resist style, the rapid fast colors and the naphthol print-on style, vat dyes being suitable for colored discharges and being equal in fastness to the naphthol grounds, the latter being stable to sodium chlorate and usable in the chlorate discharge style. He has described the uses of Blue Salt B, Variamine Blue Salt and resist combinations and recommends naphthol resists as giving very bright effects under aniline blacks.

Reserve Printing. In the reserve dyeing of mixed fabrics[2], silk and wool are reserved by adding to the bath serving for dyeing cellulose ethers or esters, the sulfuric acid esters of higher aliphatic alcohols, or their soluble salts are recommended. G. Hasse[3] produces polychromatic reserves for fabric printing by using ester salts of leuco compounds of vat dyes with a thickening agent which has a reserve action on the final alkaline vat. In an illustrative example, the printing material is composed of the sodium salt of the sulfuric ester of leucoindigo, water, methylcellulose and ammonium oxalate, thiocyanate, chlorate or *o*-vanadate.

According to E. Pfeffer[4], in color reserve printing by aniline black or other colors produced by the oxidation of vat dyes on the fiber, the printing reserves comprise vat dyes, and solutions of cellulose ethers or esters, preferably the former on account of the saponifying action on the latter of alkalis contained in the bath, are precipitated to form a suitable thickening agent, starch being added if desired. In an example of carrying out the process, the dye solution contains aniline salt, aniline oil, tragacanth, sodium chlorate and potassium ferrocyanide, and the color reserve at vat dye, acetic acid, sodium acetate, and as a

1. Proc. Am. Assoc. Textile Chem. and Colorists, Am. Dyestuff Rep. 1929, **18**, 255; abst. C. A. 1929, **23**, 3576.
2. I. G. Farbenindustrie, A.-G., F. P. 703090; abst. C. A. 1931, **25**, 4413.
3. D. R. P. 519984; abst. C. A. 1931, **25**, 3497. See D. R. P. 418487, 433146.
4. D. R. P. 529969; abst. C. A. 1931, **25**, 5300.

thickener is used the sodium salt of the sulfuric ester of cellulose (sodium ligninsulfonate ?).

Color Printing. Fabrics containing cotton or regenerated cellulose with cellulose esters are printed with a color having affinity for the cellulose ester[1], steamed and rinsed, and the whites finally cleared with 0.1% solution of sodium hyposulfite. For the printing pastes, Duranol or Setacyl colors are diluted with water and thickened with gum. Basic colors are used with acetanol (a pyridine salt made by Etabl. Kuhlmann). Ionamines are excluded.

Fabrics as above may be printed in the usual manner with a coloring matter of the anthraquinone type as citronine or basic dyes mordanted with acetanol, steamed, rinsed, and finally dyed with a coloring matter that has affinity for cotton without appreciably affecting the color of the cellulose ester portion. Or[2], in the color printing of mixtures of real silk and cellulose ester fibers, the whites may be cleared by means of 0.1% sulfuric acid or by 0.2-0.3% sodium hyposulfite solution. For acetate silk-wool mixtures the hyposulfite solution may go to 0.5% concentration. In a variant of this process[3], 2.0-2.5% solution of potassium permanganate is used, followed by a bath of sodium bisulfite (sp. gr. 1.116).

Warp Printing. The British Celanese, Ltd.[4], have described a process for the local printing and coloring of fabrics containing yarns of organic cellulose derivatives and having warp print effects thereon, where there are other yarns as natural silk present a coloring material is selected whose behavior towards the cellulose derivatives is different from that of the other fiber as applied locally. This is illustrated in the following specific example:

1. Soc. Anon. des Etablissements Petitdidier, E. P. 256238; abst. C. A. 1927, **21**, 2990; J. S. C. I. 1928, **47**, 50-B; Rayon, 1928, **6**, #8, 33.
2. *Ibid.* E. P. 258562; abst. J. S. C. I. 1928, **47**, 50-B.
3. *Ibid.* E. P. 270657, Addn. to E. P. 256238; abst. J. S. C. I. 1928, **47**, 50-B; Chem. Zentr. 1927, II, 981. F. P. 32658, Addn. to F. P. 615301; abst. C. A. 1928, **22**, 4835; Chem. Zentr. 1928, I, 2998.
4. E. P. 316982; abst. C. A. 1930, **24**, 1991.

A fabric consisting of a warp of cellulose acetate yarn and having a weft or filling of silk yarn is locally printed with a paste composed of acacia 60, Turkey red oil 12, alcohol 10, concentrated ammonia, (not very definite expression) 4, soap 4 and 1.4-di-(methylamino)anthraquinone 4 parts. After printing, the fabric is dried and then steamed for about 40 min. with steam at 6 lb. pressure per square inch, the fabric being then washed, scoured and rinsed. In another described process[1], fabrics containing substances such as cellulose formate, acetate, propionate or butyrate, and having warp print effects, are made by subjecting cellulose ester material constituting the warp or weft to a treatment which imparts an affinity for dyes different from that of the untreated material, weaving the two and then dyeing with a color having a selective affinity for one of the component materials[2].

The C. Dreyfus invention relates to the production of novel color effects by the printing of warps of yarns of organic cellulose derivatives as methyl-, ethyl- or benzylcellulose[3], a warp being first made comprising a series of parallel yarns wound on a beam, this warp being fed to a loom where the weft or filling is woven in to make a fabric. When yarns of organic cellulose derivatives are employed in the warp, it is necessary to size it to impart sufficient strength to withstand the drastic conditions to which it is subjected in the loom. It is pointed out that such warps, while they have the size thereon, may be successfully printed with a paste despite the presence of a size. The warps are locally colored with the size thereon, an advantage being that the thickener of the printing paste when retained on the warp increases its strength and acts as a size during the weaving operation. A suitable printing paste for this purpose is said to be composed of basic dyestuff 10-50, 40% acetic acid 25, ethyl alcohol 25-50, diacetin 25, water 265-250 and 50% acacia solution 650-620.

1. C. Dreyfus, E. P. 306534; abst. C. A. 1929, **23**, 5048.
2. *Ibid.* E. P. 317455; abst. C. A. 1930, **24**, 2309.
3. U. S. P. 1883346.

In printing fabrics composed of cellulose acetate or cellulose ethers with a natural silk or wool foundation[1], the fabric, after printing the cellulose derivative, is passed through a bath of potassium permanganate and then through a bath of sodium acid sulfite, to remove all traces of color from the silk or wool foundation.

The presence of the usual size on yarns of organic cellulose derivatives used for warp in fabric does not prevent the satisfactory printing upon them of dyes which have an affinity for this type of artificial silk[2]. Thus for the production of a colored fabric, the warp yarn is sized and wound on a beam, then suitably printed, dried, and woven into fabric, using a weft yarn of any suitable fiber or color. scribed a method of printing on non-resilient materials as metal, wood, artificial resins and vulcanized rubber, color-

Printing Inks. The I. G. Farbenindustrie[3] have deless or colored coatings or designs being obtained by the use of practically anhydrous lacquers containing cellulose ethers or esters, by an intaglio, offset, lithographic printing process, the ink being formed of a water-repelling composition of a cellulose ether or organic ester, a plasticizer, resins and coloring matter[4]. Nitrocellulose may also be employed in preparing the ink, an ink suitable for a lithographic printing machine with wiping mechanism being prepared from 235 parts low-viscosity nitrocellulose, 30 parts castor oil, 100 parts diethyl phthalate, 125 parts ethyl benzoate, 60 parts dammar and 250 parts zinc white.

The H. Platt and C. Dreyfus fabric marking ink[5] comprises lead chromate 10, raw linseed oil 3, nitrocellulose 10 and ethyl acetate 45. A *p*-dihydroxy compound of the benzene series has also been patented as color[6], and in another

1. Soc. Anon. des Etablissments Petitdidier (ancienne Maison Jolly-Belin), E. P. 256238, 270657. See H. Dreyfus, E. P. 339300.
2. British Celanese, Ltd., E. P. 318840; abst. J. S. C. I. 1931, **50**, 292-B.
3. E. P. 318567; abst. C. A. 1930, **24**, 2316.
4. I. G. Farbenindustrie, A.-G., E. P. 335074; abst. C. A. 1931, **25**, 1399; J. S. C. I. 1930, **49**, 1120-B.
5. Can. P. 317112.
6. G. Ellis, Can. P. 317111.

patented method[1], use is made of 10 parts octadecadiene-9.11-acid-1-triglyceride (glyceryl octadecadiene-9.11-acid) with 10 parts nitrocellulose, 30 parts ethyl acetate and 40 parts butyl acetate. J. Clewell[2] prefers diacetone alcohol 20, National nigrosine base N, 2, and orange shellac 8, while C. Dreyfus and H. Platt[3] advocate as a marking or printing ink, unaffected in dyeing or bleaching processes, lead chromate, raw linseed oil or China wood oil, and nitrocellulose dissolved in ether-alcohol or in ethyl acetate. The ink, which may be applied by means of a stylograph pen having a rounded point, is particularly adapted for marking cellulose ether or ester fabrics.

An ink which will penetrate and merge with coatings of shellac varnish and other products[4] so as to be proof against erosion and to withstand the action of acids, alkalis and other chemicals which ordinarily remove surface inks, is obtained by mixing 2 parts absolute alcohol, 1 part diethyl phthalate, 17 parts ethyl lactate or ethyl oxalate, any suitable coloring matter being incorporated. The intaglio printing ink of the I. G. Farbenindustrie[5], suitable for printing on celluloid, cellulose esters or cellulose ethers, comprises an organic cellulose derivative soluble in ethyl alcohol, coloring matter, and a solvent consisting of at least 70% ethyl alcohol free from aliphatic homologues of 1.4-dioxane.

Resist Effects. White or colored discharge or resist effects are obtained upon fibers or fabrics comprising cellulose ethers or esters in the presence of ammonium thiocyanate or other water-soluble thiocyanates, the discharge being assisted by acids such as citric or tartaric, and prefer-

1. J. Scheiber, D. R. P. 544697, Addn. to D. R. P. 522486; abst. Chem. Zentr. 1932, I, 2242.
2. U. S. P. 1806965; abst. Chem. Zentr. 1931, II, 2820; Plastics, 1931, **7**, 577.
3. E. P. 296759; abst. C. A. 1929, **23**, 2585.
4. C. Cunningham, U. S. P. 1562544; abst. Plastics, 1926, **2**, #2, 62. C. A. 1926, **20**, 513. Can. P. 265988.
5. E. P. 339733; abst. C. A. 1931, **25**, 2865.

ıbly assisted by the presence of swelling agents[1]. Resist ːffects on acetylcellulose with azoic and vat colors have ɔeen shown with formulas by W. Bennett[2] in a series of ırticles, covering the subject in considerable detail.

Effect Threads. Dyed effect threads, fast to cross-dyeng[3], are obtained on cellulose ether or ester fibers with lyes of the azo, polyazo, stilbene, sulfur or vat dyes pro-ʼided they are fast to acids, are insoluble in acetic acid or ıcetic anhydride, and contain no free amino group capable ɔf acetylation. Thional Black T and Indanthrene Blue GCD ıre examples of suitable colors. Effect threads resistant ɔ substantive dyes may be obtained by acetylating cellulose n any form in a mixture the activity of which has been ıo moderated by adjustment of temperature and ıuantity of catalyst used, that the cellulose is converted lirect into the mono- or di-acetate without change in orignal structural form[4]. The reaction is allowed to proceed ıt 15°, and after 2 days a dye test is made to see if acetyla-ːion has proceeded sufficiently far to render the fiber comɔletely resistant to substantive dyes.

Producing Woolly Effects. According to the disclosures ɔf R. Clavel[5], soft, woolly effects on threads of yarns of ıcetylcellulose may be produced by heating them with solu-ːions of formic or acetic acids of suitable concentration at ıbout boiling temperature, in the presence of protective colɔids or similarly acting salts. It is also known that when ːellulose acetate artificial silk is immersed in boiling water t rapidly becomes curly and wool-like and loses a conːiderable proportion of its luster and transparency. For ınstance, when acetylcellulose silk is heated for 3 min. in

1. British Celanese, Ltd., G. Ellis and W. Miller, E. P. 342333. Can. P. 298757. F. P. 702353.
2. Silk J. 1927, **3**, #35, 52; abst. C. A. 1928, **22**, 872.
3. Chemische Fabrik vorm. Sandoz, E. P. 324680; abst. C. A. 1930, **24**, 3911.
4. *Ibid.* E. P. 280493; abst. J. S. C. I. 1928, **47**, 812-B. F. P. 635304. D. R. P. 525084. A. Rheiner, Can. P. 278731. U. S. P. 1861320. E. P. 318366.
5. Can. P. 249726. E. P. 206818.

boiling water, it swells, becomes woolly in appearance and opaque.

Crepe Effects. Crepe cloths have recently assumed considerable importance, especially crepes made solely or in part from filaments of cellulose derivatives, in which the crinkled, cockled or puckered effect may be varied at will and within comparatively wide limits[1]. The characteristics of the finished cloth depend primarily on the type of yarn, the degree, direction and compactness of the twist, and the treatment to which it is subjected while in the twisted condition. The material is usually piece dyed and finished. In a true crepe, the cockled appearance is due to the high number of turns in the weft, the warp ordinarily consisting of twisted yarn, but in certain specialty cloths the warp also may be more highly twisted. The extra twist imparted to the weft causes the yarn to curl up even in the woven material, which is particularly the case after wetting, when the tendency to curl should persist after several washings, this degree of shrinkage being indicative of the quality of the crepe.

Real silk crepes being comparatively expensive, it is but natural that investigators of thought should exercise their ingenuity in endeavors to place upon the market artificial fibers as nearly as possible simulating the desirable characteristics of silk crepe. It was only when artificial cellulose filaments came to be used for this purpose that goods closely approaching the beauty and attractiveness of natural silk became possible. The primary factors which have contributed most to the popularity of cellulose ester and cellulose ether crepes have been their improved strength and the very fine filament yarns now being spun. Most of the so-called "non-crushable" fabrics are crepes, until a short time ago about the only fabrics which could be guaranteed as uncrushable being pile fabrics. Crepes are seldom finished with full shrinkage, otherwise the cloth would appear dead and lifeless. Where an artificial cellulose ester or ether

1. Anon., Silk J. 1932, **8**, #97, 40.

warp and a cotton crepe weft are used, the shrinkage may amount to 10-15% in length and 20-30% in width, most of which is regained in finishing. The final appearance depends almost entirely on the degree to which the fabric is pulled out in finishing. Where the crepe is composed entirely of cellulose ester or ether filaments the gray width is usually about 42 inches as against about 39 inches in the finished width. On the other hand, the shrinkage will be about 7% in the length and 8-9% in the width. Due to this shrinkage, the threads per inch are more after finishing. The tension applied at all stages of manufacture must be the minimum, otherwise the benefit of the hard twist will be considerably lessened if not lost. When extra softness and improved handle are desired, the material is given an extra treatment with dilute caustic soda, acetate yarn being more affected by this alkali treatment than cellulose ether filaments.

Regulation of degree of shrinkage or contraction induced may be regulated by substituting partially or wholly, glycerol or glycol for the water of hydration, and by allowing the water to be absorbed by deliquescent salts which are embodied with the fabrics that are being treated[1]. In the case of union goods, shrinkage of the artificial silk portion induces the crepe effect. A mixture of glycerol and zinc chloride, or glycerol and zinc acetate, or calcium or magnesium chlorides may be used for this purpose.

It is to be remembered that artificial fibers and threads obtained from cellulose ethers or esters, generally speaking, have a rectilinear structure, whereas many natural fibers as those of wool, are more or less strongly crimped. Such crimped artificial fibers may be obtained, it is claimed[2], by treating threads, bands or strips obtained from polymerization of condensation products of butadiene or its homologues, introduced in the form of a loose skein into

1. C. Cross and Viscose Development Co., Ltd., E. P. 236336; abst. J. S. C. I. 1925, **44**, 707-B; Rayon J. 1926, 41.

2. I. G. Farbenind., A.-G., E. P. 346799; abst. J. S. C. I. 1931, **50**, 674-B.

dipentene and slowly kept in motion therein about 1.5 hrs. at 45°. The product is crimped similar to wool, and has a silky luster. The crimp effects of acetate silk are said to be heightened by dehydrating the filaments as completely as possible before sizing[1].

Crepe effects are obtainable by incorporating substances as calcium chloride, nitrate or lactate[2], with organic cellulose derivatives, making cloth from the highly twisted threads, and then treating the cloth obtained with water or an aqueous solution. Where crepe yarn is produced from natural and artificial silk filaments[3], the raw material is wound on bobbins and sized between the winding and throwing operations. A crepe effect may be imparted to artificial silk fabrics by using as weft highly twisted acetylcellulose fibers which have been spun from a solution to which has been added a substance such as sodium or potassium acetate which gives a high solution tension in water[4]. Another method is to treat the highly twisted cellulose ester yarns in a bath with a material having a pronounced swelling action[5], but little or no peptizing effect on the esterized cellulose. Among the substances which may be advantageonsly used for this purpose are methyl or ethyl alcohol, benzene, toluene, trichlorethylene, carbon tetrachloride, guaiacol or aniline emulsions, or aqueous solutions of ethyl acetate.

Fabrics may be formed containing both shrunk and unshrunk yarns of cellulose ethers or esters[6], so that by treating them with a shrinking agent as nitric acid of 20-45°

1. Inoxi (S. A. R. L.), F. P. 34071, Addn. to F. P. 639197; abst. C. A. 1929, **23**, 4353.
2. Soc. pour la Fabrication de la Soie Rhodiaseta, F. P. 715047; abst. C. A. 1932, **26**, 1803.
3. D. Pächt, E. P. 345396; abst. C. A. 1932, **26**, 318.
4. Deutsche Acetat-Kunstseiden, A.-G., D. R. P. 529800; abst. C. A. 1931, **25**, 5301; Chem. Zentr. 1931, II, 3564.
5. Soc. pour la Fabrication de la Soie Rhodiaseta, E. P. 335020; abst. C. A. 1931, **25**, 1393; J. S. C. I. 1930, **49**, 1107-B. F. P. 696865; abst. C. A. 1931, **25**, 2862. Aust. P. 123395; abst. Chem. Zentr. 1931, II, 1788.
6. British Celanese, Ltd., W. Dickie and R. Moncrieff, E. P. 335180; abst. C. A. 1931, **25**, 1393; J. S. C. I. 1930, **49**, 1148-B.

Tw., crepe, semi-crepe, pebble or other ornamental effects may be produced while the fabric is capable of being dyed on a level shade. The shrinkage agent may be applied locally if desired, thus producing local designs or differential effects. The British Celanese have described a process in which yarns or fabrics formed in part only of cellulose ethers or esters, and which may contain cotton, wool and silk, are treated with a reagent which causes more drastic shrinkage of the other material, NaOH solution being suitable for inducing greater shrinkage if cotton fibers are present[1]. Threads of degummed silk or of organic derivatives of cellulose may be impregnated with materials containing casein, rubber or gelatin[2], which are then heated with formaldehyde or tannin to prevent softening during the swelling process. The coated threads after highly twisting, are woven into fabrics which are treated with water, aqueous ethyl alcohol or salt solutions, to cause swelling of the coating without rendering it relatively soft or yielding. The coating is subsequently removed in the swelling bath, if necessary after adjustment of its temperature and/or composition.

Another variation in the production of fabrics having crepe-like, cockled or pebble effect comprises using in the weft or warp or both[3], yarns which have been permanently stretched in combination with unstretched yarns, by alternating yarns which have been stretched to one degree with yarns which have been stretched to a different degree. Subsequent treatment of the fabric with water or with aqueous liquids containing soap, effects a shrinkage of the stretched yarns and a consequent crinkling of the unstretched yarns, or those yarns having the lesser degree of

1. British Celanese, Ltd., E. P. 345022; abst. C. A. 1932, **26**, 319; J. S. C. I. 1931, **50**, 584-B; Chem. Zentr. 1931, II, 3176. H. Dreyfus, F. P. 707250; abst. C. A. 1932, **26**, 856.

2. British Celanese, Ltd., and W. Dickie, E. P. 348589; abst. J. S. C. I. 1931, **50**, 716-B. H. Dreyfus, F. P. 705159; abst. Chem. Zentr. 1931, II, 3176.

3. British Celanese, Ltd., E. P. 349121; abst. Silk J. 1931, **8**, #90, 61. E. P. 352113; abst. J. S. C. I. 1931, **50**, 836-B.

stretch. Low or high twist yarns of cellulose ethers or cellulose acetate may be used. Creping of textile materials composed of cellulose derivatives may be carried out by impregnating with a swelling agent which becomes effective on dilution with water fabrics woven with tightly twisted yarns[1] which are afterwards woven into fabrics, and then scouring or otherwise treating with aqueous liquids[2]. Suitable swelling agents include zinc chloride with calcium thiocyanate, acetone, acetic acid or ethyl alcohol suitably diluted with benzene are satisfactory for yarns composed of cellulose ethers or esters, particularly cellulose acetate.

The C. Dreyfus invention relates to the production of crepe effects having yarns of natural silk and yarns of methyl-, ethyl- or benzyl-cellulose filaments[3], where the yarns of the latter have a natural luster or sheen. The silk yarn is degummed to the desired extent prior to weaving, having imparted to it as high a twist as 50-75 turns per inch and is then associated with the organic cellulose derivative yarn to form a woven fabric. It is then treated in an aqueous bath such as a scouring bath, whereupon the natural silk yarn crepes to form the desired effect[4]. It has been found that the shrinking tendency of fabrics of cotton wool, flax, natural silk or regenerated cellulose[5], when exposed to aqueous liquids is diminished or even overcome by incorporating with the fibers from which the fabrics are made, fibers of cellulose ethers or of cellulose acetate, in staples which may vary from 0.5-8 inches in length.

In the manufacture of fabrics exhibiting crepe effects[6], especially those containing highly twisted crepe threads

1. British Celanese, Ltd., and W. Dickie, E. P. 351999; abst. J. S. C. I. 1931, **50**, 880-B. See E. P. 348589.
2. *Ibid.* E. P. 352000; abst. J. S. C. I. 1931, **50**, 880-B.
3. U. S. P. 1813530; abst. C. A. 1931, **25**, 5301. British Celanese, Ltd., E. P. 352112; abst. Silk J. 1932, **8**, #92, 54.
4. British Celanese, Ltd., W. Dickie and R. Moncrieff, E. P. 356233; abst. J. S. C. I. 1931, **50**, 1008-B; Textile Mfr. 1932, **51**, #686, 79; Silk J. 1932, **8**, #94, 54.
5. British Celanese, Ltd., E. P. 356681; abst. Textile Mfr. 1932, **51**, #686, 80.
6. British Celanese, Ltd., W. Dickie and R. Moncrieff, E. P. 357084; abst. J. S. C. I. 1931, **50**, 1090-B.

with filaments made from an organic cellulose derivative, they are first subjected to a padding treatment, locally if desired, with solutions which exert a dehydrating action upon the cellulose derivative, as ethyl alcohol, calcium or zinc chlorides, sodium acetate, sodium dihydrogen phosphate, methylamine or hydrochloric acid, and after keeping for 0.5-2 hrs., are washed and dried without tension. Alternatively, the threads may be treated with these dehydrating liquors before weaving or even before twisting, the woven fabric made therefrom being subsequently washed with water.

Another patented method discloses the coating of threads composed of cellulose ethers or esters either with a layer of cellulose as by surface hydrolysis or by coagulation of viscose or cuprammonium solutions, or if the original threads are a non-etherified or non-esterified cellulose[1], the threads are coated with a cellulose ether or ester in which the etherifying or esterifying radicals contain hydroxyl or carboxyl groups, e.g., cellulose acetotartrate, and after highly twisting and weaving with other fibers, the resulting fabric is scoured with water or soap solution to cause swelling of the coating.

High twist crepe yarns of cellulose ethers or acetylcellulose[2], for the production of crepe fabrics, have their high twist imparted in two or more stages, a relatively large proportion of the twisting being done preferably in the first or an early stage. The sizing may be effected between the stages of twisting or after. Filaments of 1-2 denier may be used[3]. These twisted yarns may be formed by varying the ratio of the rate of twisting and travel dur-

1. British Celanese, Ltd., H. Dreyfus, W. Dickie and C. North, E. P. 357169; abst. J. S. C. I. 1931, **50**, 1090-B; Silk J. 1932, **8**, #95, 50; Textile Mfr. 1932, **58**, #687, 116. H. Dreyfus, F. P. 715185; abst. C. A. 1932, **26**, 1803. H. Platt, Can. P. 308209.

2. British Celanese, Ltd., W. Dickie and R. Moncrieff, E. P. 357576; abst. J. S. C. I. 1931, **50**, 1090-B; Silk J. 1932, **8**, #95, 52. H. Dreyfus, F. P. 715930; abst. C. A. 1932, **26**, 2066.

3. *Ibid.* E. P. 357577; abst. Silk J. 1932, **8**, #95, 52.

ing manufacture[1], so that a corresponding fluctuation or irregularity of twist is induced along the length of the yarn. Improved effects are said to be obtained if the thread is superficially hydrolyzed at intervals along its length instead of continuously[2].

Crepe fabrics having highly twisted weft threads are preferably woven on a loom having stationary weft supplies[3], the highly twisted weft thread being given a sufficient coating of size after twisting to overcome the retractive effort due to the twist, so that the lengths of weft severed from the supply will lie straight in the shed until the beat-up. The threads may comprise continuous cellulose ether or acetylcellulose filaments. Another variation in the production of creped textiles comprises utilizing fabric made from yarn of cellulose artificial silk or natural silk[4], or cellulose ethers or esters[5], coated at spaced intervals with a casein, rubber, albumin or algin size and then scoured, whereby the size is removed and the fabric acquires a cockled appearance[6].

Crepe, pebble and crinkled effects may be produced on netted, woven or knitted fabrics formed of organic derivatives of cellulose[7], by the local application of a solution of nitric acid of 10-60° Tw., which may be applied by means of engraved or embossed rollers or by brushing or spraying through stencils, with or without a dye or thicken-

1. British Celanese, Ltd., W. Dickie and R. Moncrieff, E. P. 358585; abst. J. S. C. I. 1931, **50**, 1137-B; Textile Mfr. 1932, **58**, #687, 119. H. Dreyfus, F. P. 715998; abst. C. A. 1932, **26**, 2066.

2. *Ibid.* E. P. 362523; abst. J. S. C. I. 1932, **51**, 227-B; Silk J. 1932, **9**, #98, 44. See E. P. 357169.

3. British Celanese, Ltd., and W. Dickie, E. P. 364057; abst. Silk J. 1932, **9**, #98, 46.

4. British Celanese, Ltd., W. Dickie and R. Moncrieff, E. P. 365040; abst. J. S. C. I. 1932, **51**, 338-B.

5. *Ibid.* E. P. 365041; abst. J. S. C. I. 1932, **51**, 338-B.

6. H. Chadwick, Dyer, Calico Printer, 1931, **66**, 43; abst. Chem. Zentr. 1931, II, 3044. See A. Crispe, Russa, 1931, **6**, 243; abst. C. A. 1931, **25**, 2571.

7. C. Parker, W. Kershaw, F. Barrett and Bleachers' Assoc., Ltd., E. P. 274584; abst. C. A. 1928, **22**, 2279; Rayon, 1927, **5**, #9, 24. British Celanese, Ltd., E. P. 335138; abst. C. A. 1931, **25**, 1393; J. S. C. I. 1930, **49**, 1106-B. E. P. 335139.

ing substance. Another method of forming crepe fabric consists in weaving together yarns of organic cellulose derivatives and highly twisted degummed natural silk yarn, and then subjecting the fabric to a creping bath[1].

In the H. Dreyfus process[2], permanent crepe effects may be obtained on fabrics consisting wholly or in part of cellulose ethers by using yarn which, after receiving a protective coating of gums, gelatin or starch, has been given 44-86 twists per inch, with or without previously drying. The twisted yarn is preferably treated when in fabric form, to remove the coating medium to any desired extent, as by hot water or application of a hot soap solution, this operation serving as the wetting treatment required for the development of the crepe effect. In the production of twisted threads[3], especially for the production of highly twisted or crepe threads, the yarn is drawn off from a rotating yarn package, causing the yarn, upon leaving the package, to pass in a balloon-shaped path to a light floating member surrounding the driving spindle of the yarn package, thus permitting the yarn to rotate about the spindle axis, and to pass to a point above and in alignment with the driving spindle axis.

In producing crepe effects[4], yarns of artificial filaments and wool fibers may be twisted together to form a double strand, a fabric being formed of such strands, one of the yarns being then subjected to a shrinking process (as by soap and water to shrink the wool yarn), to the extent that the other yarn is looped. J. Eccles[5] and W. Young[6] have given formula and details for producing various crepe effects using cellulose derivatives.

1. C. Dreyfus, Can. P. 313166.
2. U. S. P. 1538030; abst. C. A. 1925, **19**, 2136. E. P. 226256; abst. J. S. C. I. 1925, **44**, 201-B; Chem. Zentr. 1925, I, 2117. Can. P. 247234.
3. H. Dreyfus, Can. P. 297858. W. Dickie, Can. P. 325060.
4. J. Farber, U. S. P. 1825586; abst. C. A. 1932, **26**, 319.
5. Textile Colorist, 1931, **53**, 741; abst. C. A. 1932, **26**, 1448. Textile World, 1932, **61**, 98; abst. C. A. 1932, **26**, 1448.
6. Textile World, 1930, **78**, 423; abst. C. A. 1930, **24**, 4935. Cellulose, 1930, **1**, 136; abst. C. A. 1931, **25**, 3840. Textile World, 1930, **78**, 3031; abst. C. A. 1931, **25**, 819.

Damask Effect. Damask effects are produced on material of cellulose ethers or acetylcellulose by printing with caustic alkali to saponify the ester where cellulose acetate is used, then washing, and finally treating with a delustering agent as boiling water, formic, acetic or lactic acids, acetone, furfuraldehyde or pyridine,[1] by which the unsaponified portion is delustered without producing any change in the luster of the saponified portion. The material may be treated with a dye having no affinity for cellulose acetate as chrysophenine, by which the saponified portions only are dyed, or the unsaponified portion only may be dyed with such basic dyes as Malachite green.

To produce damask effects on table cloths, napkins and other textiles, or polka dots, stripes or patterns, hydrated cellulose acetates soluble in acetone as Sericose L, are applicable[2]. Goods printed with cellulose acetate may afterwards be slop-padded with direct colors, with basic and mordant colors and with aniline black, which may afterwards be discharged or resisted. For basic dyes, either 40% acetic acid solutions, or alcoholic solutions may be used and directly added to the partially hydrated acetylcellulose mixture, thus admitting of the production of fancy effects in color printing. A little tannin in acetic acid solution is often helpful in the fixation of the colors.

In the production of a permanent damask effect by the R. Chatham method[3], the material is padded with a solution of cellulose ether or ester in a mixture of phenol, formaldehyde and ethyl alcohol, then immersed in water to precipitate the cellulose derivative, and dried, after which it is hot pressed. Printed luster effects may be had on cellulose ether or ester materials by printing with a paste containing a solvent or gelling agent[4], then drying, steaming

1. Calico Printers' Assoc., Ltd., J. Whinfield and C. Levin, E. P. 273011; abst. C. A. 1928, **22**, 1860; J. S. C. I. 1927, **46**, 964-B.
2. See E. Worden, "Technology of Cellulose Esters," 1915, VIII, 2785.
3. U. S. P. 1640596; abst. J. S. C. I. 1927, **46**, 872-B.
4. British Celanese, Ltd., and G. Ellis, E. P. 335583; abst. J. S. C. I. 1930, **49**, 1147-B.

with dry steam under pressure, and subjecting to delustring by boiling in soap, whereby only the printed parts retain their original luster. F. Grove-Palmer[1] has discussed the production of plushes and velvets using cellulose acetate.

Producing Moire Effects. In the natural silk industry water-wave effects on fabrics have a successful commercial history dating back many years. It is said the first effects were obtained unintentionally in the ordinary finishing of fabrics, and silk manufacturers, keen to turn an apparent defect to profit, investigated the problem to bring it under factory control, and these watered cloths are known under the general name of moire fabrics[2]. True moire is an ingenious mechanical finish induced by simply passing a double thickness of fabric through the heated rolls of a calender, thereby producing a drawing or flattening of the weft at certain points, which exhibits the well known light and shade effect arising from the coexistence of differently inclined light-reflecting surfaces. The best results are obtained on fine warp and weft rib structures, in which the warp is fine and dense, and the weft straight, hard and round. Theoretically, when two pieces of the same fabric are placed together and passed between pressure rollers, the extreme limits of the effects possible are, either the whole of the weft ribs would be flattened or merely squeezed. Inasmuch as the cellulose ethers and organic cellulose esters are thermoplastic *per se,* and have approximately definite softening and melting points, it is obvious that they readily lend themselves under the simultaneous application of heat and pressure, to the formation of moire effects substantially permanent.

The H. Dreyfus process for the manufacture of materials presenting moire effects is characterized in that close line-patterns or grid-patterns are impressed in or on the opposite faces of relatively thin sheets or bands of

1. Text. Colorist, 1929, **51**, 834; 1930, **52**, 29, 31, 34, 54.
2. H. Chadwick, Textile Mfr. 1931, **57**, 258; abst. C. A. 1932, **26**, 310.

transparent or translucent plastic material, so that optical interference is created by the effect of the lines on the opposite faces, the sheets or bands being preferably composed of cellulose ethers or organic esters[1]. The effect is heightened by the application of heat and pressure. In weaving velvets containing both natural silk and cellulose ether or ester yarns[2], the silk yarns are degummed prior to weaving, the cellulose derivative yarns comprising either the pile or the back. The fabrics may be dyed, scoured or printed.

The essence of the A. Milhomme process for forming moire patterns, especially scratch patterns[3], is to moisten the fabrics of cellulose ether or ester composition prior to scratching the pattern thereon, the fabric being saturated in a liquid bath or dampened by spraying. It is then folded transversely or longitudinally, passed between an embossed pattern roll and a scratching roll having flexible blades. The treated fabric is dried, and subsequently subjected to heat and pressure.

In carrying into effect the process as evolved by British Celanese, Ltd.[4], ribbed or other fabrics made wholly or largely from organic cellulose derivatives, ethylcellulose being particularly specified, are submitted to combined heat and pressure with engraved rollers and in the presence or not of liquids exerting a solvent or swelling action on the cellulose compound. Moire Francaise and Moire Renaissance, for example, are obtainable of these thermoplastic fabrics, the markings being very pronounced and beautiful.

Pattern Effects on Textiles. Patterned or effect materials, sheets, slabs or blocks having a basis of methyl-,

1. Can. P. 262843; abst. Chem. Zentr. 1929, II, 1904. E. P. 250658; abst. Chem. Zentr. 1926, II, 2367.
2. British Celanese, Ltd., E. P. 344410.
3. U. S. P. 1781296; abst. C. A. 1931, **25**, 218; Chem. Zentr. 1931, I, 2286. E. P. 346561; abst. Silk J. 1931, **8**, #88, 54; J. S. C. I. 1931, **50**, 801-B; Textile Mfr. 1931, **57**, #680, 306.
4. E. P. 280195; abst. C. A. 1928, **22**, 3052; J. S. C. I. 1929, **48**, 279-B; Chem. Zentr. 1928, I, 1119. F. P. 643058; abst. C. A. 1929, **23**, 1515.

ethyl- or benzyl-cellulose or other esters or ethers of cellulose[1], such patterns being colored or other imitations as of ivory, tortoise shell or pearl, may be produced upon knitted, woven or other fabrics which have been suitably dyed, printed or stencilled, by placing thereon a molding powder of the thermoplastic cellulose compound and applying heat and pressure. For instance, the fabric is soaked in a solution containing a plasticizing agent dissolved in a substance not a solvent of the cellulose ether or ester, xylenemonomethylsulfonamide being satisfactory as plasticizer, and the fabric then dyed. The design or pattern required is then applied by printing, using dyes in volatile solvents also containing a plasticizing agent. The printed fabric is then dried and cut to shape and inserted in a mold box between layers of thermoplastic powder, the same plasticizing agent being used as employed in soaking the fabric, and the whole made into a unitary-appearing mass by hydraulic pressure and heat. Or the design may be imprinted on the fabric which is then treated with a plasticizer in a solvent mixture which dissolves the plasticizer but is a non-solvent for the cellulose ether or ester fabric, and after dissipation of the volatile solvent, heat and pressure are applied simultaneously[2].

It has been found that subjecting cellulose ether or ester fabrics to the action of heated rollers or plates, engraved or otherwise formed with a pattern[3], a pattern is produced on the fabric as an attractive glazed effect by the incipient melting action exerted upon the filaments, and is especially applicable to the production of ornamental or pattern fabrics. In the printing of "mixed" fabrics made with threads of cellulose ethers or esters with threads of

1. British Celanese, Ltd., W. Dickie and J. Rooney, E. P. 248832.

2. British Celanese, Ltd., W. Dickie and H. Halkyard, E. P. 273406; abst. J. S. C. I. 1927, **46**, 747-B.

3. C. Dreyfus, E. P. 254354; abst. J. S. C. I. 1926, **45**, 785-B; Chem. Zentr. 1927, I, 1374. U. S. P. 1634613; abst. C. A. 1927, **21**, 2990; J. S. C. I. 1927, **46**, 774-B. F. P. 609483; abst. Chem. Zentr. 1927, I, 1374.

cotton, wool or silk[1] and applicable to plain fabrics or pile fabrics, the fabric is printed upon by first applying a paste comprising the mixture of a solvent for the cellulose compound, an inert powder and a thickening agent, and contacting the mixture with the fabric at 125° until at least a part of the cellulose derivative is removable on washing with water, a discharge printing apparatus being suitable. Suitable solvents are acetic or lactic acid, acetone or other high boiling point soivents. As inert powder for the printing paste may be used powdered cellulose or barium carbonate or sulfate. Starch, casein, dextrin or water-soluble methylcellulose are suitable thickening agents. The process is intended primarily for application on velvets.

Differential effects are also producible on fabrics, especially a mixed fabric containing both cellulose acetate and a cellulose ether[2], by the local application of substances which modify the action of delustering agents and then treating with such agents. Among the substances which may be used for this purpose are waxes, resins, gums, pigments, phenols, chlorphenols, aromatic amines or substituted amines or halogenated hydrocarbons. If the fabric has been subjected to a delustering as by submission to boiling water or moist steam[3], there is locally applied an agent which will modify the delustring effect, such compounds being formic, acetic, propionic, butyric, chloracetic,

1. American Cellulose & Chemical Mfg. Co., Ltd., E. P. 263355; abst. C. A. 1928, **22**, 172; J. S. C. I. 1927, **46**, 185-B. British Celanese, Ltd., G. Ellis and W. Miller (E. P. 324683) obtain pattern effects on fabrics of cellulose ethers or cellulose acetate by (1) applying locally an agent inhibiting oxidation as a hydrosulfite, oxalate or sodium formaldehyde-sulfoxylate, (2) applying an oxidizing agent as a chlorate or bichromate, and (3) applying an aromatic compound as *p*-aminodiphenylamine, *α*-naphthylamine, benzidine or aniline, and developing the color by oxidation, using catalysts as the salts of iron, copper or vanadium.

2. British Celanese, Ltd., and G. Ellis, E. P. 266777; abst. C. A. 1928, **22**, 875; J. S. C. I. 1927, **46**, 406-B; Rayon, 1927, **5**, #2, 24.

3. G. Ellis and R. Mann, U. S. P. 1773975; abst. C. A. 1930, **24**, 5168; J. S. C. I. 1930, **49**, 945-B; Cellulose, 1930, **1**, #8, 223. British Celanese, Ltd., G. Ellis and R. Mann, E. P. 277414; abst. J. S. C. I. 1927, **46**, 874-B; Silk J. 1927, **4**, #41, 66. Belg. P. 342818.

aminoacetic, glycollic, lactic, citric and succinic acids, applied in a thickened solution form.

Designs may be produced on methyl- or ethyl-cellulose fabrics by printing a design with thickened viscose or copper-ammonia cellulose, the alkali present in either not affecting the cellulose ether[1]. The viscose is then converted into cellulose by acidification, washed and dried. When now dyed, differential effects will be observable due to the variation in dye receptivity of the cellulose ether or ester portion as compared with the regenerated cellulose. Or, the design may be produced in another material as gelatin or casein having differential dyeing properties, the gelatin or casein being removed or not after dyeing. If stiff fabrics are desired[2], yarns of cellulose ethers or esters with or without other fibers as those of cotton, wool, mohair or silk, are given a high twist, and preferably are above 200 denier. The fabrics may be made of "staple" fiber, being small lengths of acetate or ether filaments, and spinning them.

If a woven fabric is composed of real silk and artificial filaments of cellulose compounds[3], both in the warp and weft, and if a portion at least of the artificial filaments is acetylcellulose fibers, upon imprinting a design thereon by means of engraved rollers with an alkaline saponifying paste, the cellulose acetate is saponified, the real silk little changed and the cellulose ether affected not at all. Luster pattern effects are obtainable by completely delustring acetate silk fabrics, then embossing in the usual manner at about 150°, the fabric being then wetted and lightly calendered, whereby the embossing marks are removed[4].

1. British Celanese, Ltd., E. P. 295582; abst. J. S. C. I. 1930, **49**, 54-B.
2. *Ibid.* E. P. 302361; abst. C. A. 1927, **23**, 4353; J. S. C. I. 1930, **49**, 53-B; Silk J. 1929, **5**, #58, 80.
3. *Ibid.* E. P. 302363, Addn. to E. P. 274074; abst. C. A. 1929, **23**, 4352; Silk J. 1929, **5**, #58, 80.
4. Bleachers' Assoc., Ltd., W. Kershaw, F. Barrett and R. Gaunt, E. P. 303286; abst. C. A. 1929, **23**, 4581; J. S. C. I. 1929, **48**, 204-B; Silk J. 1929, **5**, #59, 74. E. P. 301567, 301568; abst. J. S. C. I. 1929, **48**, 127-B. Bleachers' Assoc., Ltd., F. P. 660022; abst. C. A. 1930, **24**, 249.

In the production of photographic or other effects upon fabric or films of cellulose esters[1] and containing diazotizable amino compounds, are diazotized and exposed to the action of light of locally varying intensity, the pattern or effect being fixed by development with a component capable of converting the diazo body into an azo compound. On the prepared fabric a light impression is suitably obtained as by direct photography, and after suitable exposure is subjected to development, the developer being applied as in dispersed form. The amino compounds recommended are *p*-nitraniline, *p*-nitro-*o*-anisidine, *m*-nitro-*p*-toluidine, *p*-chloraniline, benzidine, dianisidine or *p*-aminobenzene-azo-*α*-naphthylamine, suitable developers being *α*-naphthol, *α*-naphthylamine, dimethylaniline, and *m*-phenylenediamine.

Pattern effects are producible on either cellulose ether or ester fabrics[2] by locally applying a composition containing a chlorate and then locally or uniformly applying one or more colors dischargeable by the chlorate composition. By applying to a cellulose ether or ester fabric a solution or paste containing effect materials, a non-solvent for the cellulose derivative[3], and an "effect material" such as a pigment, beautiful and various results may be obtained. If ethylcellulose is employed in the composition, then benzene or toluene may be used as the solvent, and a paste of ethylcellulose in an aromatic hydrocarbon may be employed for producing effects on a fabric which contains cellulose acetate, or which contains cellulose ethers insoluble in benzene or toluene.

If the textile is first treated with an amine as aniline,

1. British Celanese, Ltd., and G. Ellis, E. P. 310773; abst. C. A. 1930, **24**, 733; J. S. C. I. 1929, **48**, 679-B. E. P. 312655; abst. C. A. 1930, **24**, 973; J. S. C. I. 1929, **48**, 978-B; Chem. Zentr. 1930, I, 288.

2. H. Dreyfus, F. P. 667211; abst. C. A. 1930, **24**, 1227; Chem. Zentr. 1930, I, 2168. Can. P. 287773, 293051, 293053, 293070.

3. British Celanese, Ltd., E. P. 314396, Addn. to E. P. 274841; abst. C. A. 1930, **24**, 1524; J. S. C. I. 1930, **49**, 1106-B.

p-aminodiphenylamine or 2.4-diaminodiphenylamine[1], and then with a compound capable of yielding a coloration on oxidation, differential effects and patterns are producible by applying locally an agent inhibiting the formation of such coloration.

If the cellulose ether or ester fabric is to be colored for the formation of pattern effects[2], as by impregnation with amines followed by diazotization on the fiber and developing with a coupling component, resist or discharge effects are readily obtained by the local application of chlorates, chromates, sulfoxylates or hyposulfites, which prevent diazotization of the amine. For colored discharge effects, a color resistant to the particular discharge applied is added, as acetylated aminoanthraquinone. For a white pattern on a white background pad with 5-nitro-*o*-anisidine, print with sodium chlorate, diazotize and couple with 2.3-hydroxynaphthoic acid. For a red pattern on a navy blue ground pad with dianisidine, print with Durindone-red Y, alkali, anthraquinone, hyposulfite and Formosul, steam, diazotize and develop as above.

A method has been described for the treatment of filaments and yarns so as to produce intermittent colored or multi-colored effects along their length[3], by the application, continuously with the production of the filament of one or more suitable dyestuffs, operated so as to rotate, oscillate or reciprocate into contact with the travelling yarn. In preparing white or colored pattern effects on materials of cellulose ethers or esters[4], the discharge in printing by

1. H. Platt and C. Dreyfus, E. P. 314501; abst. C. A. 1930, **24**, 1523; J. S. C. I. 1931, **50**, 390-B; British Plastics, 1931, **3**, #26, 44; Silk J. 1929, **6**, #66, 68; **7**, #81, 50. C. Dreyfus, F. P. 676830; abst. C. A. 1930, **24**, 3119. See E. P. 337746.

2. British Celanese, Ltd., G. Ellis and W. Miller, E. P. 324650; abst. C. A. 1930, **24**, 3910; J. S. C. I. 1930, **49**, 458-B; Chem. Zentr. 1930, I, 3727.

3. British Celanese, Ltd., E. P. 332565, Addn. to E. P. 332263; abst. C. A. 1931, **25**, 421; J. S. C. I. 1930, **49**, 1063-B; Chem. Zentr. 1931, I, 1973. H. Dreyfus, F. P. 687265; abst. C. A. 1931, **25**, 826; Chem. Zentr. 1931, I, 1525. See E. P. 325823, 332263, 332290.

4. British Celanese, Ltd., G. Ellis and W. Miller, E. P. 342333; abst. C. A. 1931, **25**, 5043; J. S. C. I. 1931, **50**, 391-B.

means of reducing metallic salts as stannous and titanous chlorides is much facilitated by the presence of potassium thiocyanate, so that complete discharge of very deep shades as navy blue, brown or black may be obtained; and also basic dyes may be used for securing colored discharges without the possibility of their destruction. Pattern effects are also obtainable by applying locally reducing discharge or resist preparations, including pyrazoline dyes, preferably unsulfonated. As reducing agents may be used formaldehydesulfoxylates, hyposulfite and stannous chloride[1].

By the use of colors in volatilized form[2], colored pattern effects are producible, the color being applied uniformly or through a stencil in a current of steam or other vapor, or by use of a transfer sheet subjected to heat and pressure, with or without a simultaneous embossing operation. Or[3], a molding powder comprising a plasticizable cellulose derivative as methyl-, ethyl- or benzyl-cellulose is placed in contact with a colored fabric composed of at least one substituted cellulose derivative locally colored, and the materials united by heat and pressure. In forming differential fabric[4] of methyl- or ethyl-cellulose, a design of viscose or cellulose solution is imprinted on the fabric, and then dyed by dyes that do or do not color the viscose or the organic cellulose compound.

The production of prints having dark backgrounds and lighter colored designs on fabrics containing organic cellulose derivatives has presented serious problems due to the fact that dyestuffs dyeing a deep blue are not readily

1. British Celanese, Ltd., and G. Ellis, E. P. 346751; abst. C. A. 1932, **26**, 2065.

2. British Celanese, Ltd., E. P. 349683; abst. Textile Mfr. 1931, **57**, #683, 419; Silk J. 1931, **8**, #90, 62.

3. W. Dickie and J. Rooney, U. S. P. 1655677; abst. C. A. 1928, **22**, 1041; J. S. C. I. 1928, **47**, 295-B. E. P. 249946; abst. J. S. C. I. 1926, **45**, 532-B.

4. C. Dreyfus and H. Platt, U. S. P. 1689426; abst. C. A. 1929, **23**, 289; J. S. C. I. 1929, **48**, 514-B; Chem. Zentr. 1929, I, 1619. E. P. 295582; abst. C. A. 1929, **23**, 2305; J. S. C. I. 1930, **49**, 54-B; Silk J. 1928, **5**, #55, 76; Chem. Zentr. 1928, II, 2754. Can. P. 308604.

discharged, but it has been found that if a paste containing an alkali and a metallic oxalate, with or without a vat dyestuff, is locally applied to the fabric and then an aniline black base, after steaming or otherwise oxidizing, lighter colored designs on black or dark backgrounds may be produced[1]. An alkali and a reducing agent induces the same effect[2].

Multicolored effects are also possible[3] by forming azo coloring matters on the fabric containing a diazotizable amino group and developing discharge effects by rendering the amino body, before diazotization and development, incapable of diazotization and development in selected areas only, with the aid of a reduction discharge. This same principle has been carried out by H. Dreyfus in another way[4] in which the fabric is treated by local application of a substance which diminishes and one which accentuates the delustering action of hot or boiling aqueous media or moist steam, and afterwards subjecting the material to the action of moist steam.

Figured and patterned fabrics may be prepared by means of the variation in solvent action upon cellulose ether or organic ester fibers, and fibers as of regenerated cellulose[5], by dissolving, softening or otherwise modifying the cellulose compound using such liquids as chloroform, acetone, pyridine or epichlorhydrin, the compound fabric being printed with a reserve and subsequently treated to dissolve or modify the cellulose compound portion.

In the P. Schlochoff process[6], designs are produced on sheet material having a base of cellulose acetate or other cellulose derivative by applying the material, by a roller, to a glass plate having a design with two or more depths

1. G. Rivat, U. S. P. 1870786.
2. C. Dreyfus and H. Platt, U. S. P. 1870837. Can. P. 295825.
3. G. Ellis and W. Miller, Can. P. 316194. Belg. P. 362989.
4. H. Dreyfus and G. Ellis, Can. P. 281352; abst. C. A. 1928, **22**, 3052. Belg. P. 357298. R. Van Buggenhoudt and R. Homeyer, Belg. P. 357710.
5. G. Heberlein, U. S. P. 1667892; abst. C. A. 1928, **22**, 2280. E. P. 237909; abst. J. S. C. I. 1926, **45**, 485-B.
6. E. P. 359072; abst. C. A. 1932, **26**, 4186.

of engraving, while a solvent of the material is interposed between the sheet under treatment and the plate. The application of coloring material produces a two-tone effect. In order to overcome one of the disadvantages of knitted goods, that which causes a kind of conversion into single filaments with consequent unravelling when the fabric is injured, R. Sallmann[1] claims that these "ladders" will not form if the goods are submitted to a swelling action in the knitted state, using for this purpose such reagents as sulfuric, hydrochloric, nitric or phosphoric acids, zinc chloride solution, or copper-ammonia solution. After the swelling treatment, the knitted goods are washed under slight tension and dried.

According to A. Fischesser[2], mottled effects are produced by dyeing the filaments or textile with a dye that is decomposed by chlorates, then printing it with a composition containing a chlorate and a dye that is stable thereto. In the preparation of strips of cellulose derivatives carrying monochromatic or multicolored figuring[3], the figuring is applied to a supporting surface by printing or pigment spraying, and after being dried, the surface is covered with a cellulose acetate solution by pouring or spraying on to the moving surface. When the film is stripped from the support it carries the figuring with it. The cellulose ethers are also claimed as suitable in the above process.

The I. G. Farbenindustrie[4] produce designs on surfaces composed of cellulose derivatives by incorporating in the surface, products capable of changing under the influence of light, and the physical or chemical properties of the cellulose ethers or esters, afterwards exposing the layers to light under a negative and rendering the image visible by an appropriate treatment. Ethylcellulose may

1. E. P. 309153; abst. C. A. 1930, **24**, 511; Chem. Zentr. 1929, II, 1103. See E. P. 2718, 1892; 224077.
2. I. G. Farbenindustrie, A.-G., E. P. 288592; abst. C. A. 1929, **23**, 703; J. S. C. I. 1929, **48**, 203-B.
3. *Ibid.* E. P. 288592; abst. C. A. 1929, **23**, 703.
4. *Ibid.* F. P. 689007; abst. C. A. 1931, **25**, 887; Chem. Zentr. 1930, II, 3891.

be dissolved in acetone and a solution of sodium bichromate in methyl alcohol added, the mixture being applied in a thin layer on a sheet of glass, dried, exposed to light under a negative and developed by acetone in which the unexposed parts remain soluble, the image remaining being colored by appropriate dye solutions. The cellulose layer may be applied to a textile backing as well.

Fabrics made of or containing organic cellulose derivatives may be colored uniformly or locally by spraying with a solution of one or more coloring matters in solution in a volatile solvent as (for the cellulose ethers) benzene, toluene, alcohol, trichlorethylene or carbon tetrachloride. A swelling agent for the cellulose derivatives as acetone, tetrachlorethane or chloroform may be incorporated in the mixture[1]. To obviate the tendency of a fabric comprising yarns of organic cellulose derivatives to develop faults by treating them with shrinking agents[2], C. Dreyfus and H. Platt treat the fabrics with nitric acid of 10-60° Tw., at temperatures up to 60° for 1-10 min., the lower the acid concentration the higher the temperature which may be used with safety, and the lower the acid concentration the longer the time of treatment.

B. Gmelin[3] has discussed the current technic in printing acetate silk alone or in mixtures.

1. British Celanese, Ltd., and G. Ellis, E. P. 314208; abst. C. A. 1930, **24**, 1228; J. S. C. I. 1929, **48**, 716-B; Chem. Zentr. 1930, I, 133; Silk J. 1929, **6**, #65, 80.

2. U. S. P. 1883348. F. P. 718725. Can. P. 324628. H. Dreyfus, W. Dickie and R. Moncrieff, Can. P. 316203. H. Dreyfus, Belg. P. 362542.

3. Melliand's Textilber. 1928, **9**, 225. He shows that basic dyes can be applied by using antimony-tannin mordant or Celloxan, and that several acid dyes made up with Glyezin A or Fibrit D will resist cold washing. Most mordant dyes are suited only to cotton-acetate mixtures, but certain chrome mordant acid colors as Alizarin Yellow GG, may be fixed on acetate filaments alone as in cotton printing. Glyezin A and butyl alcohol are desirable additions to the gum thickener. The vat dyes, by careful working, can be applied in the usual manner without destroying the muster of the filaments, while the Indigosols may be applied as to cotton, but a longer development at higher temperatures is desirable. When prepared with nitrite and ammonia, the Indigosols may be developed after steaming in dilute

Ornamental Effects on Textiles. In producing differential ornamentation effects on fabrics, the British Celanese, Ltd.[1], weave the fabric from yarns of organic derivatives of cellulose having different degrees of resistance to delustring, as a mixture of cellulose ether filaments and acetylcellulose fibers, so that after treatment with delustring agents such as wet steam or hot soap solutions, parts of the fabric will appear more lustrous than others. Matt effects are produced on fabrics made of or containing cellulose ethers or organic esters[2] by applying to them an effect composition containing a water-insoluble thickener, an effect material and a solvent for the thickening agents which is a non-solvent for the cellulose derivative contained in the fabric.

Selected portions of the back of a pile fabric, the pile of which comprises filaments of cellulose ethers or acetylcellulose with a ground of other materials[3], are treated with a substance which will soften or weaken the cellulose derivative pile filaments, the loosed pile being removed by brushing or suction. Seersucker (crinkled or puckered) fabric consisting of cellulose ether or ester silk[4] is produced by printing or spraying woven or knitted materials with a nitric acid solution (sp. gr. 1.05-1.30), allowing it to react for 1-10 min., and then washing. Shrinkage of the treated parts induces puckering of the non-treated portions of the fabric[5]. Fabrics in which the warp or weft

sulfuric acid containing urea. The Celliton and Celliton Fast colors are prepared with Glyezin A, ethyl acetoacetate or butyl alcohol, desirable additions for certain dyes being calcium thiocyanate, these prints being steamed 15-30 min. without pressure, and soaped at 60°.

1. C. Dreyfus and W. Whitehead, E. P. 310845; abst. C. A. 1930, **24**, 734; Silk J. 1929, **6**, #63, 68.

2. British Celanese, Ltd., E. P. 314396; abst. Silk J. 1929, **6**, #65, 80.

3. British Celanese, Ltd., G. Ellis, H. Olpin and E. Walker, U. S. P. 1783608; abst. C. A. 1931, **25**, 421; J. S. C. I. 1931, **50**, 154-B. E. P. 302208; abst. C. A. 1929, **23**, 4352; J. S. C. I. 1929, **48**, 202-B. Belg. P. 362032.

4. British Celanese, Ltd., E. P. 335138; abst. J. S. C. I. 1930, **49**, 1106-B. See E. P. 274584.

5. C. Parker, W. Kershaw, F. Barrett and Bleachers' Assoc., Ltd., E. P. 274584; abst. J. S. C. I. 1927, **46**, 747-B.

(or both) contain yarns of cellulose ether or ester, and yarns of another fiber as cotton, silk, wool or regenerated cellulose, are treated with a reagent causing shrinkage of one only of the materials, and then dyed with a color having a selected affinity for but one of the fiber classes[1]. The shrinking tendency of woven knitted or netted fabrics of cotton, wool, flax or silk when exposed to aqueous liquids may be diminished or even overcome by incorporating with the fibers from which the fabrics are made[2], fibers of ethyl- or acetyl-cellulose in staples varying from 0.5-8 in. in length, the latter constituting 10-90% of the mixture, and they may be fluffed into voluminous form by mechanical means or by injection of air or other gas.

Where it is desirable that a fabric should, in addition to possessing a good handle, at the same time be smooth, stiff and free from gumminess, materials made of organic cellulose derivatives are treated with gelatin or other albuminoid substance and then with formaldehyde or a substance yielding formaldehyde, which imparts a stiff finish[3]. Methyl-, ethyl- and benzyl-cellulose fabrics are specified as applicable to this treatment. In the manufacture of cellulose ether filaments and the treatment of fibers and textiles made therefrom[4], there is concentrated upon the ether a substance having a solvent or swelling action but initially present in concentration insufficient to exert such action. The degree of action depends upon the solvent avidity. The process may be applied with or without stretching, and the concentration carried to the point of coalescence.

The impermeability of a cellulose ether or acetylcellulose fabric may be increased by subjecting to heat and pressure to flatten the filaments and thereby diminish its

1. British Celanese, Ltd., E. P. 342075; abst. C. A. 1931, **25**, 5043; J. S. C. I. 1931, **50**, 391-B.
2. *Ibid.* E. P. 356681; abst. Silk J. 1932, **8**, #95, 50.
3. British Celanese, Ltd., G. Langdon, A. Flower and S. Fulton, E. P. 358593.
4. H. Dreyfus, E. P. 359971; abst. Silk J. 1932, **8**, #97, 55.

porosity[1]. For finishing and flexilizing cellulose ether or ester materials[2], they are treated with higher fatty acid esters (glycol or glyceryl oleate, palmitate or stearate), and to this treating medium there is added a di- or poly-valent alcohol as diethylene glycol, olive oil and lecithin. The ester can also be added even to the spinning bath. If the above treatment is applied at 75° or over, there is a subduing of the luster. To prevent textiles from becoming fluffy and losing appearance[3], the yarns may be treated with a solution of cellulose acetate or cellulose ether to impart a permanent finish and cause the noil to lay down permanently. In order to reduce the tendency of a textile to shrink when treated with aqueous fluids[4], the textile is prepared from fibers that tend to shrink, and then relatively short lengths of a cellulose ether are interwoven. In ornamenting fabrics by producing patterns on them by stamping prepared sheets laid on the surface[5], the prepared sheet comprises two layers of pliable material, the lower layer of which softens when heated, and the upper layer of which does not become sticky when warmed, so that the fabric may be ironed. The lower layer may comprise rubber, higher aliphatic cellulose esters (cellulose oleate, stearate, palmitate or laurate), or resinous substances of higher melting point. Fillers or dyes may be added, and a sheet of cellulose acetate used as a carrier and subseqently removed.

In the production of water-resisting coloring on pellicles of cellulose derivatives[6], a solution of cellulose ether containing coloring matter is locally applied to the pellicle

1. T. Woodman and W. Dickie, U. S. P. 1716255; abst. C. A. 1929, **23**, 3818.
2. C. Dreyfus, F. P. 715183; abst. Chem. Zentr. 1932, I, 2256. H. Dreyfus, F. P. 719703; abst. C. A. 1932, **26**, 3936. C. Dreyfus, Belg. P. 363405, Addn. to Belg. P. 362600.
3. *Ibid.* U. S. P. 1829983. F. P. 635028; abst. C. A. 1928, **22**, 3997. Can. P. 280645; abst. C. A. 1928, **22**, 3051. Can. P. 315773. Belg. P. 351906.
4. *Ibid.* Can. P. 318186.
5. I. G. Farbenindustrie, A.-G., E. P. 311741; abst. C. A. 1930, **24**, 975.
6. *Ibid.* E. P. 284999; abst. C. A. 1928, **22**, 4815; J. S. C. I. 1929, **48**, 637-B; Chem. Zentr. 1928, I, 2874.

of cellulose derivative, which latter may consist of either a cellulose ether or ester or regenerated cellulose.

Embossing. According to the R. Felgate and British Celanese, Ltd., invention[1], effect or other materials are locally applied to textile fabrics composed of or containing cellulose ethers or esters, by embossing the fabric in the required design, and applying the effect material by means of a roller or other device adapted to contact with the embossed portions only of the fabric. Preferably, the embossing operation is continous with the application of the effect materials. If the fabric is composed of a cellulose ester, the effect may be produced by a saponification treatment, as by a paste applied to the embossed or raised portions, the embossing and saponifying effect being carried out in one operation. The fabric may be passed around or between an embossing roller, and then directly passed into contact with a roller coated with or supplied with a paste containing a strong alkali. The embossing roller should be covered with a gum to impart sufficient rigidity to the fabric to enable a fine adjustment of the roller carrying the saponifying paste to be made.

In another embossing process[2], fabrics formed at least in part of cellulose acetate are impregnated with a solvent as ethyl acetate or ethyl lactate, lactic or acetic acids, or ethyleneglycol monoethyl ether and then embossed, this process involving the softening of a plastic cellulose derivative including the cellulose ethers with a swelling agent to the point of swelling but not direct solvency, so the surface is impressionable but not sufficiently dissolved as to be tacky. If cellulose acetate fabric is to be embossed, after dissipation of the solvent, the fabric is subjected to localized heat treatment to regenerate the luster in selected

1. E. P. 323210; abst. C. A. 1930, **24**, 3119; Silk J. 1930, **6**, #70, 64. See C. Dreyfus, E. P. 254354. Can. P. 324227.

2. Bleachers Assoc., Ltd., W. Kershaw, F. Barrett and R. Gaunt, E. P. 311306, Addn. to E. P. 303286; abst. C. A. 1930, **24**, 975; J. S. C. I. 1929, **48**, 640-B; Silk J. 1929, **6**, #64, 64.

areas. With cellulose ether fabrics, this operation is unnecessary.

In the production of embossed knitted fabrics containing methyl- or ethyl-cellulose[1], especially permanent circular knitted fabrics as stockings, the fabric is first dampened with a swelling, softening or plasticizing agent such as acetone, methyl acetate, triacetin, *p*-toluenesulfonamide or diethyl phthalate, and then, while still in the double thickness, subjected to an embossing operation. Embossed designs on cellulose ether fabrics may be made of such permanent character that waterproofing compositions may be applied thereto without materially affecting the embossed design, thus enabling the production of a permanently embossed waterproof fabric[2], by applying a rubber solution, which is sprayed on the back of the material.

Embossed effects which are not changed by ordinary laundering operations[3], and cause no substantial weakening of the fabric, are produced on fabrics composed of or containing thermoplastic cellulose derivatives by impregnating the fabric with a volatile liquid which causes the cellulose derivative to swell but not to dissolve, and exposing the treated fabric to a heat of 110-120° supplemented by pressure. Suitable liquids are water, or aqueous solutions of ammonium thiocyanate, alcohol, acetone, cyclohexanone or ethyl lactate in conjunction with organic volatile solvents which have no action on the cellulose derivative, such as benzine, plasticizing agents and lubricants being added if desired. The C. Dreyfus process is essentially the same[4].

Fabrics of organic cellulose derivatives may be simultaneously embossed and printed by first wetting the fabric with a liquid exerting a softening effect and at least par-

1. C. Dreyfus, E. P. 291445; abst. C. A. 1929, **23**, 1289; J. S. C. I. 1929, **48**, 848-B; Silk J. 1928, **5**, #51, 76. See E. P. 254354, 273406.

2. C. Dreyfus and W. Blume, E. P. 296451; abst. C. A. 1929, **23**, 2582; J. S. C. I. 1930, **49**, 370-B; Silk J. 1928, **5**, #55, 78; Chem. Zentr. 1929, I, 169.

3. British Celanese, Ltd., W. Dickie and H. Halkyard, E. P. 273406; abst. C. A. 1928, **22**, 2068; J. S. C. I. 1927, **46**, 747-B.

4. Can. P. 308623.

tially dissolving the dyestuff to be used[1], and then contacting the fabric with a transfer sheet containing a dyestuff dispersed in a wax by means of an embossing device.

Creasing. The scouring, dyeing and other liquid treatments of textile fabrics of cellulose ethers of organic cellulose esters is commonly accomplished on a machine having a winch mounted over a vat containing the liquid[2], the material bunched together in "rope" form being continuously or intermittently drawn through the solution. Much of the creasing that takes place unavoidably in these operations, and which leads to the formation of permanent defects in the goods, may be obviated if the material is allowed first to absorb the maximum content of water before being allowed to attain a creased condition, such as takes place when the fabric is allowed to get into the rope form. Unlike viscose rayon, wherein the regenerated cellulose almost immediately becomes saturated with water, the cellulose ethers and organic esters have a much diminished water absorptive capacity, explainable by the fact that the OH groups in the cellulose are largely etherified or esterified, experience having shown that the presence of hydroxyl groups in an organic substance usually imparts water-absorbing properties, and as these groups are replaced by acyl or ether radicals, so does the water-absorbing power correspondingly decrease. The application of wetting-out agents as saponin, triethanolamine and similar bodies overcomes this tendency to creasing, which may be done commercially by forcing a wetting-out liquid outwardly through the fabric, or sucking a liquid inwardly through it. Mere steeping in water for several hours is usually not sufficient.

A process for permanently pleating fabrics containing thermoplastic cellulose derivatives as the cellulose ethers[3]

1. C. Dreyfus, W. Whitehead and H. Platt, U. S. P. 1825342; abst. C. A. 1932, **26**, 319.

2. British Celanese, Ltd., and G. Ellis, E. P. 338190; abst. C. A. 1931, **25**, 2305; J. S. C. I. 1931, **50**, 244-B. Can. P. 321954.

3. C. Dreyfus, U. S. P. 1793915; abst. J. S. C. I. 1931, **50**, 969-B. Can. P. 302432.

comprises treating the fabric with a 25% aqueous solution of acetone or other suitable solvent or solvent combination, and then subjecting the fabric to the desired pleating operation while the material is in a plastic or semi-plastic condition. The excess of liquid is removed before pleating.

To form a secure edge in woven fabrics[1], the fabric threads are softened during weaving by applying liquid to the threads of the fabric at the edge during weaving in a shuttleless loom, so as to cause the warp and weft threads to coalesce. Heat and pressure may be applied to the edge to increase adhesion.

Weaving. In the preparation of pile fabrics containing both natural silk and organic derivatives of cellulose as cellulose ethers or acetylcellulose[2], the practice is to weave the silk yarn while it still has the natural gum therein in order that the silk may better withstand the drastic strains incidental to the operations to which it is subjected. In order to partially or wholly remove the natural silk gum and allow the silk to exhibit its characteristic properties, the fabrics are then usually subjected to a "boiling off" step with a soap solution. However, in the case of mixed fabrics containing both real and artificial silk filaments, the yarns of organic cellulose derivatives, especially if they happen to be acetylcellulose, lose some of their luster or sheen, even if the boil-off takes place as low as 80°.

However, with pile fabrics containing both natural and artificial silk, especially if the natural silk constitutes a part or the whole of the backweft or of the pile or both, the silk may be woven in the degummed state, it having been found that silk, after degumming, resists well the strains to which pile threads or backweft threads are ordinarily subjected in the weaving of pile fabrics.

1. W. Dickie and F. Hale, Can. P. 324417. With cellulose acetate fabrics, according to H. Platt (U. S. P. 1802956. E. P. 339429), creasing marks on cellulose acetate goods may be avoided if the fabric to be dyed is first subjected to a surface saponification and then dyed on a winch in the usual manner.

2. British Celanese, Ltd., E. P. 344410.

If the natural silk is degummed, it is preferable to size it before weaving in order to impart additional strength, and after weaving, knitting or other textile operation, the size is removed[1]. Sizes are used which may be easily removed with hot water. The size may be applied to the silk in the hank form, or to the yarn during winding from package to package. A warp knitting machine for weaving artificial filaments has been recently patented[2].

Sealing Edges of Thermoplastic Fabrics. In the formation of stockings and other knitted fabrics containing cellulose ethers or esters[3], they are cut or stamped with a hot tool which serves to fuse or melt the threads together and prevent "laddering." In producing webs or ribbons from a wider fabric (see also Topic *Bristles*) composed wholly or substantially so of thermoplastic cellulose derivatives as the cellulose ethers or esters[4], the edges are sealed against fraying or ravelling by fusing the edges at a temperature just above the melting point of the cellulose compound, and then allowing them to solidify. If the fabric is union, e.g., contains other filaments as cotton, wool or silk, the severing may be accomplished by a hot knife so as to combine a severing and a fusing surface. In ribbon manufacture, the material as ethylcellulose after cutting into strips of the desired width is first treated along the line to be severed with a solvent to soften the same, and then a hot edge prepared, whereby the cut edge is doubly fused by a combination of heat and solvent action[5]. The cutting may also be accomplished by the fusing action of a flame impinging on the goods to be severed[6].

1. British Celanese, Ltd., E. P. 339896; abst. C. A. 1931, **25**, 2861. Silk J. 1931, **7**, #83, 52.
2. British Celanese, Ltd., S. Welch, A. Guyler, J. Ashby and W. Boaler, E. P. 357141; abst. Silk J. 1932, **8**, #95, 50.
3. C. Dreyfus, E. P. 281271; abst. C. A. 1928, **22**, 3537.
4. British Celanese, Ltd., E. P. 293858; abst. Silk J. 1928, **5**, #54, 88; Chem. Zentr. 1928, II, 2087. C. Dreyfus, Can. P. 308248. H. Dreyfus, Can. P. 305537.
5. *Ibid.* E. P. 297712; abst. C. A. 1929, **23**, 2838; J. S. C. I. 1929, **48**, 242-B; Chem. Zentr. 1929, I, 818.
6. *Ibid.* E. P. 298207, Addn. to E. P. 293858; abst. C. A. 1929, **23**, 2838; J. S. C. I. 1929, **48**, 254-B. See E. P. 297712.

If the perforations are button holes or holes for producing lace or embroidery[1], either hot or cold dies, flat or in the form of rolls, may be used, the pattern being so heavily imprinted as to cut through the thermoplastic cloth. The heat, if heat be used, must be very carefully regulated as to its maximum, or the pattern will adhere to the mold or engraved roller or plate. Use of solvent, of course, enables the actual severing to be made at substantially lower temperatures than if no solvent be employed[2]. In the cutting of woven, knitted or other fabrics in dividing, parting, trimming or perforating operations[3], the fabric is first treated with a thermoplastic material which materially lowers the softening point of the cellulose compound, effecting at least a partial scission of the fabric by means of a heated cutting tool.

In the preparation of plasticizing selvages in looms[4], one or both edges of a fabric composed of cellulose ether or ester is woven in a shuttleless loom and treated with a solvent or softener, which softens the warp and/or weft threads at the edge treated, and renders them sticky or tacky so that they adhere to contacting threads in the fabric edge. Then the threads are softened by heat, adherence being assisted by pressure. The heat may be applied continuously by passing the fabric edge between rotating rollers, one or both of which may be heated. Alternatively, a solvent may be applied by a pad communicating with a container by means of a wick passing through a tube, a hammer on a cam-controlled bell-crank lever moving the fabric into contact with the pad at intervals.

An ornamental fabric has been described[5] composed of or containing a multiplicity of holes of equal or varying

1. British Celanese, Ltd., E. P. 299042; abst. J. S. C. I. 1929, **48**, 242-B; Silk J. 1929, **5**, #57, 72.
2. British Celanese, Ltd., and W. Dickie, E. P. 305257; abst. J. S. C. I. 1929, **48**, 279-B; Silk J. 1929, **5**, #60, 66; Chem. Zentr. 1929, II, 512. See E. P. 299042.
3. W. Dickie, U. S. P. 1871046.
4. British Celanese, Ltd., E. P. 343436.
5. C. Dreyfus, Can. P. 308436.

diameter, the edges of which are partially liquefied and then sealed by means of contacting with a hot surface, thus obviating raveling without sewing. The "sticking" point of a fabric is increased and its safe-ironing temperature raised[1] by treating the fabric with a solution of 50 gms. basic aluminum acetate per liter and 50-100 cc. acetic acid (strength?) per liter, for 45 min. at 40°.

W. Stelkens and C. Lietke[2] repair knit or woven fabrics with patches of cellulose ether or ester fabric by laying the fabric to be repaired on a flat surface, dampening it with a solvent for the thermoplastic cellulose derivatives, applying the patch thereto and amalgamating by simultaneous heat and pressure.

Metallization of Textiles. In the fixation of insoluble metallic compounds or particles, and the production of a permanent metallic effect on fabrics, films, leather and wooden articles[3], a cellulose ether or ester is used which is soluble in chloroform or ethyl acetate, a base of nitrocellulose film is coated with a solution of methyl-, ethyl- or benzyl-cellulose in a solvent which is a non-solvent for the nitrocellulose, such as benzene, toluene or xylene, the base film first having been rubbed with certain metallic salt crystals. The invention is made clear by the following examples:

1. A dark, highly polished surface is first produced by coating a fabric with a cellulose ester solution in acetone, preferably dyed black with nigrosine (spirit soluble). The cellulose ester used while soluble in acetone is insoluble in ethyl acetate, as acetylcellulose, and insoluble or but very slightly softened by chloroform. The dark surfaced fabric is given a metallic effect by thoroughly rubbing it with fine crystals of bismuth or antimony oxychlorides, but the metallic effect has the drawback that it is readily removed by rubbing. This may be overcome and the metallization

1. H. Platt and C. Croft, Can. P. 308437; abst. C. A. 1931, **25**, 1686.
2. E. P. 302858; abst. C. A. 1929, **23**, 4353.
3. G. Schneider, U. S. P. 1883412.

rendered perfect and permanent by then applying a coating of cellulose ester or ether which is insoluble in the base coat.

2. Instead of the plain metallic effect producible by operating according to the example above, an iridescent or fluorescent silvery effect may be obtained by applying several very thin coatings of the ester, the solvent being a non-solvent of the base. These numerous thin coatings induce a beautiful iridescence due to the refraction of light. By the use of finely ground metallic bronzes and alloys, either with or without the presence of lakes admixed therewith, shimmering, glittering, gleaming and lustrously versicolor effects are possible.

A decorative and ornamental material has been described[1], in which a cellulosic base has a coating thereon formed of scintillating particles suitably anchored. The M. Mueller[2] composition comprises a cellulose acetate base containing metallic powders in a solution formed from a solvent mixture consisting of a high and a low boiling solvent. The A. Bodmer[3] process for ornamenting fabrics in order to give brocade effects comprises using a fabric woven with yarn in warp and/or weft which is coated with a mixture of a pigment, especially a bronze or other metal powder, and a cellulose ester or ether binding substance, the fabric being afterwards embossed by heat and pressure. Methylcellulose partially or substantially soluble in water should be suitable for this purpose.

Coloring or metallizing particles may be applied to films or textiles by means of a bath treatment of finely divided graphite, or graphite and latex[4]. The Farbenfabriken vorm. F. Bayer & Co., for instance, prepare threads with metallic luster by coating them with organic cellulose

1. A. Allen, Can. P. 325148.
2. Can. P. 264991; abst. C. A. 1927, **21**, 996; Chem. Zentr. 1927, II, 353.
3. U. S. P. 1829849; abst. J. S. C. I. 1932, **51**, 722-B.
4. C. Dreyfus, G. Miles and H. Platt, U. S. P. 1870408. C. Dreyfus and W. Whitehead, Can. P. 316587.

esters containing bronzes or metallic powders[1], with or without the addition of colors or pigments. If wire or ribbon is to be metallized[2], a better adhesion of the coating is to be had by first wrapping the wire with tissue paper or cotton, and then applying the cellulose ester or cellulose ether solution with the solid metallic particles therein.

In the treatment of fabrics containing cellulose ethers or esters to obtain metallic or colored effects by the R. Clavel process[3], and to obtain fabrics resembling old Venetian tapestries of the Renaissance period, a coating or printing is applied to the fabric with a paste containing a thickener, a finely divided metal or pigment and a solvent or swelling agent for the cellulose ether, the powder being fixed on the fabric by rapidly drying the coated material. After drying the fabric may be dyed at 80°, washed and stretched, the object of stretching being to cause fracture of some of the partially or completely dissolved ether threads to give a metallic effect on a white or dyed background.

Ornamental effects may also be produced by applying to the filaments while still in a tacky condition[4], bronze, aluminum, colored luminous and phosphorescent powders, as barium, zinc or calcium sulfides. Dull or matt effects are produced by applying inorganic materials as barium sulfate, titanium or zinc oxides or condensation products of urea or thiourea with benzidine, α-dinaphthylurea, α-dinaphthylthiourea, diacetylbenzidine or dibenzoylbenzidine. In the A. Wagner method[5], gold-bronze, mother-of-pearl or other nacreous or iridescent materials are incorporated, or precipitates of calcium phosphate or barium sulfate.

Hollow Filaments are of a porous nature and a more or less cellular or tubular structure and abnormal volumin-

1. F. P. 408370; abst. J. S. C. I. 1910, **29**, 624.
2. Farbenfabriken vorm. F. Bayer & Co., First Addition to F. P. 408370; abst. J. S. C. I. 1910, **29**, 1299.
3. E. P. 269128. See H. Dreyfus and G. Ellis, Belg. P. 365077.
4. British Celanese, Ltd., and W. Taylor, E. P. 341057.
5. D. R. P. 137255; abst. Jahr. Chem. 1903, **49**, II, 415.

osity, the latter as shown by the cross-sectional area of the filaments, being susceptible of considerable variation. The production of filaments of this character, usually designated as hollow filaments or "alveolar silk" may be accomplished by a very quick, drastic and vigorous elimination of solvent while the filament is still in the plastic state, e.g., usually directly after spinning, but the coherence and hence the strength of filaments so produced may be impaired as the result of the violence with which the solvents are disengaged, or the luster may be diminished or even destroyed at the high spinning temperatures requisite to drive off the solvent with the requisite rapidity—the higher the spinning temperature, the less the luster of the filament produced. Moreover, in consequence of the rapidity with which the solvent is volatilized, the filaments cannot be drawn out to any considerable extent before the solvent has been removed to the point where the plasticity of the filament becomes too low, and therefore it is difficult to obtain hollow filaments of low denier, i.e., under 10-15 deniers. When attempts have been made to produce low deniers it has been found that owing to the rapid removal of the solvent and the consequent weakness of the filaments, breakages are usually so frequent as to render their commercial production unduly expensive.

According to the invention of H. Dreyfus[1] the foregoing effects may be obviated by introducing into the spinning solution one or more plasticizers or high-boiling solvents which are not materially dissipated until the major portion of the low-boiling solvent has been evaporated. The high boiler should boil from 50-100° above the boiling point of the low-boiling solvent for best results. The residual high boiler may afterwards be removed by solvent extraction, especially where plasticizers are used. High boilers suitable for this purpose specified are (assuming the cellulose derivative is dissolved in acetone): diacetone al-

1. E. P. 317097; abst. C. A. 1930, **24**, 1979; J. S. C. I. 1929, **48**, 937-B. F. P. 666898; abst. C. A. 1930, **24**, 1218. F. P. 678400; abst. C. A. 1930, **24**, 3647. Can. P. 292895

cohol, acetyl carbinol, acetylacetone, acetophenone, ethylidene acetone, cyclopentanone, cyclobutanone, di- and triacetin, diethyl phthalate, methyl- or ethyl-benzene(or toluene)sulfonamide, and the mono- and di-alkyl ethers of ethyleneglycol. The boiling points of the so-called low and high solvents should differ at least 35-40° from each other, in which case the lower boiling solvent should comprise about 75% of the solvent mixture[1]. Where methylene chloride or methyl alcohol comprises the low boiler[2], the cellulose ether in solution may be projected into a mineral or vegetable oil as coagulating medium in which one constituent at least of the solvent mixture is insoluble or incompletely so; this liquid is heated above the b. pt. of the insoluble component. With a mixture of acetone and acetic acid, the spinning temperature recommended is 65°[3]; with acetone, acetic acid and ethyl alcohol at 70°; with methyl formate and cyclobutanone at 85°; and with acetone and water at just below 100°. It is recommended[4] to concentrate the supply of heat necessary for solidification of the filaments near the point of extrusion, thereby generating solvent vapors within the filaments and causing hollows to appear in them during solidification.

It is claimed advantageous to so manipulate the liquid portion of the cellulose ether or ester being spun by adding one or more non-solvents of boiling point higher than that of the solvents[5], and to spin into a gaseous medium the temperature of which is lower than the boiling point of the non-solvent. Acetone with benzene or toluene is specified. Hollow artificial fibers are also obtainable by spinning a

1. H. Dreyfus, E. P. 317098. See also E. P. 165519, 182166, 198023, 203092, 209125, 210108, 317097.
2. British Celanese, Ltd., E. P. 341388; abst. C. A. 1931, **25**, 5028; J. S. C. I. 1931, **50**, 342-B; Silk J. 1931, **7**, #84, 53.
3. H. Dreyfus, F. P. 667209; abst. C. A. 1930, **24**, 1217. See F. P. 664064, 664065.
4. H. Dreyfus and R. Roberts, Can. P. 311593. C. Dreyfus and W. Whitehead, Can. P. 316422.
5. I. G. Farbenindustrie, A.-G., E. P. 356327; abst. J. S. C. I. 1931, **50**, 1044-B; Textile Mfr. 1932, **51**, #686, 79. F. P. 697329; abst. C. A. 1931, **25**, 3168.

cellulose ether or ester solution into a cell through which there is rapidly circulated a gas having a temperature substantially above the b. pt. of the solvent[1].

Structures which are hollow or contain gas bubbles or have a tubular texture prepared by using one or more threads or solid film supports which may or may

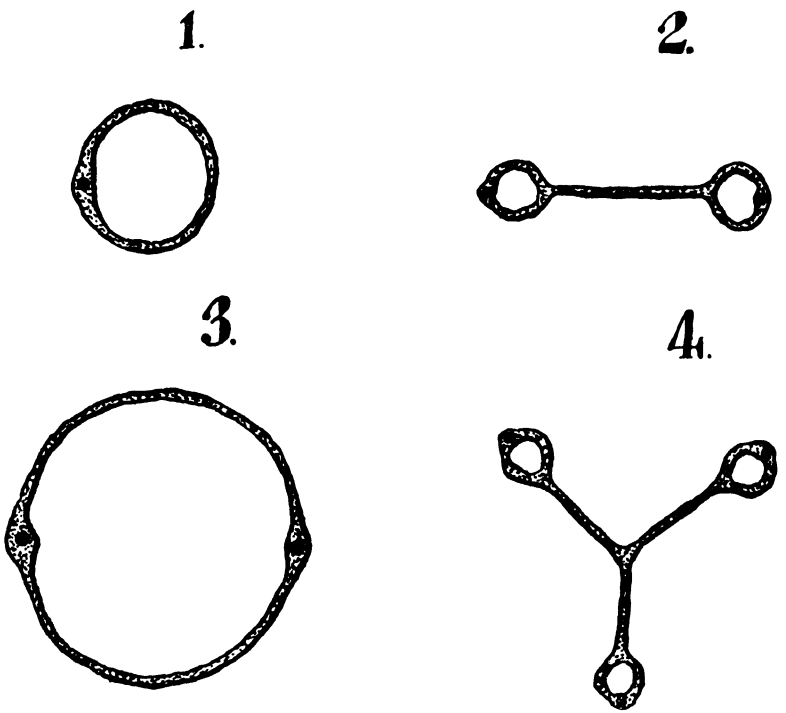


Fig. 10. Rhone-Poulenc Method of Hollow Filament Formation.

not have the same composition as the cellulose derivative, are coated with the solution and the whole heated so as to cause ebullition of the volatile solvent. The supports may be separated or remain imbedded in the manufactured product. The process is shown in Fig. 10, in which *1, 2, 3*

1. Soc. pour la Fabrication de la Soie Rhodiaseta, D. R. P. 496085; abst. C. A. 1930, **24**, 3369; Cellulose, 1930, **1**, #7, 198. See D. R. P. 370471.

and *4* are sections of tubular bodies obtained by the process, *1* representing a traverse section of a tube obtained by causing a natural silk thread or wire in the midst of a cellulose ether solution in a volatile solvent, to which has been added a softening agent or a heavy solvent, and subsequently drying the whole of the thread and its coating. For such manufacture, machines similar to those used in the production of enamelled electric wire may be employed. *2* represents a transverse section of a ribbon with tubular edges obtained by drying a liquid film formed between two thread supports. The products of *1* and *2* are obtainable with a solution of water-insoluble ethylcellulose in acetone and a drying temperature of 110°. With sufficiently active vaporization, tubes could be obtained having a transverse section like that shown in *3*. With an 18% acetone, this result is obtained at a drying temperature of 150°. By using three thread supports, solids are obtainable of a star and tubular section, as shown in *4*[1].

According to Ruth-Aldo Co.[2] hollow silk filaments may be made by dry-spinning a solution of a cellulose compound as a cellulose ether in a mixture of two volatile liquids such as acetone and *iso*propyl ether, the former being the solvent and the latter the non-solvent, and the difference between their boiling points being not greater than 40°. The essence of another process is to distribute liquid or solid particles in the solution to be spun[3] into filaments, the particles being subsequently removed from the finished or partially finished filaments by suitable solvents. Suitable liquid or solid substances are oils as lubricating and paraffin oil; fats, waxes, metallic soaps, naphthenic acids and resins. If the dispersed substance is to be formed in the filaments during the process of manufacture, then a substance is added to the spinning solution that will give rise during

1. Soc. des Usines Chim. Rhone-Poulenc, E. P. 318970; abst. C. A. 1930, **24**, 2603; J. S. C. I. 1931, **50**, 242-B. F. P. 674391; abst. C. A. 1930, **24**, 2601. Swiss P. 142757. See E. P. 302115.
2. F. P. 722719; abst. C. A. 1932, **26**, 4175.
3. Erste Bohmische Kunstseidefabrik, A.-G., E. P. 258582; abst. C. A. 1927, **21**, 3129; J. S. C. I. 1927, **46**, 774-B.

the spinning operation under the chemical action of the precipitating bath, to the desired substance. An inert organic compound boiling below 350° as nitrobenzene may be added to the solution[1], and removed after fixation of the fibers by the application of a vacuum.

O. v. Kohorn and H. Schupp[2] claim a process for the manufacture of hollow filaments by dry spinning solutions of cellulose ethers or esters, there being added to the spinning solution a non-solvent such that there is formed on the periphery of the extruded filaments a firm skin, which is stretched during the escape of the still-fluid core of the enclosed solvent. The characteristics of the finished product depend on the size of the internal cavities of the filaments; these may be varied by adjusting the proportion of added substance and varying the spinning conditions. When large cavities are formed the product is dull and lusterless, while with decrease in cavity size the luster increases. It is said to be possible to obtain a product having a half-matt luster simulating the appearance and feel of wool.

The porous artificial threads of H. Karplus[3] are prepared by incorporating high-boiling petroleum fractions with the spinning solution, which are afterwards removed by subjecting the filaments to heat and vacuum, thereby leaving voids in the places previously occupied by the petroleum hydrocarbons. Bone oil or sodium oleate which do not produce bubble-forming vapors may be added to the spinning solution[4], and are subsequently removed by solvent extraction with a non-solvent for the cellulose ether or ester. A novel method for preparing tubular filaments has

1. Erste Bohmische Kunstseidefabrik, A.-G., D. R. P. 538483, Addn. to D. R. P. 517355; abst. C. A. 1931, **25**, 2290.
2. E. P. 314543; abst. C. A. 1930, **24**, 1509; J. S. C. I. 1931, **50**, 153-B; Silk J. 1929, **6**, #66, 68. F. P. 677204; abst. C. A. 1930, **24**, 3113; Cellulose, 1930, **1**, #8, 228. Belg. P. 361480.
3. U. S. P. 1770310; abst. C. A. 1930, **24**, 4633; J. S. C. I. 1931, **50**, 342-B.
4. H. Karplus, U. S. P. 1707164; abst. C. A. 1929, **23**, 2294.

received patent protection in England[1], solutions of cellulose derivatives as methylcellulose being dry-spun through dies having conical holes tapering to a greater diameter outwardly. Thus, metal thickness of dies 0.4-0.5 mm., holes 0.05-0.07 mm. inside and 0.09-0.11 mm. outside diameter.

W. Snelling makes a preliminary fiber from sugar, sulfur, glue, rosin or casein[2], and this is covered with a thin film of organic cellulose ester carried on a suitable coating wheel. After coagulation of the coating, the preliminary fiber is dissolved out. This results in the formation of a true tubular structure. The process appears unduly expensive. C. Kohler[3] has detailed a heat-insulating material comprising hollow threads of artificial silk or of metal, the interior of the threads being evacuated. The hollow core space is preferably evacuated by spinning the hollow filament in a vacuum chamber from which it is withdrawn through a liquid seal. Each filament may be subdivided into cells by producing transverse walls at predetermined distances, e.g., by providing within the vacuum chamber means operative at regular intervals, to nip or crush the wall of the hollow thread.

The investigations of H. Schupp have shown him that hollow artificial silk produced, by dry-spinning at the usual spinning temperature, a solution of acetylcellulose containing a suitable percentage of non-solvent giving a product (sp. gr. 0.8) having much greater covering power than ordinary cellulose acetate (sp. gr. 1.3), viscose (sp. gr. 1.5) or hollow viscose (sp. gr. 1.37) silk[4]. Although its normal luster is slightly less than that of ordinary acetate silk, the spinning conditions may be adjusted so that it is perfectly white and opaque. This latter matt appearance resists scouring, bleaching and dyeing processes. 100-denier of this material has a covering power in textile form equiva-

1. Cellulose Acetate Silk Co., Ltd., and H. Curtis, E. P. 353041; abst. J. S. C. I. 1931, **50**, 878-B; Textile Mfr. 1931, **57**, 461; Silk J. 1932, **8**, #93, 54.
2. U. S. P. 1713679; abst. J. S. C. I. 1929, **48**, 639-B.
3. E. P. 343632; abst. J. S. C. I. 1931, **50**, 422-B.
4. Kunstseide, 1931, **13**, 424; abst. J. S. C. I. 1932, **51**, 177-B.

lent to 150-denier yarn of ordinary acetate silk, and is much warmer in handle. It has a tensile strength of 1.2-1.3 gms. per denier with a 25-30% loss in strength when wetted. It is indicated for the production of crepe and plush materials.

F. Grove-Palmer[1] has described the properties and application of the hollow yarn "Celta." H. Barthelemy[2] has pointed out that hollow filaments are obtainable from cellulose acetate solutions, and also, it appears, from cellulose ether solutions as well, by mixing with the solution of the cellulose derivatives an organic liquid which is a non-solvent, this liquid being such that it will evaporate rapidly when a hot current of air comes into contact with the filaments just after they are spun, thus leaving the filaments hollow and with outside surfaces that possess a low luster. The dissolving combination recommended is acetone 90, *iso*propyl ether 10, and hot air circulating preferably at 115-150° F.

In the production of filaments of cellulose derivatives containing lumens or hollow spaces therein[3], especially by the dry spinning method, the solution is extruded from the spinnerett orifices into a substantially uniform evaporative atmosphere, and the formed filaments drawn off at a comparatively high speed. This effect is heightened when the spinning solution, as it is extruded from the orifices, is subjected to such evaporative conditions that it first starts to dry or skin on the surface only, and is then submitted to more drastic evaporation so that the interior of the filaments solidifies with the formation of hollow spaces therein. In another published method[4], a slow rate of spinning is employed such as 0.025-0.15 meters per min., the size of the extrusion orifices varying with the denier of the filament

1. Textile Colorist, 1928, **50**, 666; abst. C. A. 1929, **23**, 283.
2. U. S. P. 1876130. Can. P. 318891.
3. British Celanese, Ltd., E. P. 318629; abst. C. A. 1930, **24**, 2294; Rayon Record, 1930, **4**, #2, 99.
4. C. Dreyfus, U. S. P. 1883347. W. Tennant, E. P. 267187; abst. J. S. C. I. 1927, **46**, 361-B. British Celanese, Ltd., E. P. 318632; abst. C. A. 1930, **24**, 2294; Silk J. 1929, **6**, #67, 72. See E. P. 189973.

being produced, and the rate of spinning inversely with the weight of the filaments. After spinning, the filaments are preferably drawn out.

Filaments of the cellular or tubular type are also producible by extruding a solution of cellulose ether or ester into a cell through which passes a current of evaporative medium, the heat concentration being applied close to the extrusion dies, so as to maintain in that region an air temperature greater than that necessary to produce normal solid filaments[1]. In the L. Drut[2] process of producing filaments characterized by containing a series of spaced bubbles of air or inert gas therein, the spinning solution before extrusion is agitated with air to produce an "emulsion" by means of a homogenizing apparatus, and then extruded. Nothing is said by the patentee as to the breaking strength of filaments so produced, which in our judgment would be comparatively low. In the J. Rousset method[3], there is incorporated in the spinning solution a substance which will react chemically with a component in the coagulating bath to produce a series of gas bubbles in the filaments, as a soluble alkali carbonate spun into an acid setting bath.

According to the G. Tocco process[4], films or filaments of organic cellulose derivatives are fed onto an endless band in a sealed chamber where a vacuum is maintainel until the solvent has been substantially expelled, thereby increasing the porosity of the film.

Staple Fiber. In 1912, P. Girard[5] devised a method for the cutting up and spinning of artificial silk waste fibers, the product being known as staple fibers or staple artificial silk, or according to the fineness of the fibers, is termed

1. British Celanese, Ltd., H. Dreyfus and R. Roberts, E. P. 324899; abst. C. A. 1930, **24**, 3901; J. S. C. I. 1930, **49**, 368-B. See J. Lahousse, U. S. P. 1652206; abst. C. A. 1928, **22**, 868. H. Dreyfus, E. P. 324061; abst. C. A. 1930, **24**, 3370. See E. P. 267187.
2. E. P. 143253; abst. C. A. 1920, **14**, 2862. D. R. P. 346830.
3. U. S. P. 1427330.
4. E. P. 365484; abst. J. S. C. I. 1932, **51**, 336-B.
5. F. P. 438131 and Addn. 15399; abst. Kunst. 1912, **2**, 271, 437.

artificial chappe or artificial wool. Whereas artificial silk and rayon consist of substantially endless filaments, staple fiber consists of these filaments usually cut to about the length of long natural cotton fibers (1-1.5 inch) and then spun as such. The production of staple fiber enables in many instances, the profitable utilization of rayon waste, otherwise practically valueless, being usually without twist.

The H. Dreyfus[1] apparatus for the production of staple fiber from continuous lengths of filaments comprises a conduit for the passage of the lengths of filaments, an impeller in the conduit to impel the filaments forward and a movable and adjustable cutting blade, with shaft to the impeller and movable cutting blade. Or the continuous filaments may be led to a common thread guide and traversed from end to end of a roller, swift or similar collecting device provided with longitudinal slot, being cut into substantially equal lengths with a knife[2]. By providing two such rollers, continuity of working may be assured, the rollers being brought into operation alternatively.

C. Dreyfus[3] prepares "spun" yarn containing comparatively short lengths of filaments made of cellulose ethers or esters by incorporating a finely divided insoluble material in the filaments, and then associating the comparatively short filament lengths by a twisting operation. W. Taylor[4] takes a fibrous mass of irregularly disposed filaments which are independent and continuous, and prepares staple lengths therefrom either by breaking or tearing

1. E. P. 322417; abst. J. S. C. I. 1930, **49**, 100-B. Can. P. 299012, 321716.

2. British Celanese, Ltd., and W. Taylor, E. P. 357565; abst. J. S. C. I. 1931, **50**, 1090-B; Textile Mfr. 1932, **58**, #687, 117; Silk J. 1932, **8**, #95, 52. Traveling rayon filaments may be subjected to a fluid blast, stream or jet (E. P. 323221) to produce a tangled mass or submitted to an air blast by means of an ejector device (E. P. 322557). See E. P. 165519, 198023. In another process (E. P. 373406) continuously with their production, the filaments are stretched and immediately cut into staple fiber.

3. Can. P. 323603.

4. U. S. P. 1883424. For mechanical arrangement for cutting up filaments into staple fiber, see Celanese Corporation, E. P. 317025, 317026.

into suitable lengths after the fibrous mass has been teased or combined until the filaments all run in the same direction, or are cut in the usual manner. The I. G. Farbenindustrie method is somewhat similar[1].

Delustered staple fiber may be formed in accordance with the process of F. Williams[2] which comprises cutting the filaments to the length desired and then submitting them to a roughening or abrasive treatment to diminish their luster, the fibers being afterwards associated by a twisting operation. It is claimed[3] that the tendency of cotton, wool, flax, silk and cellulose rayon yarns to shrink during washing may be reduced by incorporating in such yarns cellulose ether or cellulose acetate fibers cut to a staple of 0.5-8 in. A knitted fabric made from yarn consisting of 25% cellulose acetate fibers and 75% cotton shrinks only 4% in area after repeated washing.

Artificial Bristles, Straw, Ribbons and other comparatively large filaments, irrespective as to whether the finished material is of substantially circular or rectangular cross-section, are produced primarily by either extruding the filament or strip of the approximate size desired, and this is usually the case where ribbons are produced or artificial straw, or else to extrude a plurality of smaller filaments and coalesce them into a unitary thread, or by a third method, that of cutting strips from a fabric of a thermoplastic cellulose ether or ester, and preventing the raw edges from raveling by the application thereto of sufficient heat to incipiently melt the material to the edge.

In the physical union of a plurality of artificial silk filaments into a composite whole[4], after extrusion from the

1. E. P. 366546; abst. J. S. C. I. 1932, **51**, 303-B.
2. Can. P. 318146.
3. C. Dreyfus, U. S. P. 1829983; abst. J. S. C. I. 1932, **51**, 722-B.
4. British Celanese, Ltd., and W. Taylor, E. P. 328312; abst. C. A. 1930, **24**, 5497; J. S. C. I. 1930, **49**, 554-B. Can. P. 321116. H. Dreyfus, F. P. 701269; abst. C. A. 1931, **25**, 3833. Can. P. 316196. According to E. P. 349999, continuously with their production, filaments of cellulose ethers or esters while in a sticky condition brought about by incomplete evaporation of solvent, are stretched and caused to merge together into a single filament, which is afterwards treated

spinnerett orifices and while still in the tacky and semi-plastic condition from evaporation of but a portion of the solvent therefrom, they may be united by the agency of pressure alone and then allowed to harden by solvent dissipation, the resulting product being a single filament of flattened cross-section. By applying pressure to the whole length of the filaments a straw-like ribbon results, whereas by applying the pressure intermittently, alternating lengths of flattened and roundish cross-section may be formed. Furthermore, crinkled effects are producible, giving a product having an appearance simulating millinery straw. The degree of flattening will depend upon the pressure exerted and the comparative plasticity of the cellulose derivative. A combination of heat as well as pressure is advisable where the cellulose derivative has incorporated therewith a thermoplasticizer[1].

In another method[2], solutions of cellulose ethers or esters in organic solvents miscible with water are passed through narrow and relatively long extruding orifices, and the ribbons received in coagulating baths composed of water, aqueous solutions of salts, or dilute mineral acids. Before or after drying, the ribbons may be passed through a heating chamber to soften them, or solvents or swelling agents may be added, and the ribbon further attenuated by pressure while in the heated condition[3].

Ribbons may be made from wider fabrics composed of or containing cellulose ethers or esters[4] by cutting the fab-

with a lubricant to remove stickiness. Wool, metal or other threads may also be incorporated in the composite thread. In the method for making straw, bristles and ribbon of British Celanese, Ltd., A. Tidmus, F. Reeson and R. Riley (E. P. 339670), two spinning jets are arranged in series and in proximity to each other on a single supply pipe in such a way that the second jet may be removed or replaced without interfering with the first jet. When the first jet is removed, spinning proceeds through the second jet, which also serves as a pressure retaining member.

1. British Celanese, Ltd., E. P. 354233; abst. C. A. 1932, **26**, 4482. See E. P. 328312.
2. H. Dreyfus, F. P. 695843; abst. C. A. 1931, **25**, 2850.
3. *Ibid.* F. P. 695844; abst. C. A. 1931, **25**, 2862.
4. British Celanese, Ltd., E. P. 293858; abst. J. S. C. I. 1929, **48**, 14-B. Can. P. 300045.

rics into strips and sealing the severed edges against fraying or raveling by fusing, dissolving or softening the edges and then allowing them to solidify and harden. In the case of thermoplastic fabrics such as those made from methyl or ethylcellulose of maximum etherification, the fabric is cut into strips by means of a heated knife adapted to fuse the severed edges. Solvents such as acetone, diacetone alcohol, chloroform or cyclohexanone may be employed for dissolving a portion of the material at the edge of the fabric, coalescence of the cut yarns taking place on evaporation of the solvent.

In the physical mergence, coalescence or union physically of a plurality of filaments of the same or varying cross-section areas into a unitary larger filament, the filaments are brought into intimate contact while there is considerable solvent therein and then caused to blend together[1]. Methyl-, ethyl- or benzyl-cellulose solutions containing thermoplasticizers in addition to the inherent thermoplasticity of the cellulose ether[2] may be fabricated into filament form and then passed between heated rollers in order to fashion ribbons or straw therefrom. Artificial resins which in themselves soften by the application of heat may be incorporated with the cellulose ether before spinning by means of a harmonious solvent or solvent combination, and then treated as indicated in one of the above methods[3]. Such suitable synthetic resins specified are diphenylolpropane-formaldehyde resin, diphenylolpropane-acetone resin, toluenesulfonamide-formaldehyde resin, benzene- or xylene-sulfonamide-formaldehyde resin or phenol-furfural resin.

In order to cause the individual filaments of a bundle

1. British Celanese, Ltd., E. P. 326462; abst. C. A. 1930, **24**, 4931; J. S. C. I. 1930, **49**, 553-B.

2. H. Dreyfus, E. P. 341034; abst. C. A. 1931, **25**, 4720; J. S. C. I. 1931, **50**, 343-B; Silk J. 1931, **7**, #84, 53. F. P. 702209, 702210; abst. C. A. 1931, **25**, 4125. Compare E. P. 248147, 249946, 328312. F. P. 700876, 701269.

3. C. Dreyfus and British Celanese, Ltd., E. P. 342340; abst. C. A. 1931, **25**, 5029; J. S. C. I. 1931, **50**, 388-B; Brit. Plastics, 1931, **3**, #25, 37. Can. P. 324240. Cites E. P. 317456, 318630, 318631, 318643.

to merge into a single strand[1], the associated filaments either before or after the initial adherence, and while they are still in a sticky or tacky condition, are subjected to stretching, thereby producing in general a round cross-section and a comparatively smooth surface. Threads and straws made of or containing cellulose ethers or esters may be treated with a mixture of a solvent for the cellulose derivative and a non-solvent less volatile than the solvent used, so that in the normal evaporative process there is a gradually increasing increment of non-solvent until a point is reached where the cellulose compound gelatinizes, the luster at the same time becoming more subdued[2]. In the formation of heavy filaments as bristles[3], the individual smaller filaments are brought into direct contact immediately upon extrusion, and coalescence assured by spinning into a heated, evaporative atmosphere. In such a case, the cellulose derivative solution should be so concentrated as to be relatively non-flowable and a correspondingly higher pressure used to force the same through the microscopic orifices.

Beautiful effects are producible where the plurality of filaments are united in the presence of a pigment or effect material[4]. An unusually high flexibility in artificial horsehair is possible[5], by leading a number of elementary filaments through a solvent or swelling agent at such speed that the thread is softened at the outer surface only, so that a welding of the filaments takes place through a small thickness of the thread (the peripheral portion), the filaments within the sheath so formed retaining their individuality. The process may be combined with the spinning

1. British Celanese, Ltd., and W. Taylor, E. P. 349999; abst. Textile Mfr. 1931, **57**, #683, 419. H. Dreyfus, F. P. 710135; abst. C. A. 1932, **26**, 1441. C. Dreyfus and W. Whitehead, Can. P. 318759.
2. British Celanese, Ltd., E. P. 364020; abst. Textile Mfr. 1932, **58**, #680, 249.
3. W. Whitehead, Can. P. 306830.
4. *Ibid.* Can. P. 323782. Ital. P. 223260.
5. Soc. pour la Fabrication de la Soie Rhodiaseta, E. P. 352414; abst. Silk J. 1932, **8**, #92, 56.

of the threads themselves, the superficial agglutination being carried out on the threads, which may be twisted or not, after they have been completely freed from solvent.

Liquid films may be formed from solutions or pseudo-solutions by surface tension between two or more solid threads or plates serving as supports, and then coagulated[1]. The supports which may be of silk, wire or the same composition as the ribbon, straw or film, may be removed from the manufactured product or not, as desired. W. Sachs[2] has described a textile material made from ethylcellulose, obtained by cutting a flat structure in small strips, turning these strips into a more or less twisted yarn, claiming the textile material so prepared shows all the good properties of ethylcellulose as flexibility, water-resistant capability, and non-sensitivity towards dampness, being capable of taking up dyes, and therefore indicated for the manufacture of overcoats, raincoats, hats and weavings. The yarns may be made woolly or flocky by admixture with other fibers.

In producing ribbons, films and tapes[3], the pliability is improved by adding 2.5-10% of a high-boiling solvent to the solvent liquid used for moistening the filaments. Coalescence is then effected by application of both heat and pressure. Waterproof properties are imparted by passing the ribbons during or after coalescence between smooth rollers coated with carnauba wax. Or[4], the threads from a group of spinneretts may be united into a ribbon of parallel strands after coagulation by passing through a set of friction rollers.

In the J. Bongrand and L. Lejeune process[5], threads are impregnated and coated with a cellulose ether under pressure so that the elementary fibers are bound together,

1. Soc. des Usines Chim. Rhone-Poulenc, E. P. 318250; abst. Brit. Plastics, 1931, **2**, #21, 433.
2. D. R. P. 342097; abst. Textilber. 1922, **3**, 114.
3. British Celanese, Ltd., E. P. 354233, Addn. to E. P. 328312; abst. J. S. C. I. 1931, **50**, 1044-B.
4. Soie Charentaise, E. P. 341009.
5. E. P. 344415.

and the constituent parts of a twisted or cabled thread are isolated from one another by the cellulose ether. This is effected by placing the threads in contact with a cellulose ether in a volatile solvent or in the form of an aqueous dispersion for a sufficient length of time, penetration being accelerated by vacuum or pressure. C. Dreyfus[1] forms heavy filaments such as artificial bristles or straw, by extruding a concentrated solution of an organic cellulose derivative in a volatile solvent through large orifices into an evaporative atmosphere, the concentration being such that it is relatively non-flowable. With a denier of 20-2000[2], the heavy filaments, while still in the heated metier casing and containing solvent, are supported by passing over or round one or more heated feed devices, which rotate, each with a linear speed greater than the one preceding.

In another variant[3], a number of cellulose derivatives filaments are rendered sticky by treatment with a solvent or softening liquid containing such high-boiling solvents as triacetin or tritolyl phosphate, and are then heated to cause them to adhere together. Or[4], a number of filaments, after passing through a die, are softened either by heat or the application of a solvent or swelling body, and then passed through a further die so that they cohere into a product, the cross-section of which is the same as the die.

The British Celanese, Ltd.,[5] have described goods obtained by uniting fabrics by means of heat and pressure or by use of solvents, with artificial straws made of methyl-, ethyl- or benzyl-cellulose, the product being afterwards embossed and used for making hats.

Pile Fabrics. It has been found that those artificial filaments which are not deleteriously affected by merceri-

1. Can. P. 306830.
2. British Celanese, Ltd., E. P. 318630; abst. J. S. C. I. 1931, **50**, 59-B.
3. British Celanese, Ltd., R. Riley, W. Lowe and W. Taylor, E. P. 366070.
4. British Celanese, Ltd., and W. Taylor, E. P. 371428; abst. J. S. C. I. 1932, **51**, 675-B.
5. E. P. 355860; abst. C. A. 1932, **26**, 3377.

zation as the cellulose ethers, may be made to resemble bro cades by treating them with alkalis in certain areas, such treatment also causing variation of receptivity of color, so that many variations in effects are possible. A fabric woven in a sateen weave on a cotton back is printed with starch paste and dried, and then immersed in 96.5° Tw. sulfuric acid at 55° F. for 10 seconds, washed and dried. The luster of the unprinted portion is more or less subdued and the effect thus obtained is of a woven brocade.

The ornamental fabric of the British Celanese, Ltd.[1] comprises cellulose ether or ester filaments associated with fibers of cotton, silk, wool or regenerated cellulose, either the weft or warp containing one or some of both classes of fibers, being treated with a reagent which, while not appreciably affecting the cellulose ether or ester yarns, causes shrinkage of the other yarn. Thus yarns of cellulose derivatives of low twist may be associated with highly twisted yarns of natural silk, the compound fabric being treated in an aqeous bath, whereupon the highly twisted natural silk yarn shrinks to a large extent, while the other yarns shrink inappreciably. The fabric is then subjected to a wet treatment with soap, washed and dried. A cockled or pebbled appearance results.

In weaving velvets containing both silk and cellulose ether or ester yarns liable to lose luster on treatment with hot liquids, the silk threads are degummed prior to weaving, the cellulose derivative yarns comprising the pile and the silk the back, or conversely. The fabric may be dyed in the usual manner[2]. Such mixed fabrics as velvets having a cellulose acetate pile on a silk or wool back[3], are printed with mineral acids or their acid salts (sulfuric acid, sodium

1. E. P. 344155; abst. C. A. 1932, **26**, 319; J. S. C. I. 1931 **50**, 486-B; Chem. Zentr. 1931, II, 3176. See E. P. 342075.

2. C. Dreyfus, U. S. P. 1818540; abst. C. A. 1931, **25**, 5580 British Celanese, Ltd., E. P. 344410; abst. Silk J. 1931, **8**, #86, 53 Can. P. 312945.

3. *Ibid.* E. P. 302592; abst. C. A. 1929, **23**, 4352; abst. J. S C. I. 1929, **48**, 976-B; Silk J. 1929, **5**, #59, 72. H. Dreyfus, Can. P 303274.

acid sulfate), the pile being locally destroyed and removable by subsequent neutralization. A softener, solvent or swelling agent for the cellulose ester may advantageously be added to the printing paste.

The tendency to shrink in textile materials as cotton, wool or silk[1], is lessened by weaving with them filaments or fibers of cellulose ether or cellulose ester to tend to counteract this otherwise normal shrinkage tendency. C. Dreyfus[2] plaits a fabric containing methyl- or ethylcellulose yarns by subjecting the fabric to a suitable plaiting operation in the presence of a softening agent for the cellulose ether, whereby the plaiting becomes permanent upon the application of heat and pressure, and produces pile fabric either by the use of yarns of organic cellulose derivatives of increased opacity[3], or else incorporation of an opacity-inducing material in the yarns as such. Or[4], the pile fabric may be prepared by softening and shaping at least a portion of the yarns of organic cellulose derivatives and then permitting them to harden by solvent evaporation, or regenerated cellulose may be locally preciptated thereon, the fabric, after treatment with the solution, being dried and the alkali neutralized and washed away[5].

G. Holden[6] has described several processes for obtaining color effects on acetate pile fabrics and for preparing art velveteen.

Milanese Cloth. The milanese warp loom has been known for some time in the industry in connection with the making of fabric gloves[7], usually conceded as a monopoly of Saxony, where the fabrics as well as the gloves have been made for some time. An outstanding feature in this

1. C. Dreyfus, U. S. P. 1829983; abst. C. A. 1932, **26**, 856.
2. U. S. P. 1793915; abst. C. A. 1931, **25**, 2306. See E. P. 313992.
3. C. Dreyfus, U. S. P. 1873862. Can. P. 324242.
4. *Ibid.* U. S. P. 1873863. Can. P. 324452.
5. J. and J. M. Worrall, Ltd., H. Livsey and G. Holden, E. P. 365132; abst. Textile Mfr. 1932, **58**, #691, 287.
6. J. Soc. Dyers & Col. 1931, **47**, 222; Rayon Record, 1931, **5**, 564.
7. W. Davis, Silk J., June 1927, p. 56.

fabric is that the finish is such as to impart a very agreeable handle, the fabric being sueded and processed with a chemical finish of desirable softness. With the advent of the use of yarns of thermoplastic cellulose derivatives in this art, milanese warp looms have been applied to the manufacture of under-garment fabrics which by their attractiveness have captured the fancy of a wide public. Although milanese is generally classified as a knitted fabric, it really stands by itself as a textile medium, having a warp, the threads of which are knitted on each other in the form of loops. Its threads are migratory, and no end in the warp occupies the same place for more than one course of loops. It is also virtually a double cloth texture, for there are a series of stitches on the face which migrate course by course towards the right, and this is underlaid by a series of threads which migrate similarly towards the left. These two sets intersect intimately with each other, and the resulting cloth is virtually ladder proof. Although the stitches unravel locally, the entire texture is not disintegrated as is the case with the plain knitted fabric.

There is an enormous advantage of the knitted stitch itself in an intermediate garment, for it has been found to possess appreciable heat-retaining properties compared with the weight, especially when prepared from the organic cellulose esters or cellulose ethers. The knitted texture is interspaced, and these inter-loops function as so many tiny air containers which, when covered by an outer garment, present a complete unit in resisting the radiation of heat from the body. That is, these packets or pockets of air when so enveloped serve as the equivalent of material in so far as conservation of body heat is concerned, and the cost of this added resistance to loss of body heat is practically nil.

Preparation of Lace. The J. Harold process for lace making utilizes primary nitrocellulose[1], the method being to provide a ground or foundation of cotton, which is solu-

1. U. S. P. 1835866; abst. C. A. 1932, **26**, 1136.

bilized by nitration with a bath of nitric and sulfuric acid. The lace is then attached to this backing during its formation, and when the operation is completed the nitrocellulose backing is dissolved away by means of an appropriate solvent. Cloth may be given the appearance of lace, gauze or other perforated effects by submitting cloth composed of filaments derived from cellulose acetate or the cellulose ethers[1], and threads composed of vegetable fibers as cotton or linen, to a carbonization treatment wholly or in part. The cloth may also contain animal fiber as natural silk or wool, and the designs applied by means of different mixtures. See also Topic, *Carbonizing.*

Elastic Fabric. The C. Dreyfus elastic fabric that does not readily soil and is easy to clean is prepared from cellulose ether or organic ester yarns[2], on account of its relative imperviousness to dirt, grease, moisture and perspiration, and also from the fact that when it has become soiled a mild soap cleansing is sufficient, and does not impair the desirable properties of the imbedded rubber threads. The elastic fabric is manufactured in the usual way for elastics for garters, belts, corsets, girdles, brassieres, trouser braces and elastic bands for bloomers and trousers, and being insoluble in water and not hydrolyzed thereby, it is especially resistant to repeated perspiration. The F. Brigman elastic thread does not use thermoplastic cellulose derivatives[3].

Hosiery. Taking advantage of the fact that the cellulose ethers and esters have substantially definite melting points, and when in the molten or semi-molten condition are adhesives *per se,* their agglutinating properties being enhanced by plasticizers previously incorporated therewith, C. Dreyfus[4] has devised a method for the fabrication of stockings by cutting a blank from a piece of fabric contain-

1. C. Dreyfus, F. P. 36860, Addn. to F. P. 636608; abst. C. A. 1931, **25**, 1103.
2. U. S. P. 1869958. See E. P. 306050.
3. U. S. P. 1868690.
4. Can. P. 305048. U. S. P. 1802634. British Celanese, Ltd., E. P. 281271.

ing the cellulose derivative, simultaneously melting the edges of the cut portion of the fabric as it is being cut, and subsequently joining the longitudinal edges of the blank by pressure, aided by sewing.

A knitted hose has been described containing, in at least a part of its length, highly twisted yarns of continuous textile filaments of cellulose derivatives, having about 10 to 30 turns to the inch[1]. To enable the length of loop to be changed gradually[2], particularly in silk and artificial silk hose, reduction gearing is provided between the cam for adjusting the relative height of the knitting-cams and the needles, and the driving means. In the process of D. Young[3], lustrous yarn, the individual component threads of which have been given a twist in one direction while the final yarn is given a twist in the opposite, is employed in the manufacture of seamless hosiery, the first twist comprising 32-48 turns per inch, while the final twist has 28-44.

Electrical Discharge. In the operations of working up fibers having a low degree of hygroscopicity, as the artificial threads from cellulose ethers and esters, the more or less intense electrical charge produced by friction is often very troublesome. This charge is the more disagreeable the lower the atmospheric humidity in the workroom, consequently in attempts to overcome this drawback humidifiers have been installed.

A simple method of avoiding the electric charge consists in treating the threads with a solution of soap or of a water-soluble oil, and the *modus operandi* has been described in reference to the handling of acetate silk prepared by the wet-spinning method. Where artificial threads prepared by a dry-spinning method are concerned,

1. W. Cameron and F. Williams, Can. P. 315771. In W. Cameron (Can. P. 325063) process for producing circular knit hose the foot portion of which has a configuration approaching that of the wearer's foot, this is accomplished by cutting away a part of the foot and sewing the cut edges, leaving the ankle portion intact.
2. W. Holmes, L. Leedham and Wildt & Co., Ltd., E. P. 357619.
3. E. P. 357360; Grant of Patent opposed. Abst. Silk J. and Rayon World, 1932, **8**, #95, 52.

one tends to avoid treatment with aqueous solutions and emulsions and the subsequent necessary drying method, preferring to use anhydrous fatty oil mixtures with fat acids[1]. Whereas when operating with fibers which have been impregnated with a soap solution or an oil emulsion, on account of the presence of electrolytes (soap, Turkey red oil and other emulsifying agents) frictional electricity which may have been generated is quickly dissipated, but in the case of mixtures free from water and containing no Turkey red oil, the position is much less favorable. Although the electric charge is considerably reduced in comparison with the unoiled threads, and the mutual repulsion of the single threads or bundles of threads which otherwise becomes apparent is less noticeable on account of the agglutinating action of the oil, the further treatment of the thread, particularly in warp knitting, involves considerable difficulties.

The discharging properties of the oils in certain cases can be somewhat enhanced by the addition of oleic acid. Metallic soaps are more active than the free acids, but their solubility in oils is small, so that there is danger of separation, causing smearing of the oiling devices with consequent damage to the threads.

According to the Aceta Ges.[2], a very good antistatic effect is produced by adding appropriate quantities of oil-soluble organic bases or oil-soluble soaps of the same, to the mixture of oils and/or fats. For this purpose, there may be used cyclohexylamine, dibutylamine, piperidine, mono-, di- and tri-ethanolamine, "Sapamines," or aminoethylamine oleate. It is preferable to use the bases in combination with fat-acids of low melting point, particularly oleic acid or

1. Knoll & Co., D. R. P. 286173; abst. J. S. C. I. 1915, **34**, 1138; Chem. Zentr. 1915, **86**, II, 450; Chem. Ztg. Rep. 1915, **39**, 828; Kunst. 1915, **5**, 188; Wag. Jahr. 1915, **61**, II, 254; Zts. ang. Chem. 1915, **28**, II, 439.

2. E. P. 346912; abst. J. S. C. I. 1931, **50**, 626-B. F. P. 689984; abst. C. A. 1931, **25**, 1103.

technical olein. The process is stated to be applicable to filaments of the cellulose ethers.

It has been suggested in the preparing or spinning of yarns from artificial fibers[1], to cover with cellulose acetate or a cellulose ether the parts of the machine over or near which the materials pass while in a substantially untwisted state, to prevent attraction towards those parts of the fibers which have come electrified during the preparation or spinning operation.

The I. G. Farbenindustrie have given particulars for the manufacture of masses and structures from partially or wholly water-soluble alkylcelluloses[2] especially methylcelluloses[3], without the use of organic solvents by allowing the methylcellulose to dry first out of an aqueous solution in the form of foils or sheets, which are then pressed together into layers by means of the interposition of a solution of a water-soluble alkylcellulose as an adhesive between the individual sheets. In this manner artificial materials are obtained which are either transparent, opaque or colored depending upon the fillers or addition agents with which they are compounded, and may be used for the fabrication of celluloid-like masses or objects.

The operation is indicated preferably in the following two examples:

1. Methylcellulose foils are painted with a thin layer of a 20-50% swelling solution of methylcellulose in water by means of a coating apparatus. The pre-treated sheets are then laid on each other according to the thickness desired in the final product, and at 40-60° are subjected to a pressure gradually increasing to 100-150 atms. There is thus obtained unitary appearing sheets or blocks from

1. British Celanese, Ltd., W. Dickie and F. Hale, E. P. 349990.
2. G. Balle and K. Sponsel, D. R. P. 516751.
3. The methylcellulose being prepared according to the method of W. Denham and H. Woodhouse (see page 24), or according to F. P. 447974 (see p. 30, n. 2; 91, n. 2; 415, n. 6, 1180, n. 2). See also Aust. P. 73001.

which objects may be prepared as by turning, planing or sawing.

2. Foils from water-soluble ethylcellulose are painted or sprayed with a thin layer of water so that a light surface swelling takes place of the exterior surface of the individual foils, and these are then agglomerated into a unitary appearing sheet by a gradually increasing pressure aided by heat as before. The temperature is so adjusted that it reaches the maximum with the highest pressure.

In an improvement on this process[1] it has been shown that the method may also be applied to cellulose sheets regenerated from viscose, if one or several layers are coated with an aqueous alkylcellulose solution and then subjected to pressure, or pressure aided by heat, the small amount of water present in the alkylcellulose solution being readily absorbed by the regenerated cellulose. In this manner it is claimed, the close relationship between regenerated cellulose which swells in water and the water-soluble alkylcelluloses, results in a perfect union of the regenerated cellulose layers so that no fissures or bubbles are formed and an optically uniform mass results, free from brittleness and with no tendency to crack or split.

For example, foils of regenerated cellulose (the patent calls it hydrocellulose) are led continuously over rubber rollers and coated with a thin layer of a 30% aqueous solution of methylcellulose. These foils are united with each other in pairs, and finally welded together in a rolling mill to a firm, elastic, flexible mass that is perfectly transparent and indistinguishable as to having been formed from a plurality of layers, the product remaining homogeneous when warmed, being readily susceptible to drilling, rolling and stamping.

1. I. G. Farbenindustrie, D. R. P. 547665, Addn. D. R. P. 516751.

CHAPTER XIV

COMMERCIAL APPLICATIONS OF THE CELLULOSE ETHERS

Having detailed the methods of manufacture and physical constants and relationships of the cellulose ethers in Chapters VI to XI inclusive, and having indicated that these etherified celluloses in contradistinction to the cellulose nitrates have little or no technical applications in the undissolved condition, Chapter XII was concerned with a statement of the solvents, softeners and plastifying bodies which have been proposed from time to time for incorporation with these bodies to increase the range of their commercial usefulness. Chapter XIII detailed those uses in the arts of the cellulose ethers in the filament, fiber, or textile form, and this Chapter continues the uses of the etherified celluloses in fields other than those in which individual filaments are the first solid form of these bodies.

This Chapter is roughly apportioned into three sections as follows:

Section One. Those uses which have been proposed in which the ethers are used in the liquid or fluid form and without loss of the volatile solvent portion, and include Lacquers (page 2388); Production of Crystal Effects (2428); Cellulose Ether Coated Cigar and Cigarette Tips (2431); Cellulose Ether Coated Paper (2434); Cellulose Ethers for Insulation (2438); Cellulose Ethers in Pharmacy (2445); Emulsification with the Cellulose Ethers (2451); Cellulose Ether Ultra-Filters (2458); Cellulose Ethers in Leather Industry (2461); Cellulose Ethers and Tannin (2465); Cellulose Ethers in Explosives Industry (2470); Shoe Stiffener (2471); Cellulose Ether Inks (2474); Pigmentation of Cellulose Ethers (2476); Solid Alcohol (2480); Airplane and Balloon Fabric Lacquers (2481); Stencil Sheets (2486).

Section Two. Solid Cellulose Ether compositions, in which the solid is devoid of or low in thermoplasticity, in which softeners may be added, but not appreciable amounts of solvent plasticizing bodies, including Films (2499); Cellulose Ethers in Color Photography (2530); Artificial Sponge (2535); Cellulose Ethers in Prosthetic Dentistry (2536); Pencils, Crayons, Sealing Wax (2539); X-ray Screens (2540); Tracing Cloth (2542); Rubber with Cellulose Ethers (2542); Cellulose Ether Transfers (2547); Artificial Wire Glass, Glass Substitutes (2552).

Section Three. Products involving the use of the cellulose ethers in which a noticeable degree of thermoplasticity is involved, and to which thermoplastic function the adaptability of the product owes its primary value. Plastics (2556); Laminated Glass Cheets (2582); Laminated and Composite Sheets (2597); Phonograph Records (2599); Artificial Horn (2606); Playing Cards (2608); Artificial Pearls (2609); Recent Cellulose Ether Data (2621).

Cellulose Ether Lacquers and Coating Compositions. The modern cellulose derivative lacquer industry perhaps had its inception in the observation of J. Hyatt about 1860, that "liquid cuticle," a pyroxylin solution in ether-alcohol would stick to wood upon evaporation of the solvent portion and thereby produce a transparent, water-repellent film, as he observed in Albany, New York, one day, when he went to the closet to get the bottle, and found that it had tipped over, run over the shelf and solidified to a polished-appearing pellicle difficult to remove. However, J. Stevens really laid the foundation by his observations on the solvent capacity of the high-boiler amyl acetate, since substituted by *n*-butyl acetate in many of the arts, and supplemented by harmoniously acting plasticizing bodies. This work is not concerned with the development of the inorganic cellulose esters (nitrocellulose), and only with the organic cellulose esters insofar as their closely analogous properties indicate a suitability in the cellulose ether field. Inasmuch as the formulation of lacquers in the main is a manipulation of solvents, non-solvents, diluents

and high-boiling and extensifying bodies, and likewise inasmuch as the cellulose ethers as a class have a much wider solvent capacity than the organic cellulose esters in the same solvent and in the range of solvents, a majority of the fluid preparations which have been exploited and made the basis of patent grant in the cellulose acetate field are applicable in connection with the solvation of the cellulose ethers.

Cellulose derivatives in the dissolved condition are roughly classifiable as to the content of cellulose compound, those of least percentage being the bronzing liquids, followed by the general lacquers, then the paint and enamels which gradually blend off in cellulose compound content to the semi-solid and solid thermoplastic compositions used in the plastic arts. However, due to the ready modification of viscosity of solutions in which the solvent portion may be materially reduced without a corresponding increase in the viscosity, the classification of these lacquers based upon total solid evaporable content does not possess the significance that it did a few years ago (see Topic, "Viscosity Reduction"). The addition to fluid cellulose ether and ester preparations of the modern synthetic resins in the dissolved state has also materially altered the art in the deposition of films upon rigid and semi-rigid surfaces.

The great expansion in the field of non-evaporable plastics and suppleness-inducing and toughness-producing bodies as adjuncts to the cellulose ethers and organic esters as used for protective coatings has basically modified our conceptions of the components in a lacquer of this general classification when intended to impart specific properties in the dried condition. The breadth of this subject is so wide as to justify a separate tome for its proper development. As in the previous topics, the intention is primarily to touch only upon the high lights, leaving the references to literature and to patent issuance for those requiring exhaustive information in a narrowly proscribed field. The upwards of thirteen thousand separate patents issued in the cellulose

ether and organic ester art as found in the indices of this work, are primarily involved in the preparation or utilization of liquid preparations,—a lacquer in its broadest significance, since these non-explosive cellulose derivatives only have found technical usefulness when in the dissolved state, or as the result of once having passed into solution. Up to the present time, price considerations have militated against their usefulness in many fields in which otherwise they would undoubtedly find a wide applicability, but with the numerous foci of research now progressing, cost of production is being steadily lowered, while the desirable qualities of the finished preparations are being materially enhanced.

The purposes of this topic can perhaps be best developed by dividing these fluid preparations roughly into those which read upon the sole use of the organic cellulose esters (formate, acetate, propionate, butyrate and the mixed organic esters) on the one hand, but which in their disclosures indicate also a suitability in the analogous cellulose ether field, and those methods, processes and formulas in which some form of the cellulose ethers are either specified, claimed or recommended, little attempt in either classification being made to classify the preparations based upon the relative percentage of cellulose content contained therein.

1. *Cellulose Acetate Lacquers.* The acetylcellulose lacquer as described by G. Austerweil[1] involves the use of polymerized vinyl esters as polymerized vinyl acetate, which for proper stability should be free from traces of chlorine. The cellulose ester and the vinyl resins are preferably placed in solution separately, and then admixed in varying proportions, depending upon the properties required in the film producible therefrom. J. Brandenberger[2] dissolves cellulose acetate in the usual solvents and then adds a small amount of alkaline silicate for the dual purpose of increas-

1. Aust. P. 78983; abst. Chem. Ztg. 1919, **43**, 733.
2. E. P. 24811, 1908; abst. J. S. C. I. 1910, **29**, 17. F. P. 405429; abst. J. S. C. I. 1910, **29**, 345.

ing rigidity and diminishing inflammability. In the application of a cellulose ether or ester lacquer[1], a process has been recommended, especially suitable to application to non-rigid surfaces, of floating a layer of lacquer on an aqueous body of greater density (of course) than the lacquer, and then dipping the object to be lacquered through the floating lacquer. On account of the property of some of the lower etherified celluloses of swelling in water, this bids fair to be an important method for attaching methylcellulose and ethylcellulose films to rigid and non-rigid supports, by virtue of the high contractility of such cellulose ethers upon drying whereby their adhesion to the object is materially enhanced. The R. Carruthers[2] lacquer combines celluloid dissolved in acetone-benzene-alcohol, with a cellulose acetate solution, alleging better adherence as the result of the presence of the thermoplastic nitrocellulose complex.

For application to non-porous structures as metal sheets, a mixture of cellulose acetate 5 to nitrocellulose 6 in a combined solvent of methyl acetate, diphenyl acetate, cresyl formate, an acetin and dimethyl-, diphenyl- or tolylurea as antacids[3] represents the composition of L. Collongy as patented in France. The camouflage acetate enamel of W. Doerflinger[4] as adapted to the covering of airplane parts, adds stannic oxide as a fire-retardant, with diacetone oil and nigrosin. The uses of "Albertat 175 A," a trade name for the aluminum salt of a high acid Albertol resin[5], has been suggested as a flatting medium for oleo-varnishes, but owing to the proneness of oxidation spontaneous ignition sometimes takes place. It therefore, should be stored in small metal containers.

As a coating for fibers and textile products made there-

1. R. Beausejour, U. S. P. 1572461.
2. E. P. 319978; abst. C. A. 1930, **24**, 2621.
3. F. P. 502538; abst. Chim. et Ind. 1921, **5**, 571.
4. U. S. P. 1345354.
5. E. Fonrobert, Farben-Ztg. 1932, **37**, 1084; abst. C. A. 1932, **26**, 3682.

from[1], the fibers may be steeped in a solution containing cellulose acetate, methyl acetate, acetone and benzene, to which 15-30% of plasticizing agent may be added, depending upon the coarseness or fineness of the fibers, the threads being then drained and dried. The artificial fiber solution of J. Huebner[2] involves dissolving the cellulose acetate in either formic or acetic acids, to which methyl and ethyl alcohols are added (probably forming some methyl and ethyl formates and acetates), claiming such a solution may be clarified readily by the usual methods of filtration. The use of acetate lacquers in the industry in general[3] has been made the basis of a review of M. Jenett and and M. List, and the preparation of iridescent layers has been explained by A. Kraus[4], who claims the most exquisite color action is produced on a black background by incorporating in the lacquer bismuth oxychloride powder, a most charming play of colors being obtained. Cellulose distearate dissolved in xylol[5] has been advanced as especially useful for coating tennis racquet strings.

In coating metal airplane and airship parts, especially the metal portions as duralium, magnesium alloys and steel[6], a zinc chromate-synthetic resin primer is applied, followed by a plurality of coats of an acetylcellulose lacquer. If it is intended to use the lacquer for cementing glass joints[7], the borders are sprayed or dipped with acetylcellulose dissolved in a mixture of acetone, acetic acid and methyl acetate. The L. Rado[8] collapsible tube is formed of aluminum-covered metal foil coated on both sides with a cellulose acetate protective solution as a unitary or plur-

1. A. Girard and M. Roumazeilles, F. P. 611899.
2. E. P. 127027; abst. C. A. 1919, **13**, 2443.
3. Chem. Techn. Wchschr. 1918, **2**, 287; abst. Chem. Zentr. 1919, II, 428.
4. Farbe u. Lack, 1932, 110; abst. Chem. Zentr. 1932, I, 3000.
5. R. Lant and W. Koreska, E. P. 343117; abst. C. A. 1931, **25**, 4421. F. P. 689991; abst. Chem. Zentr. 1931, I, 548.
6. J. McCloud, I. E. C. 1931, **23**, 1334; abst. J. S. C. I. 1932, **51**, 314-B.
7. F. Howe and M. Misener, D. R. P. 491726; abst. C. A. 1930, **24**, 2567.
8. E. P. 312262; abst. C. A. 1930, **24**, 933.

ality of applications[1]. Diacetone alcohol forms the main solvent portion of the G. Trumpler lacquer[2], being associated with another water-miscible solvent as acetone or ethyl alcohol. H. Tenen[3] has reviewed the general subject of acetate varnishes and lacquers, and submitted several type formulas, while F. Groff[4] condenses tung oil with phenol and adds the product to dissolved acetylcellulose to form high solid content enamels and paints. The resinous condensation product of E. Pieper[5] is obtained from phthalic anhydride, glycerol, ethyleneglycol and diethyleneglycol, while A. Rogers[6] uses coumarone resins for the same purpose.

Monoethylin phthalate[7], or glyceryl benzoylbenzoate[8], constitute the preferred high boiling portion of the F. Hahn acetylcellulose lacquers, acetone oil fractions and diacetone alcohol being added in relatively small amounts. Copper-butyl phthalate or iron-butyl phthalate may be also used, where high covering power with great tenacity is desired[9]. J. Davidson recommends certain alkylbenzenes as mono-, di- or hexa-ethyl(or propyl or butyl or pentyl(amyl))benzene, as a group of 12 high boiling solvents especially harmonious in lacquers[10], especially in conjunction with ethylglycol, to which polymerized vinyl chloride or acetate may be added[11].

In attempt to combine synthetic resin bases and certain condensation products of organic acids with products to form solid compounds applicable in the cellulose acetate and likewise in the cellulose ether industry, the British

1. G. Siebert, Farben-Ztg. 1930, **36**, 506; abst. Nitrocellulose, 1931, **2**, #1, 17.
2. F. P. 668125; abst. C. A. 1930, **24**, 1528.
3. Chemicals, 1926, **25**, #19, 9.
4. E. P. 354166; abst. C. A. 1932, **26**, 3943.
5. Can. P. 321592; abst. C. A. 1932, **26**, 3391.
6. U. S. P. 1884255.
7. F. Hahn, Can. P. 312569; abst. C. A. 1931, **25**, 4422.
8. *Ibid.* Can. P. 312568; abst. C. A. 1931, **25**, 4422.
9. C. Henning, C. Burke and E. Reid, Can. P. 320783.
10. U. S. P. 1834050; abst. C. A. 1932, **26**, 1143.
11. J. Davidson, U. S. P. 1838368. See Chemische Fabriken vorm. Weiler-ter-Meer, F. P. 606763; abst. Chem. Zentr. 1926, II, 1795.

Celanese, Ltd., and associates have been very active. Among the suitable products developed for this purpose have been described phenol-aldehyde and phenol-ketone resin types[1], phenol-furfural series of resinous products[2], sulfonamide-furfural aggregates[3], toluenesulfonamide-aldehyde bodies[4], lactic acid-resinous condensates[5], toluenesulfonamide-formaldehyde with polymerized vinyl compounds[6] especially in association with ethyl phthalate and diphenylpropane[7], diphenylolpropane-formaldehyde[8], diphenylolcycloparaffins as diphenylol-cyclopentanone, -cyclohexanone, -cycloheptanone, -methylcyclohexanone and -cyclohexane[9], and toluenesulfonamide resin types with methylglycol, ethylglycol, their corresponding acetate and dioxane. In conjunction with either the cellulose ethers or cellulose acetate in solution, they may be added in amounts up to the weight of the cellulose compound, and yield brilliant, transparent films of great permanency.

Condensates of the furfuraldehyde-aniline group[10], sulfonamide-benzaldehyde bodies[11], and formylglycerol condensed with hydroxybenzyl alcohol[12], have also been evolved as suitable for addition to cellulose acetate solutions for lacquering purposes. Among the less common solvents and high boilers found applicable to use in such lacquers may

1. G. Schneider, E. P. 300140; abst. C. A. 1929, **23**, 3588. C. Dreyfus, Can. P. 307989. British Celanese, Ltd., E. P. 316984. Can. P. 293641.
2. W. Moss and B. White, E. P. 307291; abst. C. A. 1929, **23**, 5338.
3. C. Dreyfus, W. Moss and B. White, Can. P. 319152.
4. *Ibid.* Can. P. 319151.
5. C. Dreyfus and W. Moss, Can. P. 319150.
6. *Ibid.* Can. P. 318758. See C. Dreyfus, W. Moss and B. White, Can. P. 319731.
7. British Celanese, Ltd., E. P. 352547; abst. J. S. C. I. 1931, **50**, 895-B.
8. *Ibid.* E. P. 298616. Cites E. P. 296674, 299066, 299067, 299781, 303169.
9. *Ibid.* E. P. 342429. See E. P. 342144. Can. P. 319730.
10. *Ibid.* E. P. 307290, 307291; abst. J. S. C. I. 1930, **49**, 469-B.
11. C. Dreyfus, W. Moss and B. White, Can. P. 319729.
12. G. Seymour and C. Dreyfus, Can. P. 317117; abst. C. A. 1932, **26**, 1460. U. S. P. 1828449.

be mentioned butyl tartrate[1], alkylureas as di- and tetramethyl, -ethyl and -phenylurea[2], dibenzyl tartrate[3], naphthalene[4], acetanilid and acetnaphthalid[5]. For a priming or filling coat as a base upon which to superpose the acetate lacquer[6], cocoanut oil or the fatty acids obtained therefrom has been recommended.

Acaroid or xanthorrhea resins associated with cellulose acetate and aniline, toluidine or pyridine added as stabilizers[7], these resins also being claimed as suitable for incorporation with the cellulose ethers[8]; diphenyl tartrate[9] to prevent the coatings from becoming tacky or acquiring a bloom; furfuraldehyde-acetone resin to increase the luster[10]; addition of diphenylolpropane and xylylmethylsulfonamide as plastizants and to increase the flowability of the lacquer[11]; and the use of a mixture of benzene, ethylene dichloride and ethyl alcohol as fulfilling all the requirements of a low-boiling acetylcellulose solvent[12] are other refinements of the art as evolved by British Celanese, Ltd., and co-workers[13]. If an abrasive be added to a sulfonamide in quantity sufficient to exert a solvent action[14], a polish for cellulose acetate surfaces is formed.

The R. Behin protective coating against the action of gasolene, oils and alcohol combines acetylcellulose and a

1. British Celanese, Ltd., and W. Moss, E. P. 362480; abst. J. S. C. I. 1932, **51**, 235-B.
2. H. Dreyfus, Can. P. 296775.
3. C. Dreyfus and G. Schneider, Can. P. 318147.
4. C. Dreyfus and W. Moss, Can. P. 319728.
5. C. Dreyfus, E. P. 127678; abst. C. A. 1919, **13**, 2444.
6. British Celanese, Ltd., E. P. 342211; abst. J. S. C. I. 1931, **50**, 405-B. C. Dreyfus, Can. P. 307036.
7. C. Dreyfus, E. P. 222168. U. S. P. 1742587.
8. C. Dreyfus and W. Moss, Can. P. 312235. H. Dreyfus, Belg. P. 359497.
9. Celluloid Corp., E. P. 358428; abst. J. S. C. I. 1931, **50**, 1147-B.
10. British Celanese, Ltd., E. P. 307289; abst. J. S. C. I. 1930, **49**, 469-B.
11. *Ibid.* E. P. 317454; abst. J. S. C. I. 1931, **50**, 128-B.
12. W. Moss, U. S. P. 1883395. C. Dreyfus and W. Moss, Can. P. 292644.
13. C. Dreyfus, Can. P. 307037. See Can. P. 295242, 310250.
14. *Ibid.* Can. P. 310930.

solution of a formalin-phenol derivative[1]. Another method disclosed is to first coat the surface with a polyhydric phenol as resorcinol in furfural which may also contain a plasticizer[2], and over this is flowed an acetylcellulose as a toughening agent, the coating being hardened by exposure to gaseous hydrochloric acid. Benzyl alcohol, tolyl carbinol and cyclohexanone constitutes the preferred dissolving composition in the cellulose acetate enamel of Cellon, Ltd., and T. Tyrer[3], and ethylidine diacetate in another acetylcellulose lacquer formula[4]. The Consortium für Elektrochemische Industrie[5] add a polymerized vinyl ester to the non-evaporable solids without a corresponding increase in viscosity of the lacquer. Monoethyl, monopropyl, monobutyl and monoamyl phthalates, and zinc, copper, lead, cadmium, iron, manganese, nickel and cobalt unite with these half esters of phthalic acid to form the corresponding 32 double esters, of which zinc-butyl phthalate is an example[6], being friable, transparent solid gum-like material which softens at elevated temperature and becomes liquid at about 150°. These bodies are soluble in the common solvents, and give solidity and flexibility to a cellulose ether or ester varnish when incorporated therein.

To prevent steaming and the formation of raindrops on glass surfaces[7] it is recommended to incorporate in an acetylcellulose lacquer about 50% nicotine based on the acetylcellulose, acetone, ether, amyl acetate and glycerol being the solvent portion. If it is efficient on automobile windshields, it should find a ready sale in our locality. The F. Hahn coating composition involves the use of dissolved

1. F. P. 654238; abst. C. A. 1929, **23**, 3783.
2. British Thomson-Houston Co., Ltd., A. Ward and G. Bray, E. P. 320649.
3. E. P. 130402. F. P. 510356. Ital. P. 177682.
4. Chem. Fabr. Griesheim Elektron, D. R. P. 281373; abst. C. A. 1915, **9**, 1850. H. Matheson, U. S. P. 1488608.
5. F. P. 718689; abst. C. A. 1932, **26**, 3392.
6. B. Brown and C. Bogin, U. S. P. 1591652. C. Gabriel, U. S. P. 1813735; abst. C. A. 1931, **25**, 5304.
7. Compagnie Internationale des Industries Chimiques "Interchimic" Soc. Anon., E. P. 350847.

cellulose acetate with a resin-like material prepared by heating 1 mol. of oxalic or phthalic acids with 1 mol. ethylin (or methylin, propylin or butylin), forming the corresponding monomethylin, monoethylin, monopropylin and monobutylin phthalates or oxalates. Diethyl phthalate is used in conjunction with lower boiling solvents[1]. Cyclohexyl phthalate, cyclohexylbutyl, dicyclohexyl phthalate are bodies recently described as being desirable softeners for use in cellulose acetate and cellulose ether flowable combinations[2]. Other desirable solvents which have been made the basis of patent issuance are phosphoric acids to diminish inflammability[3] and used in the proportion of 0.5-0.05 parts, methylene chloride[4], ethyl abietate[5], phenyl abietate or benzyl abietate, aniline acetate or *p*-aminoacetanilid[6], or nitrobenzene or dinitrobenzene[7].

The viscosity of cellulose acetate lacquers may be diminished by adding gall or bile in solution[8]. The adhesive of W. Stelkens[9] comprises perforated films of cellulose derivatives and provided with transverse paths through the thickness for swelling agents and solvents used in softening it to aid adhesion. If it is desired to color the lacquer[10], complex metal compounds of *o*-hydroxyazo dyes have been recommended, the original patent containing several specific examples[11]. Acetylcellulose lacquer designed especially for application to semi-stiff collars, cuffs or shirt fronts[12] com-

1. F. Hahn, U. S. P. 1812335; abst. C. A. 1931, **25**, 5049. Can. P. 312568.
2. E. Reid and G. Schwartz, U. S. P. 1778567.
3. E. Farrow, S. Sheppard and H. Clarke, E. P. 342444; abst. C. A. 1931, **25**, 4421.
4. A. Eichengrün, E. P. 243031; abst. C. A. 1926, **20**, 3826.
5. L. Bent, U. S. P. 1839529.
6. W. Lams and J. Wyler, U. S. P. 1833526; abst. C. A. 1932, **26**, 1143.
7. F. Zimmer, Farben-Ztg. 1918, **23**, 331.
8. I. de Introini, E. P. 307392; abst. C. A. 1929, **23**, 5317.
9. E. P. 364765; abst. J. S. C. I. 1932, **51**, 316-B.
10. Soc. Anon. pour l'Ind. Chim. a Bale, D. R. P. 535472; abst. C. A. 1932, **26**, 1143.
11. H. Hopkins, U. S. P. 1771538.
12. F. Fischer and B. Gotthart, E. P. 311417; abst. C. A. 1930, **24**, 977.

prises cellulose acetate in solution associated with a preponderance of high-boilers[1].

A series of patents has been issued to M. Harvey[2] for the utilization of cashew nut oil as a bland softener and suppleness-inducing body in cellulose acetate compositions. Ethyl acetylhydroxyacetate and amyl acetylglycollate[3], mixtures of isomeric xylenemethyl(or ethyl)-sulfonamides[4], and glycol phthalate[5] are examples of high boiling solvents which have been detailed as desirable adjuncts in acetylcellulose solutions. As superior lacquer bases cellulose acetopropionate or acetobutyrate[6], freely soluble in acetone and the higher ketones, have been put forward on account of an alleged enhanced stability over the acetylcelluloses. If it is desired to product non-transparent coatings[7], coloring substances or pigments are added. For transparent colored coatings[8], alkaline earth metal salts of azo dyestuffs containing sulfonic groups obtained by coupling diazotized nitroarylamines with acetoacetic acid arylides are used. Ethylglycol is a preferred solvent because it dissolves both the cellulose ester and the dyestuff[9]. Cellulose trilaurate or starch laurate in solution[10], dissolving readily in methylene chloride, chloroform or benzene, is adapted to wood fillers and priming coats in general.

The A. Zetter lacquer[11], designed for forming capsules on stoppered bottles by dipping, utilizes a viscous solution of cellulose acetate (meaning a solution of high contractil-

1. Glasurit-Werke M. Winkelmann, A.-G., E. P. 288221; abst. C. A. 1929, **23**, 721.
2. U. S. P. 1838070, 1838071, 1838072, 1838074, 1838075, 1838076, 1838077.
3. Chemische Fabrik von Heyden, Akt-Ges., D. R. P. 288267, 324786.
4. H. Dreyfus, U. S. P. 1530987. E. P. 154334. F. P. 634165.
5. I. G. Farbenindustrie, A.-G., Can. P. 297083.
6. *Ibid.* E. P. 345970; abst. C. A. 1932, **26**, 610. M. Hagedorn and O. Reichert, D. R. P. 531175; abst. C. A. 1931, **25**, 5557. F. P. 680860.
7. *Ibid.* E. P. 302280; abst. C. A. 1929, **23**, 4356.
8. *Ibid.* E. P. 339936.
9. British Celanese, Ltd., E. P. 298616.
10. I. G. Farbenindustrie, A. G., E. P. 302698, 303168.
11. D. R. P. 526467; abst. C. A. 1931, **25**, 4420.

ity) treated with a fatty oil until coagulation begins, which is then diluted with solvent until the precipitate first formed just re-dissolves. In preparing layers of acetylcellulose for coating materials[1] such as fabrics, fibers or leather, solvents which dissolve the ester only when hot are added in order to prepare very viscous solutions, and the fabric is coated by impressing the solution onto the cloth by means of rollers. Monoalkylethers of propyleneglycol have been described as suitable cellulose ether and cellulose ester dissolvants, specifically propyleneglycol monoethyl ether[2]. As an intermediate layer upon which to build top coats of the cellulose esters or ethers where extremely high adhesion and elasticity are the primary requisites[3], a mixture of cellulose dilaurate and guttapercha in benzene, xylene and chlorbenzene, or cellulose monoacetate-distearate and rubber dissolved by a mixture of methylene chloride, benzene and chlorbenzene, has been advocated. Methyl rubber W (dimethylbutadiene-heat-rubber)[4] has also been combined with the cellulose esters for an analogous purpose.

In preparing colored lacquers[5], nitrocellulose is mechanically worked with at least an equal quantity of a solid color such as Lithol Fast Scarlet R until the latter has gone into a practical colloidal state of dispersion, and this base material is then incorporated with a cellulose derivative lacquer in the proportions desired to give the effect required. Condensation products of dibasic acids with multivalent alcohols may be added[6]. Other colored lacquers result by first making a paste from the calcium salt of the dyestuff obtained from diazotized 5-nitro-2-aminobenzoic acid and acetoacetic acid-2-anisidine sulfonic acid and pouring the reaction mixture upon ice, whereupon

1. A. Eichengrün, U. S. P. 1357447. D. R. P. 287745.
2. H. Finkelstein, U. S. P. 1812145.
3. E. Richter and W. Becker, U. S. P. 1778813.
4. I. G. Farbenindustrie, A.-G., E. P. 348077.
5. C. Immerheiser and E. Knebel, U. S. P. 1830944; abst. C. A. 1932, **26**, 861.
6. I. G. Farbenindustrie, A.-G., F. P. 669278; abst. C. A. 1930, **24**, 1753.

the sulfonic acid separates, diethyl phthalate being then added. The mass is then stirred with nitrocellulose dissolved ethylglycol, acetone and ethyl alcohol, and this stock color then added to a cellulose derivative lacquer in amount desired[1]. Water-insoluble azo- or vat-dyes or color lakes prepared from water-soluble coal tar dyes may also be used for this purpose[2]. As a bronzing liquid[3], metal varnish[4], and spirit varnishes[5], processes have been detailed.

A. Van Heuckeroth[6] has compared as lacquer plasticizers, Paplex G-20, Paplex RG-2 and diphenyl phthalate as against dibutyl phthalate, tricresyl phosphate, bornyl phthalate and diethyleneglycol dibenzoate. General data, methods of preparing lacquer formulas and application of the cellulose acetate lacquers have been published by C. Newby[7], L. Clement and C. Riviere[8], E. Fischer[9], J. Frydlender[10], H. Gardner and C. Knauss[11], H. Hofmann and E. Reid[12], and others[13].

2. *Cellulose Ether Lacquers.* The interest and importance of this field is at once obvious by a glance at the multiplicity of processes which have been evolved and detailed information in the patents granted. In respect to

1. I. G. Farbenindustrie, A.-G., E. P. 339936; abst. J. S. C. I. 1931, **50**, 351-B.
2. Chem. Fabrik Griesheim Elektron, E. P. 233891.
3. J. Young, U. S. P. 1418347.
4. M. Deschiens, Chim. et Ind., Special No. May, 1927, 479; abst. C. A. 1927, **21**, 3472.
5. A. Stiel, E. P. 353389; abst. C. A. 1932, **26**, 3686.
6. Am. Paint & Varnish Mfrs. Assoc., Circ., 1931, #399, 377; abst. C. A. 1932, **26**, 608.
7. J. Soc. Dyers Colourists, 1929, **45**, 104; abst. J. S. C. I. 1929, **48**, 443-B.
8. Bull. Soc. D'Encouragement, 1914, **121**, 187; abst. J. S. C. I. 1915, **34**, 75.
9. Kunst. 1916, **6**, 210; abst. C. A. 1917, **11**, 1316.
10. Rev. prod. chim. 1930, **33**, 225; abst. C. A. 1930, **24**, 6038.
11. Am. Paint & Varnish Mfrs. Assoc., Circ. #338, 1928, p. 657; abst. C. A. 1929, **23**, 276.
12. I. E. C. 1929, **21**, 955; abst. J. S. C. I. 1929, **48**, 924-B.
13. W. Smart, Metal Industry, 1925, Sept., 367. A. Brown, Paint, Oil and Chemical Review, 1925, **80**, #10, 12. B. Brown and C. Bogin, I. E. C. 1927, **19**, #9, 968. W. Mueller, Paint and Varnish Record, 1927, Feb., 14. M. Barrett, Paint, Oil and Chem. Rev., 1924, **78**, #3, 10. Anon., Paint, Oil and Chem. Rev., 1927, **84**, #19, 13. Mehren, Kunst., 1922, **12**, 99. Andes, Farben-Ztg., 1918, **24**, 128.

lacquers as in other fields of cellulose ether activity, the art is so new comparatively speaking, that the major portion of the published information is contained in the voluminous but scattered patent literature. In fact, in lacquers as in other branches of the etherized cellulose art, pure science research apparently has not kept pace with patent process disclosures, at least up to the present time. With a much wider assortment of solvents available for the cellulose ethers, both low boiling, high boiling and those which exert a swelling or plasticizing effect, and also by virtue of the fact that the cellulose ethers are soluble in classes of bodies which do not dissolve the nitrocelluloses or cellulose acetates, such as oils, fats and waxes in the molten condition, and aliphatic and aromatic alcohols, either alone or in association with denatured alcohol (also an inexpensive solvent) the situation presents itself at the moment, that although the cellulose ethers are more expensive per unit weight than are the nitrocelluloses and acetylcelluloses, yet there is considerable saving in the use of less expensive solvents and diluents for the etherized celluloses, so that disparagement in price based upon the undissolved organic cellulose derivatives, is considerably lessened when comparing the cellulose esters and ethers in the dissolved condition, as in lacquer, paint, enamel and bronzing liquid formulas.

Ethyl *α*-hydroxy*iso*butyrate and the corresponding methyl and propyl esters[1] have been advocated as desirable solvents not only for the cellulose ethers of the higher etherification type, but also for the nitro- and acetyl-celluloses—one of the comparatively few classes of dissolvants applicable equally to these three type cellulose derivatives. They are prepared by reaction between a ketone and a cyanid or a ketone cyanohydrin and an alcohol. K. Burgemeister[2] prepares useful varnish ingredients by heating cellulose ethers with resins and/or oils to 280-300°. Thus,

1. American Cyanamid Co., E. P. 356141; abst. C. A. 1932, **26**, 4487. E. P. 312469; abst. C. A. 1930, **24**, 961.
2. D. R. P. 523300; abst. C. A. 1931, **25**, 3502.

ester gum 1, linseed oil 2 and ethylcellulose 1 part are heated at 280° until the ethylcellulose has completely dissolved in the resin-oil mixture. The composition may be dispersed with benzine or linseed oil varnish.

According to Frederking[1] the most satisfactory procedure for preserving parchment documents comprises impregnating them with solutions of cellulose ethers, especially where paper documents are to be preserved. Documents in pencil or copying-ink pencil on a poor quality of paper are treated with a solution of copal varnish in ethyl alcohol. In the production of articles with a glaze-like covering[2], especially when applied by a cold process, solutions of the cellulose ethers are indicated on account of their neutrality and stability. The method consists in making the articles to be glazed, such as wall tiles or statues from porous materials capable of readily absorbing and retaining large quantities of water, applying a glazing liquid consisting of finely ground cement and water containing small quantities of substances for rendering its colloidal condition more permanent when the article is set, and while the first coating is still plastic, a thin coating of cellulose ether solution is applied.

The French process of engraving as described by J. Guerard[3] relates to a specific varnish to be applied to intaglio, lithographic, relief and transparent plates. The negative obtained on such support presents an opaque appearance on a transparent base. The varnish is formed of dissolved cellulose ether with resins dissolved in a volatile solvent, the evaporation of which first causes the formation of a jelly from a part of the solid components of the varnish, the other solid constituents remaining dissolved within the jelly, solidifying at the end of the evaporation in subdivided form. The varnish is produced by dissolving the

1. Mitt. Materialprüf. 1931, 188; abst. J. S. C. I. 1932, **51**, 499-B.
2. K. Friedrich and C. Friedrich, E. P. 309755; abst. C. A. 1930, **24**, 704.
3. U. S. P. 1850929.

cellulose ether in acetone, the resins in a mixture of alcohol-ether, and mixing the two solutions.

An improved wooden flooring or floor covering has been patented[1], it being claimed that when parquet and strip floors or linoleum are covered with a cellulose ether solution in which camphor, plastifying agents and resins are added in conjunction with the usual volatile solvents, such an impenetrable and impervious coating results that the spilling of coffee, wine and similar liquids leaves no marks, and furthermore, the well known slipperiness of waxed and polished floors is entirely absent when the floor or floor covering is suitably covered with a cellulose ether film. Artificial resin varnishes containing a notable proportion of benzylcellulose have been described by G. Kimpflin[2].

In the coating (waterproofing) of articles prepared from cellulose hydrate material[3], such as films, fibers, bands and plates, they are first swollen in water in order to increase their porosity, then treated with a water-miscible liquid (as acetone or ethyl alcohol) which is also a solvent of the cellulose ether applied thereto. The hydrated cellulose articles are then either immersed in the cellulose ether lacquer, or the lacquer is sprayed over the hydrated cellulose surface and afterwards dried, adhering excellently. The cellulose ether enamel of A. Martin[4] involves a method of incorporating pigments with etherized cellulose or with cellulose esters, for the purpose of producing pigmented compositions either glossy or of matt finish, or for use as primers, fillers or base coats upon porous materials. The method comprises placing a quantity of cellulose ether in a high speed centrifugal either in the moist condition or purposely wetted with a liquid, and while the hydroextractor is still revolving, pouring in a slurry of water in which

1. R. Norman, H. Boldemann and S. Jeurling, E. P. 346738; abst. C. A. 1932, **26**, 2880.
2. Chim. et Ind., Spec. No., 1926, Sept., 618; abst. C. A. 1927, **21**, 827. See Bull. Soc. encour. ind. nat. 1924, **123**, 657; abst. C. A. 1925, **19**, 581.
3. F. Klein, E. P. 313410; abst. C. A. 1930, **24**, 1229.
4. E. P. 354748; abst. Brit. Plastics, 1932, **3**, 102.

the pigment as blanc fixe, chrome yellow, prussian blue or chrome green is held in suspension. The speed of the extractor is then raised to its maximum, and the coloring matter actually driven into the cellulose ether particles by the centrifugal force developed. After whizzing, the cellulose ether is dried, and may then be dissolved to a thick paste which is incorporated in lacquers in the quantity required.

I. Morozov[1] has collected the available theoretical and practical information to permit a thorough understanding of the problems of cellulose ether lacquers, particular attention being paid to problems of viscosity and to attempts to explain behavior on the basis of structural formulas. In a paint system in which the second coat is applied to the first while the latter is still wet, the paint material for the first coat is treated with a sufficient quantity of an oxide or hydroxide of an alkaline earth metal, or of the soaps of these metals with resinic acids or oleic acid[2], while the vehicle for the covering coat contains as an essential component cellulose ethers combined with caoutchouc or its decomposition products.

In the production of palette materials and surfacing compositions such as those which have a "stopping" character and which are applied to surfaces which are afterwards polished or lacquered after hardening[3], the surfacing material consists in concentrated solutions of cellulose ethers to which resins containing metals as powdered iron, copper or aluminum may be added. The mixture of powdered metals is so proportioned that the surfacing material when dried and polished shows a metallic sheen. The Bakelite Corp. have described varnishes containing synthetic resins[4], obtained by causing a phenol, a fatty oil and form-

1. J. Chem. Ind. (Moscow) 1931, **8**, #17, 23; abst. C. A. 1932, **26**, 1807.
2. M. Rensch, E. P. 326649; abst. C. A. 1930, **24**, 4945.
3. G. Trümpler, E. P. 294262; abst. C. A. 1929, **23**, 2050. F. P. 668123; abst. C. A. 1930, **24**, 1529.
4. E. P. 342286; abst. C. A. 1931, **25**, 4421. See V. Turkington, E. P. 293453, 324025.

aldehyde to react, and incorporating with this benzylcellulose to the extent of 5-10% of the total solids.

The cloth-like fabric of M. Shoemaker[1] and produced from unwoven fibers, being highly absorbent and hence suitable for wash cloths, towels or napkins, is formed of wood pulp of long fibers and in sheets preferably uncalendered upon which is placed a cellulose ether coating. In one embodiment of the process, cellulose compounds are used which may be regenerated. A coating composition has been described[2] comprising ethylcellulose or benzylcellulose of low viscosity, the viscosity reduction being obtained by heating the ether of high viscosity with a dilute acid under pressure. After removing residual acid by washing, then drying, the cellulose ether is dissolved in a mixture of low boiling solvents with dibutyl phthalate, tricresyl phosphate or ethyl lactate added.

British Celanese, Ltd., and affiliates have described the preparation and utilization of several cellulose ether compositions suitable as lacquers and for pore-filling purposes. For instance, they have divulged an adhesive composition containing cellulose ethers[3], preferably in association with a synthetic resin also in the dissolved condition, in which a base as composition board is first coated with the cellulose ether lacquer, upon which is superposed a thin layer of plastic powder, and on top of this is placed a sheet of plastic. This four-ply veneer is then compacted by combined heat and pressure into a unitary-appearing whole. Their preferred low-boiling solvent for the formation of varnishes and coating compositions comprises an alcohol, an aromatic hydrocarbon and a halide of an unsaturated hydrocarbon, such as alcohol-benzene-ethylene dichloride

1. U. S. P. 1786781; abst. C. A. 1931, **25**, 813. E. P. 317330; abst. C. A. 1931, **24**, 2296. F. P. 679615; abst. C. A. 1930, **24**, 3911.
2. D. Traill and A. Levesley, Can. P. 322054.
3. W. Moss, U. S. P. 1815444; abst. C. A. 1931, **25**, 5535. W. Moss and B. White, Can. P. 302649; abst. C. A. 1930, **24**, 4647. See E. P. 313184, 342674.

(3:4:3), the mixture being an energetic solvent for methyl-, ethyl- and benzyl-cellulose[1].

In the formation of lacquers of a methyl-, ethyl- or benzyl-cellulose base[2], synthetic resins of the phenol-aldehyde type are associated with the etherized cellulose, utilizing resins melting between 40-50°, the lacquer made therefrom comprising the usual low and high boiling solvents. Acetone is an excellent solvent for both[3]. Resin lacquers of high adhesive power are formed from condensation products of acetone and phenol to form diphenylolpropane (acetone-phenol) and this is then condensed with formaldehyde to produce a readily fusible resin soluble in organic solvents[4]. The ether and resin and then dissolved together with volatile solvents to which plasticizing bodies may be added. If naphthalene is added[5], adhesion is said to be increased.

They have found that cellulose ethers of low viscosity characteristics fulfill all the requirements for lacquers and varnishes[6], especially methyl-, ethyl- and benzyl-celluloses having a viscosity of 0.1-50 determined with an Ostwald viscosimeter, using 6 gms. cellulose ether in 100 gms. benzene, viscosity being compared with glycerol taken as 100°. Any suitable solvents may be employed in fabrication of the lacquer as ethyl acetate, methyl acetate, benzene, toluene, ether, acetone or methyl or ethyl alcohols. Softeners and synthetic resinous products may also be incorporated. As an example, a coating composition having the following non-volatile components may be prepared: ethylcellulose (viscosity 1.) 10-15, resin or gum 10, softener 1-3. To 20 parts of the above is then added ethyl alcohol 67, acetone 22, and toluene 11. Basically similar lacquers result where

1. W. Moss, E. P. 299782; abst. J. S. C. I. 1930, **49**, 676-B.
2. W. Moss and C. Dreyfus, E. P. 296674; abst. C. A. 1929, **23**, 2585.
3. *Ibid.* E. P. 296675; abst. C. A. 1929, **23**, 2585.
4. W. Moss, E. P. 299781; abst. C. A. 1929, **23**, 3588.
5. *Ibid.* E. P. 301497; abst. C. A. 1929, **23**, 4071.
6. C. Dreyfus, E. P. 309951; abst. C. A. 1930, **24**, 739.

the cellulose ether is combined with a synthetic resin of the acetone-furfural type[1], solvents and plasticizers being added as above.

Coating compositions may be prepared by combining with the cellulose ethers by means of harmonious solvent combinations[2], diphenylolcycloparaffins as diphenylolcyclohexane, with the usual range of solvents. The lacquers produced as the result of the above combination, upon evaporation yield tenacious and elastic films. If rough or porous surfaces that require to be first filled are to be lacquered[3], it is recommended to use as a priming coat a composition containing a substantial proportion of non-drying oil or fatty acid, and then coat over with a lacquer of cellulose ethers with synthetic resins associated by means of volatile solvents containing a proportion of suppleness-inducing body[4]. By high solubility and low viscosity, the British Celanese, Ltd.[5], are able to produce cellulose ether lacquers containing up to 50% ethylcellulose or benzylcellulose, the lacquer being intended as a primer or filler for use on brick, wood or metals[6]. Diphenylolpropaneacetone resin[7], or diphenylol-propane resin, associated with a cellulose ether in solution materially increases adhesiveness. Diphenylolpropane-formaldehyde resin[8] has been described as also useful, and for the same purpose.

In order to impart to surfaces a comparatively dull or opaque appearance, a cellulose ether is dissolved in a mixed solvent the higher boiling constituent of which is not a solvent for the etherized cellulose[9], and as such a solution is

1. W. Moss, E. P. 307289; abst. J. S. C. I. 1930, **49**, 469-B.
2. British Celanese, Ltd., E. P. 342429; abst. C. A. 1931, **25**, 4421.
3. *Ibid.* E. P. 342211; abst. C. A. 1931, **25**, 4422.
4. *Ibid.* E. P. 342144; abst. C. A. 1931, **25**, 4421.
5. E. P. 348266; abst. C. A. 1932, **26**, 2070. C. Dreyfus, Can. P. 318370.
6. British Celanese, Ltd., W. Dickie and E. Greenwood, E. P. 360896, Addn. to E. P. 274841 and 314396; abst. J. S. C. I. 1932, **51**, 226-B.
7. British Celanese, Ltd., E. P. 342674; abst. C. A. 1932, **26**, 2833.
8. W. Moss, U. S. P. 1883396.
9. British Celanese, Ltd., E. P. 346269.

allowed to evaporate after having been applied to the surface intended to be coated, the increment of non-solvent increases with the result that ultimately incipient gelatinization takes place, and a non-transparent film is deposited[1].

A series of cellulose ether-oxyn lacquers has been described[2], being prepared by mixing solutions of cellulose ethers with or without the addition of softening agents, with oxyn solutions. Thus, a solution of ethylcellulose in the usual solvents is combined with a solution of linoxyn in amyl acetate, forming heavy lacquers and enamels of great durability. If slower drying is required in the lacquer, the ethylcellulose may be dissolved in a mixture of acetone with butyl phthalate or ethyl lactate added. L. Clement and C. Riviere[3] have described methods of manufacture of pigmented and colored cellulose ether lacquers, the mineral pigment being first ground in a small amount of water, then made into an emulsion in water with an emulsifying agent, and then incorporating the cellulose ether. Such lacquers, it is claimed, are inexpensive to produce on account of the low amount of volatile solvent required, and of a high degree of permanency.

In preparing seals for dry cells, P. Marsal[4] applies a thin coating of a cellulose ether to the mix body of the cell, and after this has dried, an additional seal of rosin, sealing wax or pitch may be poured on. The value of a cellulose ether coating is that it is practically water-proof and there is no liberation of free acid as is possible when nitrocellulose or acetylcellulose is used for the purpose. In preparing a painter's groundwork on canvas by means of cellulose derivatives[5], a groundwork of pigment miscible with water as chalk paste with water-soluble methylcellu-

1. W. Moss and B. White, E. P. 307290; abst. C. A. 1929, **23**, 5338.
2. G. Knoeffler, D. R. P. 542889; abst. C. A. 1932, **26**, 3125.
3. E. P. 350924; abst. C. A. 1932, **26**, 3124. F. P. 709195; abst. C. A. 1932, **26**, 1439.
4. Can. P. 282684; abst. C. A. 1929, **22**, 4070.
5. O. Ernst, D. R. P. 502865; abst. C. A. 1930, **24**, 5496.

lose is used, and after drying of this coating, a lacquer of ethylcellulose in alcohol is applied as the after-treating agent. The H. Mayer[1] washable paint is prepared by mixing the coloring material with a water-insoluble cellulose ether, and over this is painted a solution of water-insoluble ethyl- or benzyl-cellulose in an organic solvent. A glossy surface is thereby produced irrespective of the amount of pigment in the base coat.

Where it is desired to combine rubber with a cellulose ether or cellulose ester[2], the plasticizer as developed by Deutsche Hydrierwerke may be used, especially if films or molded articles are to be fabricated. This dual dissolvant is obtained by the condensation of carbonyl compounds with polyvalent alcohols, such as excess of cyclohexanol with glycerol in the presence of gaseous HCl. There is produced dihydrodioxols (2.2-pentamethylene-4-oxymethyldihydrodioxol), through substituted hydroxyl groups, whose special significance lies in the fact that rubber may be dissolved in a cellulose ether containing this solvent, or into a rubber solution dry ethylcellulose may be dissolved by warming and stirring.

In the coating of articles, especially those having metal surfaces[3], there is added first a primary coat containing a mixed ester of a polyhydric alcohol and a polybasic acid, such as obtained by combining glycerol with phthalic anhydride and linseed or china wood oil, and after this coating has dried, there is applied one or more coverings of a straight cellulose ether lacquer containing the usual volatile solvents with plastifiants added. A bonding coat of drying oil or pyroxylin is optionally applied over the priming coat before the top coat of cellulose ether is brushed or flowed on. To prevent livering or gelling of the coating composi-

1. D. R. P. 535167; abst. C. A. 1932, **26**, 1141.
2. F. P. 714837; abst. C. A. 1932, **26**, 1811.
3. C. Coolidge and H. Holt, U. S. P. 1863834; abst. C. A. 1932, **26**, 4487. E. I. du Pont de Nemours & Co., E. P. 287940; abst. J. S. C. I. 1929, **48**, 989-B.

tion 0.1-5% of substances such as oxalic, phosphoric, tartaric, citric, malic, formic or acetic acids may be added[1].

C. Stine and C. Coolidge[2] prepare a coating composition containing the cellulose ethers and rubber in order to impart additional flexibility and elasticity to the film, as is indicated by the following two formulas claimed as suitable:

1. A mixture of rubber 75 and ethylcellulose 25 parts is made, and to this is added 70 parts perilla oil, 1.2 parts cobalt linoleate, 4 parts butyl phthalate, 120 parts lithopone, 100 parts turpentine, and the solvent portion composed of benzene 200, with ethyl and butyl acetates 100 each.

2. Rubber 40, ethylcellulose 30, linseed oil 100, cobalt linoleate 1, zinc oxide 60, and the solvent portion benzene 400 parts. It is observed that the dissolving portion (volatile solvent) in this formula is inexpensive.

The rubber used may be either normal or deaggregated, and the cobalt linoleate merely representative of a class of driers which is appropriate. Manganese resinate may also be used. As a thinner, benzene, butyl acetate, toluene or alcohol may be used. A coating composition as in Ex. 2, when spread out in a thin film and air dried or heated at a temperature of 130° F. for 4 hrs., gives a hard, elastic, waterproof film. The approximate limits of drying are given as 8 hrs. at 80° F. to 1 hr. at 200° F. However, if the amount of oil is reduced and rubber-cellulose ether ratio changed to give an increased amount of cellulose derivative to rubber, more rapid drying can be obtained.

The cellulose ether composition of H. Hopkins and J. Segur[3], and which relates more particularly to compositions containing binary or multiple solvents having abnormal solvent power, has been formulated to make use of a cellulose ether of high dissolvant power associated with an

1. J. McBurney and E. Nollau, E. P. 278696; abst. C. A. 1928, **22**, 2673.
2. U. S. P. 1723632; abst. C. A. 1929, **23**, 4583.
3. U. S. P. 1855744; abst. C. A. 1932, **26**, 3376. E. P. 312309; abst. C. A. 1930, **24**, 960.

inexpensive water-insoluble liquid having little or no dissolving effect upon the cellulose ether, but which does not act as a direct precipitant of the same when incorporated in the cellulose ether lacquer. The mechanics of the formula and its practical application are clarified by the four following examples:

1. An ethylcellulose is selected which is soluble in butyl alcohol but insoluble in gasolene, to prepare an 8% solution in butyl alcohol, the solution having a viscosity expressed by 2.75 poises. To this solution gasolene is added in the proportion of 1 of gasolene to 2 of butyl alcohol, the viscosity of the mixture then being 1.44 poises. The proportion of non-solvent in the above formula permits of some variation, and the fluctuation in viscosity is small for mixtures containing the non-solvent in proportions varying from 0.33-0.66 of the whole.

2. A solution is prepared of ethylcellulose 8, butyl alcohol 33 and benzine 67. In this solution the alcohol and benzine have combined solvent power distinctly in excess of the sum of the separate solvent powers.

3. A composition is prepared of ethylcellulose 25, with ethylglycol and gasolene each 50, the combined fluid having a higher solvency than the sum of the separate solvent or dispersing powers of the two taken alone.

4. Ethylcellulose 10, rosin ester 5, blown linseed oil 10 and drier 1, is dissolved in a mixture of butyl lactate 2, butyl alcohol 18.5 and gasolene 55.5. In this example, the alcohol and gasolene have a combined dispersing or solvent power in excess of the sum of the solvent powers of the two substances, gasolene being substantially the non-solvent.

As a first component of the abnormal solvent binary constituting the active cellulose ether solvent, there may be employed alcohols such as methyl, ethyl, propyl, amyl, allyl or benzyl alcohol, glycerol diethyl ether or ethyl lactate. As the second component, there may be incorporated with the ethlycellulose benzine, pentene, hexane, heptane, amylene, hexylene or heptylene.

In preparing moisture-proof materials, especially transparent regenerated cellulose pellicles, suitable for the wrapping of foodstuffs and other articles usually wrapped in waxed paper, there is applied one or more coatings of a cellulose ether in solution as ethylcellulose and containing tricresyl phosphate, triphenyl phosphate, amyl phthalate or butyl phthalate as plasticizer. The transparent reconstituted sheets are either immersed in the cellulose ether lacquer, or the etherified cellulose in solution is sprayed on the film, usually in roll form, which is afterwards passed through a drying chamber for removal of the volatile solvent portion[1].

In the preparation of cellulose ethers containing softeners of the acetal type[2], it has been found that acetals having outside the acetal nucleus more than one ether group, and having relatively low vapor pressures are compatible with various cellulose derivatives and make excellent plasticizers for cellulose ethers and acetylated cellulose. The application of these acetals is indicated in the following examples:

1. Ethylcellulose 10, and acetal of diethyleneglycol ethyl ether 3 are dissolved in 87 parts benzene-toluene (1:1). This combination yields films of unusual softness, flexibility and clarity. Tests were made extending over three months, and showed no change in these properties.

2. Benzylcellulose 10, acetal of diethyleneglycol ether 2, and 88 parts toluene-butanol (1:1), produces clear, flexible films of properties similar to those in Ex. 1.

G. Ensminger[3] has published details of a non-chalking coating composition employing pigments, and which is said to produce coatings which do not disintegrate under the influence of the elements and leave minute particles of the pigments exposed on the surface, being prepared as indicated in the following type formula:

1. W. Charch and K. Prindle, U. S. P. 1826696, 1826699.
2. E. I. du Pont de Nemours & Co., E. P. 318980.
3. U. S. P. 1860532.

9.9 parts benzylcellulose, 2.6 of dammar, 1.7 butyl phthalate, 0.8 chrome green, 4.6 leaded zinc oxide and 2.1 bone black are mixed and incorporated into a solvent mixture comprising denatured alcohol 10, ethylglycol acetate 3.6, butyl acetate 3.8, ethyl acetate 30.1, toluene 27.7 and amyl alcohol 3.1, to make 100 parts. It is said that this formula in lacquer when applied to surfaces in Florida where the weather conditions as to extremes of heat are severe, showed no signs of disintegration long after previous lacquers became bady chalked and far on the road towards entire disintegration.

P. Seel[1] has described a cellulose ether lacquer, in which ethylcellulose is made into a film-flowable composition by means of ethyl butyrate, benzene and ethyl alcohol. A similar composition[2] may be formed from ethylcellulose 4, butyl alcohol 20 and benzene 76, or ethylcellulose 3, amyl alcohol 15 and toluene 82, or else ethylcellulose and amyl alcohol 5 each, butyl alcohol 15 and xylene 75. The Farbwerke vorm. Meister, Lucius & Brüning[3] prepare cellulose ether compositions suitable for printing or staining paper, leather and fabrics by brushing or spraying lacquers consisting of a pigment dye intimately mixed with a resin or solid fatty acid suspended in a cellulose ether varnish, the pigment being either worked up directly with the cellulose ether and then solvents added, or else the coloring matter is incorporated with the fatty and resinous component, and this introduced into the cellulose ether lacquer. E. Fischer[4] has determined the proportional solubilities of the various ingredients of varnish, including the cellulose ethers.

In the waterproofing of shells to make them stiffer and for obtaining better firing patterns[5], especially in shotgun shells, either solutions of methyl-, ethyl- or benzyl-cellulose may be used as indicated thus:

1. U. S. P. 1405448.
2. A. Trivelli, U. S. P. 1458256; abst. C. A. 1923, **17**, 2645.
3. E. P. 246447; abst. C. A. 1927, **21**, 504.
4. Farbe und Lack, 1930, #30, 350; abst. C. A. 1930, **24**, 4646.
5. C. Burke and F. Hann, E. P. 315227; abst. C. A. 1930, **24**, 1741. See E. P. 316323, 356446, 357123.

1. 18 parts benzylcellulose and 100 parts of a solvent comprising ethyl acetate 25, butyl alcohol 10, toluene 35 and xylene 30, are used as a spraying lacquer over paraffin impregnated shells. One coating of the above composition is said to increase the time limit of immersion in water without swelling or opening of the crimp from 2 to 7 hrs., while with two coats, the shell is still good after 19 hrs. immersion.

2. Benzylcellulose 16 parts and 100 parts of the above solvent in Ex. 1 may be used as a dipping lacquer, two coats giving complete protection for 16-20 hrs.

3. Ethylcellulose 12 parts, kauri 6, butyl phthalate 4 and 50 parts each benzene and toluene admixed, are used as a dipping lacquer for paraffined shells. The immersion limit has been found to be increased from 2 to 7 hrs. The above compositions may be used on the shells before loading and the shells may be baked to increase the water resistance.

For the preparation of a black lacquer of cellulose ether base[1], it is directed to dissolve furyl alcohol in the lacquer and then add a small amount of sulfuric or hydrochloric acids, ethyl sulfate, benzenesulfonic acid or zinc or ferric chlorides, which react with the furyl alcohol to produce a substance of a black color, which in nowise substantially affects the glossiness or luster. Spicers, Ltd.[2], have been granted a patent which concerns a process for preparing masses from cellulose ethers by the use of hexachlorpropane or heptachlorpropane, which are said to be superior to similar lacquers employing hexachlorethane or pentachlorpropane, the amount of hexa- and hepta-chlorpropane required for plasticizing being much less.

The emulsion type of lacquer as devised by G. Davies and W. Jenkins[3] involves the use of methylcellulose of the water-soluble variety as the emulsifying agent, aqueous emulsions of nitrocellulose being producible by the use of

1. C. Fawkes, U. S. P. 1732124; abst. C. A. 1930, **24**, 252.
2. D. R. P. 514945; abst. C. A. 1931, **25**, 2289. F. P. 696603; abst. C. A. 1931, **25**, 2848. See E. P. 279139. Can. P. 275323.
3. Australian P. 23004.

aqueous solutions of methylcellulose (Colloresin D) either alone, or in conjunction with other dispersing agents as saponin, sulfonated castor oil and similar derivatives when not incompatible. Cellulose ether lacquers may also be produced by working according to the directions as laid down by W. Crooks and C. Walton[1], who first treat the etherized cellulose by means of a solvent in the vapor phase until it swells strongly, and then by a liquid solvent combination, it having been found that by proceeding in this manner, the porosity of the gaseous treated ether becomes so porous that either less quantities of solvent are required to effect solution, or a mixed solvent of lowering dissolving power and less expensive may be used.

A cellulose ether varnish has been described[2] obtained by heating drying oils as linseed oil or a mixture of linseed and china wood oil, to about 270-280° until polymerization commences. Air is then bubbled through and the heating continued to 310° or more. When the boiled oil has partially cooled, finely comminuted cellulose ether may be stirred in, or a cellulose ether solution incorporated with the cooled oil mixture in the proportions desired. To decrease the permeability to water of articles composed of regenerated cellulose or water-impressionable cellulose ethers[3], the cellulose ether is subjected to a preliminary treatment with a water-miscible liquid as formic or acetic acids capable of causing the etherized cellulose gel to swell and soften, and is also a solvent of the organic or inorganic cellulose ester which is to be applied thereto. When the product is in the swollen condition, it is then treated with (say) an acetic acid solution of cellulose acetate, or the acetic acid may be dissipated before the cellulose ester solution is applied. Diamyl phthalate is a useful addition to the acid.

1. U. S. P. 1835997. E. P. 303152; abst. C. A. 1929, **23**, 4542.
2. G. Ruth, A.-G., and E. Asser, F. P. 694074; abst. C. A. 1931, **25**, 2011. G. Knoeffler, D. R. P. 542889.
3. Wolff & Co. and R. Weingand, E. P. 298605; abst. C. A. 1929, **23**, 3097. See E. P. 245683, 257924, 262440, 273564, 274054, 276206, 277309, 298609, 304717.

For the manufacture of lacquer coatings, films and plastic masses utilizing the cellulose ethers according to directions published by I. G. Farbenindustrie[1], there are added in the manufacture non-volatile or difficultly volatile organic bases as the substituted guanidines in order to increase the stability on ageing. Such suitable bodies have been found to be triphenylguanidine, the biguanides such as *b*-naphthylguanide, aralkylated aromatic bases as benzylaniline, dibenzylaniline, carbazole, N-ethylcarbazole and methyl, ethyl and propyl aminobenzoates as examples of aminobenzoic acid esters. The invention is illustrated as follows:

1. 7 parts butylcellulose are dissolved in a mixture of ethyl acetate and benzene 11 each, toluene 5, ethylglycol 9, and xylene and alcohol 10 each, with the addition of 0.15-0.2 part by weight of N-ethylcarbazole. Coatings obtainable from this lacquer are said to be distinguished by lasting about 4 times as long as the corresponding lacquer films free from carbazole. For the producing of a covering butylcellulose lacquer, the above composition is mixed with 10 parts zinc white and 1-2 parts butyl phthalate.

2. For the manufacture of a stable film, 20 parts benzylcellulose and 2 parts tricresyl phosphate with 0.4-0.5 *b*-naphthylbiguanide, are dissolved in 75 parts benzene and 5 parts alcohol. Films obtainable from this solution are said to last approximately five times as long as the corresponding benzylcellulose films free from base, the advantage being particularly observable under the action of ultra-violet rays.

They prepare lacquers and similar coatings suitable for use on hard or porous surfaces[2] by the mechanical dispersion of water-insoluble cellulose ethers by grinding, with or without first gelatinizing by addition of water, by adding to the aqueous dispersion an aqueous emulsion of a solvent or softening agent. Hard surfaces as metals

1. E. P. 342288; abst. C. A. 1931, **25**, 4725.
2. I. G. Farbenind., A.-G., E. P. 330897; abst. C. A. 1930, **24**, 6039.

or glass are best coated by applying thereto a first or priming coat of nitrocellulose solution, and after this has dried, superimpose one or more coatings of cellulose ether lacquer[1]. Such cellulose ether lacquers may be colored by incorporating basic dyestuffs with them[2], which may also contain acid groups, together with complex salts capable of forming color lakes with the dyestuffs. Suitable acids are phosphotungstic, phosphomolybdic, silicotungstic and phosphotungstomolybdic. The dystuffs and acids may be added either in the solid form or dissolved in such liquids as alcohol, glycol, glycerol or their esters or ethers. Methyl Violet B extra and Alkali Blue B are especially suitable for this use[3]. Lithol Fast Scarlet R is also useful[4] in this connection, being freely soluble in solvents dissolving the cellulose ethers. In the use of acetals as cellulose ether solvents[5] (see p. 1873), it has been found that better results are obtained if water is omitted in the formula[6].

Plastic, filler and priming compositions for application to wood, paper and other porous materials[7] may be increased in body, and the films deposited therefrom rendered more resistant to wear, by incorporating in the cellulose ether solution inorganic fillers of a scaly or foliaceous structure, such as graphite, talcum or mica in very fine state of subdivision, all of these products being neutral in character and insoluble in water or the usual organic solvents. If it is desired to produce colored solutions or masses comprising cellulose ethers[8], lacquers are prepared with salts formed by dyes containing sulfonic or carboxylic groups with organic derivatives of ammonia in which the ammonia N-atom

1. W. Moss, E. P. 298608; abst. C. A. 1929, **23**, 3098. See E. P. 298616.
2. I. G. Farbenind., A.-G., E. P. 275969. See E. P. 302615, 302616; abst. C. A. 1929, **23**, 4307.
3. *Ibid.* F. P. 642799; abst. C. A. 1929, **23**, 1517.
4. *Ibid.* E. P. 293485; abst. C. A. 1929, **23**, 1749. See E. P. 247288.
5. *Ibid.* E. P. 286789; abst. C. A. 1929, **23**, 513.
6. *Ibid.* E. P. 289523, Addn. to E. P. 286789; abst. C. A. 1929, **23**, 704.
7. *Ibid.* E. P. 296796; abst. C. A. 1929, **23**, 2540.
8. *Ibid.* E. P. 293067; abst. C. A. 1929, **23**, 1517.

is not bound to such a C-atom as is itself directly connected with two other N-atoms. Suitable bases are alkylamines and their derivatives such as ethylamine and di- and triethanolamine, or compounds as dimethylaniline, xylidine, pseudocumene, cyclo- and dicyclo-hexylamine, pyridine, piperidine and quinoline. The original patent gives several specific examples.

For manufacturing colored brushwork lacquers[1], which will furnish coatings possessing a high gloss and without further treatment when dry, water-insoluble cellulose ethers may be used, glycolmonoalkyl ethers or esters or glycoldialkyl ethers, in association with the usual solvents. Glycol monoethyl ether is especially suitable. Where it is desired to produce a lacquer depositing as a dull or matt finish[2], a plastic mass containing a cellulose ether and a high-boiling hydrocarbon, fat or oil are dissolved together in a liquid mixture which is a solvent of all ingredients. A suitable composition for this purpose may be prepared by combining ethylcellulose in solution with a condensation product of naphthalene with xylyl chloride, which is soluble in a mixture of benzene and alcohol, as are the cellulose ethers.

In preparing cellulose ether oxyn lacquers[3] films are obtained from evaporation of the solutions said to be exceptionally stable to elevated temperatures. The solutions may be used as spraying, dipping or brush lacquers depending upon the total non-evaporable solids therein, and the adjustment of boiling point and evaporative speed of the volatile solvent portion. The following illustrates the main points in the invention:

1. 2 gms. of a 5% solution of ethylcellulose in acetone and 1.5 gms. of a 20% solution of linoxyn in amyl acetate, yield an ethylcellulose linoxyn solution, which on evaporation forms in a very short period, a tough and lustrous film.

1. I. G. Farbenindustrie, A.-G., E. P. 294158; abst. J. S. C. I. 1928, **47**, 719-B.
2. *Ibid.* E. P. 309194; abst. C. A. 1930, **24**, 509. L. Lock and E. Hubert, D. R. P. 479083; abst. C. A. 1929, **23**, 4836.
3. *Ibid.* E. P. 307361; abst. C. A. 1929, **23**, 5338. F. P. 670762; abst. C. A. 1930, **24**, 1996.

2. Two kilos of benzylcellulose solution obtained by dissolving 150 gms. benzylcellulose in a mixture of 75 gms. tricresyl phosphate, 700 gms. acetone and 75 gms. amyl acetate, are mixed with 700 gms. of a 20% solution of linoxyn in amyl acetate. The solution on evaporation yields a pliable, smooth, lustrous film.

For the protection of metal surfaces against corrosion, it is a prime requisite that the lacquer outer film shall not only adhere with great tenacity, but that the film substance shall be unduly permanent in all normal climatic changes. Such a lacquer has been described by the I. G. Farbenindustrie[1] and obtained by the utilization of a highly benzylated benzylcellulose. Particularly effective coatings are said to result if there is incorporated in the lacquer solution, a heavy metal salt of an acid of relatively high molecular weight, such as a heavy metal salt of a fatty acid, naphthenic acid or resin acid (abietic acid). Such suitable salts are copper naphthenate or oleate, lead naphthenate, or ferric stearate, laurate or resinate. By selecting a copper salt, which is destructive to lower animal and vegetable organisms, lacquers particularly useful for coating ship's bottoms and other submerged materials result. Thus:

1. A coating preparation is made of 10-15 parts benzylcellulose, 50 parts each benzene and xylene, 6-9 parts tricresyl phosphate and 5 parts copper naphthenate. Instead of copper naphthenate, there may be used a naphthenate of lead, iron, nickel or cobalt.

2. A coating composition is prepared from dissolving 15 parts benzylcellulose in a mixture of 50 parts each benzene and xylene, 10 parts alcohol, 9 parts tricresyl phosphate and 2 parts ferric stearate. Instead of the latter, the same amount of ferric laurate or resinate or cupric laurate may be used.

Lacquers and similar coatings intended primarily for

1. E. P. 323525; abst. J. S. C. I. 1930, **49**, 204-B. F. P. 685163; abst. C. A. 1930, **24**, 6040. Can. P. 304969. H. Schladebach and H. Hähle, U. S. P. 1844983; abst. C. A. 1932, **26**, 2333. See F. P. 687119.

application to absorptive material such as wood, natural or imitation leather, brickwork, asbestos, paper or textile fabrics[1] are obtained by means of solutions in which methyl- or ethyl-cellulose of the water-soluble type is used as emulsifying agent, the wood or other material to be coated being sprayed, immersed, brushed or printed. The process is made clear by reference to the following two examples:

1. 100 parts of a 4-8% nitrocellulose solution in a mixture of ethylglycol, benzyl alcohol, methyl and ethyl acetates, and which has been colored with 1-5 parts Lithol Fast Scarlet R, are emulsified in 250 parts of 5% aqueous methylcellulose solution, to which 5-10 parts butyl phthalate are introduced while shaking. The lacquer is then ready for immediate use.

2. 20 parts nitrocellulose of the alcohol-soluble variety and giving solutions of low viscosity, are moistened with 10 parts butyl alcohol, and then dissolved, together with 5 parts of a resin obtained by condensing cyclohexanone, in 62 parts butyl glycol and the addition of 10 parts tricresyl phosphate, and 3 parts Lithol Fast Scarlet R. Of this lacquer, 110 parts are emulsified with 5 parts methylcellulose and 0.5 part sodium mono- or di-butylnaphthalenesulfonate and glue in 94.5 parts water, to which a further 50-60 parts of water may be subsequently added. The emulsion thus formed gives suitable coatings on wood or leather.

The solubility or property of swelling of methylcellulose in water, while valuable in some technical applications, is precluded in others from this fact. G. Balle and K. Sponsel have discovered a method whereby the solubility of methylcellulose or its solubililty in water may be attenuated nearly to zero[2], by adding thereto in solution or in the swollen condition, materials which form colloids with

1. I. G. Farbenind., A.-G., E. P. 334567; abst. C. A. 1931, **25**, 1108. F. P. 688315; abst. C. A. 1931, **25**, 834.
2. D. R. P. 527197; abst. C. A. 1931, **25**, 4705.

the aqueous solution, and intimately mixing them. A film produced from such a solution is no longer soluble in water after drying. Among such insolubilizing materials are phenol-formaldehyde artificial resins, linseed oil and benzyl alcohol. One may proceed as follows:

1. To 100 parts of a 5% solution of methylcellulose in water, there is added 2 parts of finely pulverized ethylcellulose moistened for this purpose with water, but which is insoluble in water. The mixture is stirred until a homogeneous mixture has resulted. If now the solution is poured out on a glass plate and the water allowed to evaporate, there remains behind a clear foil or pellicle, scarcely soluble in water.

2. 100 parts by weight of 10% methylcellulose solution in water are treated with 10 parts of approximately 35% latex emulsion and uniformly stirred. When poured onto a glass plate the mixture leaves on evaporation of the water, a foil completely insoluble in water.

Where colored lacquers or varnishes are desired where composed of the cellulose ethers or organic cellulose esters[1], the color is imparted by using salts of sulfo- or carboxylic acid dyes with organic dye bases. Thus, auramine base is ground with the diazo dye from tetrazotized dianisidine and 1.8-aminonaphthol-2.4-disulfonic acid and alcohol. This material may then be directly incorporated with the cellulose ether lacquer by means of solvents harmonious to both.

An especially high water-resistance to water-soluble cellulose ethers as the methylcelluloses and not maximum ethylated ethylcellulose may be imparted by the addition thereto of oxidized or drying oils or benzyl alcohol, and especially by submitting the cellulose ether to heat or to the action of ultra-violet light[2]. Also the addition of condensation products of urea and formaldehyde or phthalic

1. K. Holzach and W. Mueller, D. R. P. 529840; abst. C. A. 1931, **25**, 5304. See E. P. 330895.
2. G. Balle and K. Sponsel, D. R. P. 542287, Addn. to D. R. P. 527197.

acid and polyvalent alcohols, esters of vinyl alcohols and acrylic acid esters, which are either water-soluble or capable of being emulsified. Thus:

1. 100 parts by weight of a 10% aqueous methylcellulose solution are treated with about 5 parts by weight of linseed oil or linseed oil foots, which is then contacted with the methylcellulose in a very finely divided condition, so that the mixture can be worked up into a film, which on evaporation of the solvent is still soluble in water, but which nevertheless completely loses this property when, with excess of air it is heated about 4 hrs. at 100-110°. The linseed oil has now been converted into linoxyn, either insoluble or soluble with difficulty in the common solvents, and the presence of which retards access of water to the methylcellulose particles. The time of heating may be made shorter, if one of the usual siccatives is added to the linseed oil. The operation can also be worked at room temperature only a longer time is required for the conversion.

2. To 1000 parts of a 15% aqueous solution of ethylcellulose there is added 15 parts of a condensation product of urea and formaldehyde which is no longer soluble in water, and this product is introduced into the ethylcellulose solution in fine, uniform condition. A film prepared from this mixture is heated 2 hrs. at 80-100°, after which it has become completely insoluble in water.

In the preparation of cellulose ether lacquers containing synthetic resins[1], use is made of resinous condensation products in a finely divided condition of urea or methylolurea, as indicated by the following example:

1. 120 parts dimethylolurea and 136 parts dimethylthiourea are introduced with stirring into a mixture of 380 parts *n*-butyl alcohol and 20 parts oxalic acid and kept at about 100°. After dissolution, the temperature is kept at 85° for another 15 min. and the solution then neutralized while stirring, by adding 50 parts trisodium phosphate, cooled to room temperature and filtered. It is then washed

1. I. G. Farbenind., A.-G., E. P. 344626, Addn. to E. P. 327673.

with ethyl alcohol and dried *in vacuo* at 30-50°. This product may be worked up into lacquers together with cellulose ethers, coatings obtained showing a high gloss.

Lacquers and artificial coatings are made from solutions of cellulose ethers and cellulose esters of the higher fatty acids as cellulose naphthenate and cellulose abietate[1], and combined by means of the usual solvents to form films upon drying which are extremely flexible and tenacious. Ethylcellulose with cellulose trilaurate dissolved together forms durable films and coatings. For example:

1. 50 parts water-insoluble ethylcellulose are dissolved in 100 parts linseed oil varnish at 140°, to which is then added an organic or inorganic pigment about 15-20 parts. The mass formed is of high viscosity and may be applied as such or thinned with solvents common to both oil and cellulose ether to the consistency desired.

2. 50 parts ethylcellulose as before are dissolved with 50 parts stearic acid and 30 parts ceresin at 130°, and in this solution is added 10 parts carnauba wax and 3 parts soluble azo color soluble in oil. Crayons are obtainable from the above without thinning, or after suitable dilution, lacquers especially applicable as filler coats are obtained.

3. An excellent lacquer is said to be obtained by mixing 30 parts water-insoluble ethylcellulose, 50 parts linseed oil varnish, and 150 parts each xylol and tetralin. This lacquer is slow drying on account of the low volatility of the volatile solvent portion.

4. 20 parts ethylcellulose are dissolved in a mixture of 50 parts copper oleate and 20 parts paraffin at 140°. When the mass has become homogeneous there is added 10 parts elemi and 10 parts of an inorganic red pigment at 130-140 with continual stirring. There is obtained a pasty mass which may be diluted with volatile solvent thinners and used as a lacquer.

5. Dissolve together 45 parts cellulose trilaurate, 30 parts paraffin and 30 parts ethylcellulose together at 160°.

1. I. G. Farbenind., A.-G., F.P. 660510; abst. C.A. 1930, **24**, 252.

The product as is may be employed for insulation purposes, or diluted with a mixture of acetone, glycol and benzene, forms an efficient lacquer for spraying, immersing or brushing.

An inexpensive lacquer utilizing the solvency of carbon bisulfide for the cellulose ethers has been devised[1], a representative lacquer formula being made by dissolving triethylcellulose in benzene to a clear solution and adding a proportion of carbon bisulfide, or dissolving the cellulose ether directly in a mixture of benzene 8%, CS_2 92%. This lacquer evaporates readily due to the rapid evaporation of the solvents, and it is to be remembered that carbon bisulfide is both very poisonous and inflammable. An excellent lacquer is said to result by dissolving 7 parts triethylcellulose in 96 parts carbon bisulfide and 4% acetone.

A cellulose ether lacquer has recently been described by the I. G. Farbenindustrie[2], in which 2 parts of a condensation product of cyclohexanone or methylcyclohexanone are mixed with 80 parts toluene, 5 parts each benzene and alcohol and 10 parts ethylcellulose. The plasticity of the solution may be augmented by the addition thereto of 4 parts dibutyl methylenetetrahydrophthalate and 4 parts iron oxide or zinc oxide. Inks, lacquers or plastic compositions result from dissolving cellulose ethers in aliphatic homologues of 1.4-dioxane, as dimethyl- or diethyl-1.4-dioxane, which are slow evaporating and leave tenuous films which do not blush or bloom[3].

A lacquer for printing on tin foil by means of an intaglio printing machine has been disclosed[4]. It may be prepared by mixing 150 parts of water-insoluble ethylcellulose with 80 parts butyl phthalate, 20 parts esterified colophony, 525 parts xylene, 150 parts butyl alcohol and 75 parts ethylglycol, and then stirring 150 parts gold bronze into the colorless lacquer. The general process involves the use of

1. I. G. Farbenind., A.-G., Swiss P. 133158. 2. D. R. P. 543825.
3. I. G. Farbenind., A.-G., E. P. 326824; abst. C. A. 1930, **24**, 4945.
4. *Ibid.* E. P. 318567; abst. C. A. 1930, **24**, 2316.

anhydrous lacquers containing cellulose ethers with addition of suitable pigments for printing by means of deeply engraved plates or rollers on non-resilient bases, which may, if necessary, be rendered smooth and even by previous application of a coating of lacquer or varnish which is allowed to dry.

In the dyeing or coloring of lacquers and varnishes[1], there is dissolved therein in the molten condition a non-sulfonated, non-carboxylated mordant dye, and treating the solution in the absence of water with a heavy metal salt of an organic acid as a resin acid or naphthenic acid. For instance, a solution of 4-chlor-*o*-aminophenol + 2.3-hydroxynaphthoic anilide in warm cellulose laurate varnish is treated with cobalt naphthenate, producing a red-violet; 4-nitro-*o*-aminophenol + phenylmethylpyrazolone in warm linseed oil with cobalt stearate produces yellow-brown; 3.5-dichlor-*o*-aminophenol + 2.3-hydroxynaphthoic anilide and triethanolamine in warm benzylcellulose varnish with cobalt naphthenate produces a violet.

A process for manufacturing cellulose ether lacquers emanated from Germany in 1931 in which cellulose ethers are utilized which contain in addition to methoxyl and ethoxyl groups[2], alkoxyl groups with more than 2 carbon atoms, when dissolved in mixtures of aromatic hydrocarbons and paraffin alcohols, the lacquer films obtained from them being completely resistant to benzine. The solvent mixtures capable of being used are said to be considerably more harmless physiologically than the aromatic hydrocarbons, and are distinguished from the simple alkylcellulose lacquers by a much higher stability. The range of suitable base products and their application are indicated in the following examples:

1. 20 parts ethylpropylcellulose (containing 32.5% ethoxyl and 12.5% propoxyl) are dissolved in 40 parts ben-

1. I. G. Farbenindustrie, A.-G., E. P. 309148; abst. Brit. Plastics (Molded Products), 1930, **2**, 134.

2. L. Rosenthal and R. Hebermehl, D. R. P. 525424; abst. C. A. 1931, **25**, 4139. L. Rosenthal, Can. P. 310150.

zine (b. pt. under 100°), 40 parts "hydroaromatic benzine" (b. pt. 130-150°), 65 parts alcohol and 35 parts butyl alcohol, with 2-4 parts butyl phthalate. There is obtained a spraying lacquer, which dries upon wood with a high polish.

2. A brush lacquer suitable for rust protection purposes results from dissolving 10 parts ethylbutylcellulose (31% ethoxyl, 13% butoxyl), 25 parts alcohol, 10 parts ethylglycol, 10 parts butylglycol, 5 parts cyclohexanol, 20 parts sanga oil and 20 parts turpentine oil. This solution also contains 5-7 parts glyceryl abietate, 5-7 parts tricresyl phosphate and 10 parts either red ferric oxide or zinc oxide.

3. A wood filler lacquer results from dissolving 10 parts ethylbutylcellulose in 15 parts butyl acetate or methylglycol acetate, 25 parts ethylglycol, 50 parts turpentine oil and 20 parts linseed oil varnish.

4. A brush lacquer may be prepared by dissolving 6-10 parts ethylbutylcellulose, 45 parts butylglycol, and 45 parts lacquer benzine, b. pt. 150-180°. Plastifiers and readily volatile solvents may also be added.

5. 10 parts methylbutylcellulose are dissolved in 35 parts alcohol, 40 parts benzine (b. pt. 80-100°) and 15 parts butyl alcohol. There is obtained a clear and completely transparent solution, drying with a high luster and of good stability.

Lacquers, priming compositions and filling and top coats for porous or non-porous bases may be prepared from ethyl-, ethylbutyl- and benzyl-cellulose with resinous condensation products of polybasic acids and derivatives of polyhydric alcohols containing at least one free hydroxyl group, which either dissolve or swell considerably in benzene[1], or other hydrocarbons. The resinous condensation products suitable for addition to the cellulose ethers for lacquer and varnish purposes, may be obtained from phthalic, succinic or maleic acid, ether-dicarboxylic acids

1. I. G. Farbenind., A.-G., E. P. 330895; abst. C. A. 1930, **24**, 6041. F. P. 687119; abst. C. A. 1931, **25**, 833. Belg. P. 366433. See F. P. 685163.

such as diglycollic or salicylacetic acids or chlorphthalic acid, or from glycerol, sorbitol, pentaerythrite, or partial esters of abietic, linoleic, ricinoleic or naphthenic acids, which esters contain at least one free hydroxyl group.

Illustrative examples of the application of this wide range of compounds to the various cellulose ethers are indicated in the following seven examples:

1. 100 parts ethylcellulose benzene-soluble and 20-50 parts of a resinous condensation product from 3.5 mols. phthalic acid with such a proportion of glyceryl linoleate containing one or two esterified hydroxyl groups as may be obtained from 3 mols. glycerol and 1 mol. linoleic acid, are dissolved in a mixture of 700 parts benzene, 100 parts toluene and 50 parts ethyl alcohol. The solution is especially applicable for wood coatings. A resin obtained from phthalic acid-glycerol-lauric acid may be employed instead of the resinous condensation product above stated.

2. 100 parts benzene-soluble ethylcellulose or of an ethylbenzylcellulose soluble in benzene-ethyl alcohol (1:1), 20 parts of a resin obtained from phthalic acid and a colophony glyceride still containing free hydroxyl groups, and 10-20 parts butyl phthalate, are dissolved in a mixture of benzene 400, xylene and alcohol each 150, butyl alcohol 100, and 60 parts butyl acetate. 10 parts Lithol Fast Scarlet RN powder are then added to the solution. A covering lacquer is thus obtained, especially suitable for application to sheet metal which has received a priming composition, or on wood.

3. 50 parts benzene-soluble ethylcellulose and 150 parts of a resin obtained from 3.5 mols. phthalic acid, 1 mol. linoleic acid and 3 mols. glycerol are dissolved in a mixture of benzene 550, toluene 200, ethyl alcohol 50. The solution, to which fillers as slate meal or aluminum bronze may be added, is applied to substrata and may then be thoroughly dried at 80-100°. In order to accelerate the drying of the coating, 0.1-0.5 parts cobalt linoleate may be added.

4. 50 parts benzylcellulose and 25 parts of a viscous resin prepared from hydroxyethyl linoleate and phthalic acid are dissolved in a mixture of benzene 300, toluene 400, 50 parts each ethyl alcohol, butyl alcohol, ethylglycol and butyl acetate. Into the solution is incorporated Lithol Fast Scarlet RN powder. The lacquer obtained, which may be incorporated with from 10-20 parts butyl phthalate for increasing the elasticity of the coatings, is indicated for coating wood or metal surfaces, and may be used with a colorless nitrocellulose lacquer.

5. 50 parts benzylcellulose, 20 parts of a resinous condensate from 2 mols. each of glycerol, colophony and palmitic acid and 1 mol. maleic acid are dissolved together with 10-20 parts butyl phthalate in the solvent mixture of Ex. 4, and 100 parts Milori blue added. The lacquer may be sprayed on wood, and the glossiness of the coating increased by spraying thereon as a top coat, a colorless nitrocellulose lacquer.

6. 50 parts benzene-soluble ethylcellulose and 25 parts of a resinous condensate of 6 mols. each of glycerol and ricinoleic acid and 5 mols. phthalic acid are dissolved in a mixture of benzene 920, ethyl alcohol 30 and 100 parts titanium white added. The lacquer gives good coatings on wood or metal, the elasticity of which may be increased by adding to the above mixture 10 parts tributyl phosphate.

7. 10 parts ethylbenzylcellulose soluble in benzene-alcohol (1:1), 100 parts of a viscous resinous condensate of hydroxyethyl linoleate and phthalic acid, and 10-20 parts benzylnaphthalene are dispersed, together with 100 parts each lithopone, iron oxide and slate meal, in a mixture of benzene 100, xylene 125, ethyl alcohol 85, and 10 parts butyl alcohol. The fillers are preferably rolled together with the resinous condensate before the dispersion. A primer suitable for spraying is obtained, the coating deposited being covered with further lacquer coatings.

Film Crystal Effects. In 1920 a process was described for the decoration of films of cellulose acetate or other

organic cellulose derivatives[1] in order to produce films simulating effects produced by snow or resembling frost on a window, and obtainable by dipping or painting objects with a solution of the cellulose compound in a volatile solvent in which is dissolved a crystalline or crystallizable material as an inorganic salt or an organic body. Upon evaporation of the solvent portion, the salt or other crystallizable product is deposited in crystalline form, the nature and extent of effect produced being modified by a selection of the crystallizable material as to its relative degree of solubility in the menstruum in which the cellulose compound is dissolved. As suitable compounds inducing crystalline effects were specified triphenyl phosphate, ureas, picric acid or alkaloids. Picric acid would be applicable only if the film were colored yellow. Nearly all the alkaloids are too expensive for this use.

Six years later appeared the disclosure of C. Ferguson[2] in which in a solution of acetylcellulose or other cellulose derivative, is dissolved a proportion of *p*-chlorbenzene, benzoic acid or triphenyl phosphate and a lacquer film made therefrom, a frosted glass effect being induced by evaporation to dryness and allowing the organic compound to crystallize out. By applying the lacquer to paper or cloth, for instance, beautiful materials as transparent or translucent lamp shades are possible. Cellulose derivative 12, to dichlorbenzene 45, is the ratio preferred. A small amount of dyestuff may be added to heighten the pleasing effect, light pinks and blues being especially attractive.

In a process patented in France[3], decorative effects are obtained by dissolving in a lacquer or varnish cholesterol, salicylic acid, *p*-dichlorbenzene, *b*-naphthol or tri-phenyl phosphate. Cellulose ether or ester varnishes are preferred

1. Societe Clement & Riviere, F. P. 529178; abst. Chim. et Ind. 1922, **8**, 644.
2. U. S. P. 1589875; abst. C. A. 1926, **20**, 3084.
3. Vernis Soehnee Freres, F. P. 707092; abst. C. A. 1932, **26**, 610.

for this purpose. A. Kraus[1] has given formulas for the preparation of iridescent nitrocellulose lacquers in which fine, crystalline metallic salts are dissolved and the solvent portion of the lacquer dissipated to induce crystallization of the salts.

In 1930 two patents were granted A. Pearl[2] for an oramental coating using a cellulose derivative lacquer as a basis which is spread on paper or other surface, after first dissolving therein such bodies as benzoic or salicylic acids, resorcinol, borneol terpene hydrate, menthol, thymol, and especially monobromcamphor, the latter forming long, radiating monoclinic crystals, subliming at 76°. After the volatile solvent has been removed by evaporation, the product is heated at a temperature above the subliming point of the added chemical, but below the decomposition point of the cellulose derivative, in order to vaporize the crystalline material. Upon its expulsion by heat, there remains on and in the coated surface the natural design or configuration of the crystal in intaglio, presenting a remarkable crystalline appearance, forming radiating crystals of a silky or satiny appearance. Of course, it is impossible to produce the same design twice.

If it is not desired to use heat to expel the crystals, a solvent for the crystal which is a non-solvent of the cellulose derivative may be used[3]. Taking salicylic acid as an example, 1.9 gms. dissolve in 700 cc. water at 20°, whereas 111 gms. sodium salicylate dissolve in the same amount of water at 15°. Therefore, in order to more expeditiously remove the salicylic acid, the dried film is treated with an aqueous solution of sodium borate or phosphate, whereas the acid is transformed into sodium salicylate readily washed away by means of water. If the film is tinted, the dyestuff used must be unattacked by the solvent used to remove the crystals. By manipulating the solvents as to

1. Farbe u. Lack, 1932, 110; abst. C. A. 1932, **26**, 2332.
2. U. S. P. 1775691; abst. C. A. 1930, **24**, 5516.
3. A. Pearl, U. S. P. 1844479.

their relative speed of evaporation, larger or smaller crystal effects are possible, and the beauty of appearance may be enhanced by the addition to the lacquer of small amounts of colored bronzes or mother-of-pearl essence to impart a fluorescent, dichroic, iridescent or nacreous appearance, as has been described by G. Klinkenstein[1].

The cellulose ethers appear especially suitable for produring crystal effects of this nature by virtue of the fact that there is no acid radical to be eliminated and cause change in color of the added bronze or alter the composition or appearance of the added crystals, and also because the solvent portion can be made up largely of benzene, toluene or xylene, in which solvents, dyestuffs and a wide range of crystalline organic bodies are freely soluble.

Cellulose Ether Coated Cigar and Cigarette Tips. E. Richter[2] has described a cigarette tip coil or roll which may be used in cigarette-making machines. Whereas it appears in the cigarette industry extremely thin films of metal powder and cellulose derivative are used as substitutes for metal foil as coverings for the tips of cigarettes, these rolls have proven defective by reason of the fact that they are easily electrified. This arises chiefly from the thinness of the film, and also partially from the paper which serves as a base for the latter. As the process of manufacture is carried out in a relatively dry atmosphere the foil and paper take up a charge of static electricity as they are unwound from the coil, which electrical charge exerts an injurious influence on the subsequent steps of production. The E. Richter tipping coil is alleged to obviate these objections when prepared as indicated herewith. Thus, to 3-4 parts of bronze are added 7 parts of a 20% solution of a mixture of 2 parts ethylcellulose and 1 part nitrocellulose in the usual solvents, and with the addition of one or more of the usual plasticizers in the amount of 5%. This solution is spread on the usual flowing apparatus, and the film

1. U. S. P. 1852581.
2. U. S. P. 1816398; abst. C. A. 1931, **25**, 5558.

thus produced wound to cigarette tip coils, which when being worked in cigarette machines do not take up electrostatic charges.

In coating cigarette tips according to the W. Becker disclosure[1], use is made of an under-layer of resinous polymerized vinyl derivative and a water-proof over-layer. The over-layer may be a cellulose ether or organic cellulose ester with triphenyl phosphate and acetone, and the under layer of bronze powder and vinyl resin. Or[2], the cigarette paper may be coated with solutions of cellulose esters of saturated higher fatty acids as cellulose stearate, together with resins and rubber. Burning rubber in a cigarette would at least, impart a distinctive odor. In the production of films which may serve as imitation ivory or cork cigarette mouth pieces[3], a 2% solution of nitrocellulose in a known solvent and containing a multiple quantity of bronze powder as compared with the amount of cellulose, is continuously sprayed on to the traveling supporting surface through a stencil; and over this figuring when dry is applied continuously a 15% solution of ethylcellulose or benzylcellulose in benzene-alcohol, colored black with 4% lampblack as compared with the cellulose ether. A black film with sharply defined figurings of golden luster is obtained.

There has been described a "near-tobacco"[4] in which tobacco waste in the form of cuttings or dust is mixed with acetylcellulose or a cellulose ether in the presence of such solvents as acetone, ether or alcohol, and is formed into a film for use as cigarette or cigar wrappers, or into a cake which may be sliced or comminuted for smoking as tobacco. Of course, those who like to inhale a blend of acetic acid vapor and tobacco, that is just the thing they would like. Upon smoking it, is it not reminiscent of being just

1. D. R. P. 516716; abst. C. A. 1931, **25**, 3139.
2. E. Richter, M. Hagedorn and W. Becker, D. R. P. 517451; abst. C. A. 1932, **26**, 305; Chem. Zentr. 1931, II, 3419.
3. I. G. Farbenindustrie, A.-G., E. P. 288592; abst. J. S. C. I. 1929, **48**, 203-B; Chem. Zentr. 1928, II, 1154.
4. A. Schaarschmidt and M. Popoff, E. P. 282369; abst. C. A. 1928, **22**, 3737; Chem. Zentr. 1926, I, 1727.

north of the "vinegar works" with the wind in the south? The process of E. Schnabel[1] is of the same order, and is concerned with the manufacture of mouth pieces for cigarette holders, in which an amount of tobacco powder is added to cellulose acetate dissolved in acetone to a 15% concentration, about 2 parts tobacco dust to 1 part cellulose acetate being the recommended ratio and 0.2-0.4% of a water-insoluble plasticizing agent.

In the manufacture of thin bands to be used more particularly in the manufacture of cigarette mouthpieces, the Chemische Fabrik von Heyden A. G.[2], employs a combination of a metallic band and a cellulose ester as acetylcellulose. A solution of acetylcellulose carrying a metallic powder suspended therein is uniformly spread by spraying over a rotating support in an exceedingly thin layer, and the dried film detached with a regular motion from the rotating support. The proportions recommended are acetylcellulose 1, bronze powder 5-15, acetone 40. The proportion of bronze powder (5) to acetylcellulose (1) appears to us as being too high for a strong film to be cast. In order to ensure proper and adequate adhesion to the paper[3], the band is formed of two continuous layers, the upper layer carrying the metal powder, and the lower one (attached to the paper) containing a material enhancing adhesion as powdered magnesia, lithopone or powdered cork.

The cigarette tip of F. Wickel[4] is a mixture of cellulose derivative in solution containing finely divided mica, while that of C. Münch[5] involves the use of a small amount of bronze powder with the cellulose derivative, and the

1. D. R. P. 473701; abst. C. A. 1929, **23**, 3099; Chem. Zentr. 1929, II, 2282.
2. E. P. 157126; abst. J. S. C. I. 1922, **41**, 541-A. F. P. 721359; abst. C. A. 1932, **26**, 4174.
3. Chemische Fabrik von Heyden, A.-G., E. P. 337501; abst. C. A. 1931, **25**, 2311.
4. E. P. 269194; abst. C. A. 1928, **22**, 1474; Chem. Zentr. 1927, II, 656.
5. E. P. 334271; abst. C. A. 1931, **25**, 1082; Chem. Zentr. 1931, I, 2290.

addition of a material which produces a matt effect to the cigarette tip so coated. W. Thiele has described a cigar (price class not stated)[1] formed with a wrapper of comminuted tobacco leaves mixed with a solution of cellulose acetate or other suitable cellulose derivative. We prepared a cigar following the patent description. Upon burning it evolved a distinctive acetous flavor and aroma.

E. Closmann prepares cellulose acetate films of a frosted and hence translucent appearance for the preparation of cigarette tubes, thereby assuming the appearance of paper of particular fineness[2], and to "completely remove the glutinous character of the ash," adds 1-2% of nitrocellulose. Undoubtedly the cigarette is "free-burning" with the nitrocellulose thereon. The method of F. Meyer[3] for protection of the lips of cigar smokers is to coat the top of the cigar with acetylcellulose solution, which is afterwards allowed to dry.

Films and bands of very high degree of fineness have been described[4], which can be made from concentrated and even pasty solutions by spreading the mass in the form of a thin layer on a smooth support and allowing it to dry. The support may be an endless band or a rotating roller or drum, so that the manufacture may be made continuous. Bronze or other metal powder is incorporated in the lacquer solution, a single spreading operation being sufficient to cast a film of the desired thinness. The process is said to be particularly suitable for the manufacture of very thin metallized films serving as substitutes for metal leaf in the cigarette industry for making gold mouthpieces. The thickness of such films is 0.003-0.01 mm.

Cellulose Ether Coated Paper. The waterproofing and decorating of paper and paper products has been a field

1. W. Thiele, U. S. P. 1716250; abst. C. A. 1929, **23**, 3807.
2. E. P. 196654; abst. C. A. 1923, **17**, 3790.
3. U. S. P. 931629. D. R. P. 193210; abst. Mon. Sci. 1911, (5), **74**, 92. Can. P. 107996.
4. Actien-Ges. für Anilin-Fabrikation, E. P. 181706; abst. Chem. Met. Eng. 1922, **27**, 755.

in which the cellulose acetates have for some time played an important part, and in which the cellulose ethers are indicated as being at least as equally useful, and in some instances show points of superiority.

H. Wandrowsky[1], for instance, adds water-insoluble cellulose esters in finely comminuted condition directly to the paper pulp in the beater, and the paper after formation and drying, is submitted to a solvent treatment to further close the pores of the paper and increase the resistance to moisture. In the case of paper textiles, the solvent is not added until after the weaving operation. The Du Pont Viscoloid Co.[2] decorate one side of a diaphanous cellulose acetate sheet, which is then united to a second sheet so that the decoration is imprisoned between the two sheets. A suitable binder is dibutyl phthalate, ethyl lactate, ethylglycol or a mixture of acetone with methyl or ethyl alcohols or acetates.

In the C. Boyce method of finishing prints[3], which is a continous process of producing prints simulating photographs, the surface of the finished print is made permanent and given a glaze finish by the application thereto of an acetylcellulose lacquer. Wall papers have been described[4] made waterproof, more sightly and durable, by coating the paper in rolls by means of an acetylcellulose varnish or lacquer, the paper being intended primarily for bath rooms and nurseries, where the paper is more prone to come in contact with water or water vapor. In another method for the waterproofing of paper and textiles[5], a suspension of flour in water is first heated with NaOH at 120° until the starch has been solubilized and completely converted into dextrin. After cooling, a solution of casein and sodium

1. D. R. P. 323816; abst. J. S. C. I. 1920, **39**, 779-A; Paper, 1921, **28**, 38. C. Dreyfus, Can. P. 294371.
2. E. P. 323473; abst. Brit. Plastics, 1930, **1**, #11, 498.
3. U. S. P. 1725699, Re-18192.
4. Akt.-Ges. für Wasserdichte Stoffe "Filmos" Oftringen, D. R. P. 521520; abst. C. A. 1931, **25**, 3484. D. R. P. 456518.
5. M. Favresse and J. Peres, F. P. 629291; abst. J. S. C. I. 1929, **48**, 241-B; Chem. Zentr. 1928, I, 608.

carbonate or silicate is added, and the articles to be water proofed are soaked in this mixture, calendered hot, dried, and then treated with a solution of cellulose acetate.

A fire-preventative treatment for paper and textiles has been evolved in Germany[1], in which the fibrous material either in sheet or textile form is treated with a solution of cellulose acetate (Cellon), and the volatile solvent evaporated therefrom. In the coating of paper by the H. Valentine and E. Simpson method[2], an iridescent film or coating is produced on paper or other surfaces by floating on the surface of water a solution of an organic derivative of cellulose in an alkyl ester of a fatty acid, with or without the addition of gums or resins, evaporating off the solvent and then applying the film to paper, preferably by raising the paper out of the water. An adhesive as starch may be added to the water.

In the application of the cellulose ethers for the dual purpose of waterproofing and inducing specific and artistic effects upon paper or textile products, K. Franz and C. Dankert[3] produce paper glazed on one side only, by moistening the side to be glazed with an alkylcellulose solution before pressing, dimethylcellulose being especially suitable. In an improvement upon this process[4], the polish on one side of the paper, carton or pasteboard may be increased by the addition of starch paste to the methylcellulose aqueous solution, and the cost of coating thereby materially reduced. The starch paste may first be applied to the paper, then dried, and methylcellulose then superposed as an after coat, or the starch paste and methylcellulose may be mixed together and applied as a unitary or plurality of coatings.

1. R. Kölliker, Papierfabr. 1925, **23**, 162; abst. C. A. 1925, **19**, 3017.
2. E. P. 202835; abst. C. A. 1924, **18**, 329; Paper, 1923, **33**, #8, 18.
3. D. R. P. 518724; abst. C. A. 1931, **25**, 3484.
4. K. Franz, D. R. P. 510855; abst. C. A. 1931, **25**, 1085; Chem. Zentr. 1931, I, 385.

Paper of pasteboard intended to furnish the outer surface of walls[1] may be waterproofed by soaking the individual pieces in a cellulose ether solution in volatile solvents and then applying after placing a polish thereon by submitting the sheets to heat and pressure, or a cellulose ether lacquer may be applied to the sheets after they are in position on the wall. Beautiful effects are producible by first coating the paper with the cellulose ether solution, and while still tacky impressing a figurine thereon. After drying the paper is then coated with a cellulose ether lacquer, thus making the colored impression substantially permanent.

H. Persiel[2] has described a process for preparing artificial materials of various kinds, which consists in finely dispersing with water a cellulose ester or ether, and then treating the dispersion after bringing it to the desired shape with an agent which is capable of causing the cellulose compound to swell. In the preparation of floor coverings, a printing paste has been evolved[3] comprising benzylcellulose, a pigment, a drying oil as linseed, and a plasticizer as tritolyl phosphate, or glycerylditolyl ether, and containing also both high and medium boiling solvents as ethyl and butyl lactates, benzene and methyl alcohol or acetone.

The carbon paper of M. Bandli[4] consists of an acetone solution of a cellulose ether or ester in admixture with suitable softening agents and optionally containing undissolved cellulose (cotton flock) in a fine state of subdivision to act as a binding material, and in which is incorporated the coloring material, usually a spirit-soluble nigrosine. Stearic anhydride has been described as an excellent waterproofing agent for paper[5], it being claimed that paper so

1. Societa Anonina Cartiere Giacomo Bosso and N. Silvestrini, F. P. 721694; abst. C. A. 1932, **26**, 4176.
2. U. S. P. 1848268; abst. Plastics, 1932, **8**, #6, 256.
3. Imperial Chem. Industries, Ltd., F. Walker and A. Hetherington, E. P. 360815; abst. J. S. C. I. 1932, **51**, 235-B.
4. E. P. 307714; abst. J. S. C. I. 1929, **48**, 470-B.
5. A. Nathansohn, E. P. 356277. F. P. 697149.

treated remains waterproof, even after extraction with volatile solvents.

Cellulose Ethers for Insulation. The Aceta Ges.[1] have shown that the electric charge formed during the working up of textile materials such as cellulose ethers may be reduced by treating the material with mixtures of oils or fats to which an oil-soluble base has been added, such as cyclohexylamine, dibutylamine, piperidine, aminoalcohols or aminoethylamide oleate (oleic acid aminoethylamide). Soaps of secondary or tertiary amino alcohols and of "sapamines" are especially suitable. Insulating tubing is formed of fabric made from threads of spun paper and impregnated with cellulose ethers alone, or in association with natural or synthetic resins[2]. The coating of a metallic arc-welding electrode is provided with a film impermeable to moisture[3], which may be formed by dipping the coated electrode in a cellulose acetate or cellulose ether lacquer, or by mixing such a lacquer with the materials of which the coating is formed.

The M. Arosio[4] impermeable, non-hygroscopic insulating material consists of vulcanized fiber coated with a film of acetylcellulose or celluloid, firmly adherent to the supporting surface. C. Avery and H. Kress[5] have given a detailed account of the acetylcellulose insulation of textile coated wire as carried out at the Western Electric Co. plant at Kearny, N. J., with illustrations of factory installation. In improving the insulation characteristics of conductors insulated with cellulose acetate[6], D. Brobst immerses the cotton coated wire in a bath of cellulose acetate solution, and an electric current is passed through the conductor

1. E. P. 346912; abst. C. A. 1932, **26**, 2066. See D. R. P. 286173.
2. Allgemeine Elektricitäts Ges., E. P. 342290; abst. C. A. 1932, **26**, 4394.
3. Alloy Welding Processes, Ltd., and E. Jones, E. P. 303996; abst. C. A. 1929, **23**, 4437. See E. P. 301221.
4. E. P. 131907; abst. J. S. C. I. 1921, **40**, 143-A. E. P. 131911. D. R. P. 331024.
5. Chem. Met. Eng. 1932, **39**, 273.
6. U. S. P. 1808520; abst. C. A. 1931, **25**, 4403.

and bath. The conductor is then passed through another bath of cellulose acetate and through a drying chamber. Electric conductors may be made by adding to a cellulose acetate solution 5-10% silver nitrate and 1-3% nitric acid, reducing with hydrogen sulfide and treating in an electrolytic bath[1].

In the insulation of electric wires and cables according to the F. Brislee system[2], a cellulose acetate composition in hard and substantially solvent-free form is applied in layers with textile supports, around a conductor under approximately atmospheric pressure, and the material then heated to about 100°, at which temperature the composition softens and flows so that adjacent layers unite, and impregnation of the textile material thus effected. According to C. Dreyfus[3], methyl-, ethyl- or benzyl-cellulose are employed in the fibrous form for heat and sound insulation, suitable fibers being of the order of 1-4 denier produced from an acetone solution of the cellulose derivative. The fibers may be 1-5 inches in length, and fluffed by agitation or blowing with air, and may be subsequently crinkled by heating with boiling water. The material is especially suitable for the insulation of pipes, rooms, aircraft cabins, portable jars and refrigerators.

A solidifiable paste for use in the manufacture of tubes and as an electrical insulating and jointing material[4] is prepared from a mixture of acetone, methyl acetate, triphenyl phosphate and cellulose acetate, the composition being agitated in a closed vessel with sufficient asbestos to impart the desired consistency, and used in this connection as an insulating medium[5]. For the production of a fast

1. A. Borensztedt, F. P. 644430; abst. C. A. 1929, **23**, 1577; Chem. Zentr. 1929, I, 171.
2. U. S. P. 1795994; abst. C. A. 1931, **25**, 2498. E. P. 330552; abst. C. A. 1930, **24**, 5899; J. S. C. I. 1930, **49**, 775-B. E. P. 337052; abst. J. S. C. I. 1931, **50**, 70-B; Brit. Plastics, 1931, **2**, #21, 432.
3. E. P. 315280; abst. C. A. 1930, **24**, 1685. W. Wirz, Can. P. 293068. C. Dreyfus, Can. P. 315581.
4. C. Castro, E. P. 252999; abst. C. A. 1927, **21**, 2558. F. P. 605770; Kunst. 1926, **16**, 206.
5. A. Rheiner, Can. P. 321040.

adhering metal coating to insulating bodies, especially for the preparation of electric condensers[1], by the use of a cellulose ether or ester, the metal coating being rendered adherent by colloidally depositing an intermediate layer of metal or metal oxide. For best adherence, superficial roughening of the surface if a cellulose ether is used, or peripheral saponification of the surface if an organic cellulose ester be employed is necessary, and a metal salt is added to effect a milder action.

A. Dunton has apparently shown[2] that if the right type of cellulose acetate is selected, there need be no fear as to deterioration upon ageing. It has been found that the life of acetylcellulose foils actually exceeds that of many insulating materials formerly used. From tables given, it appears cellulose acetate ranks next to mica products as a desirable insulating medium. His opinions in general, coincide with those of A. Eichengruen in this respect[3]. In the manufacture of uniformly loaded conductors used for signalling purposes[4], a strip of cellulose ether is tightly wound round the conductor, the cellulose ether being soluble in a liquid which does not attack copper or the loading material, then surrounding the conductor with the loading material, and placing it in a liquid which dissolves the strip, and finally annealing it.

In improvements in papers for use as a dielectric for electrical conductors, F. Haigh[5] employs very thin paper coated with acetylcellulose. An electric resistance material is made by mixing a finely divided conductor such as nickel or iron reduced from the oxide without fusion, with a cellulose acetate binder, the mixture while viscous, being spread on glass plates[6]. In the production of insulating

1. Dubilier Condenser Company, Ltd., and E. Pfiffner, E. P. 261392; abst. C. A. 1927, **21**, 3461; Chem. Zentr. 1927, I, 1911. D. R. P. 482282; abst. C. A. 1930, **24**, 177.
2. Electrician, 1931, **107**, 483.
3. Kunst. 1924, **14**, 92; abst. Chem. Zentr. 1924, II, 100.
4. Felten & Guilleaume Carlswerk, A.-G., Can. P. 257645.
5. E. P. 138226. See E. P. 24981, 1911.
6. Howards & Sons, Ltd., and M. Bandli, E. P. 314306; abst. C. A. 1930, **24**, 1305.

fabrics[1], the I. G. Farbenindustrie have found that if a mercerized cotton fabric is impregnated with a cellulose ether lacquer, an insulating fabric is obtained of excellent dielectric properties.

In the formation of electrical conductors, according to the E. Jodrey formula[2], paper is coated with an adhesive, continuous, conducting layer of copper foil coated with organic cellulose esters. L. Lilienfeld[3] has called attention to the great suitability of the cellulose ethers for insulating goods, and has pointed out the following advantages:

1. Extreme permanency and stability as well as neutrality, withstanding being heated in the presence or absence of water to comparatively high temperatures without decomposition.

2. Resistance to hot alkaline solutions, in which respect they exceed that of all known cellulose derivatives. This stability of the alkylcelluloses and their resistance to water results in an insulating power far surpassing all other cellulose derivatives, such as the cellulose esters which lose their insulating power under the influence of humidity owing to a slow and gradual hydrolytic decomposition.

3. The unusual suppleness and resistance to chemical and physical influences, and the notable toughness and hardness of the plastic masses produced from their solutions or jellies.

4. Their property of dissolving easily in a large number of relatively inexpensive solvents.

5. Their relative non-inflammability as compared to cellulose, and of course, as compared with the cellulose nitrates.

The L. Lilienfeld insulating material is formed from ethylcellulose or benzylcellulose in admixture with a hydro-

1. E. P. 297749; abst. C. A. 1929, **23**, 2772. E. P. 322540, 322541, 322542, 322543; abst. C. A. 1930, **24**, 2905. E. P. 342848; abst. Brit. Plastics, 1931, **3**, #29, 75. F. P. 687702; abst. C. A. 1931, **25**, 754; Chem. Zentr. 1931, I, 1954. D. R. P. 519457; abst. C. A. 1931, **25**, 2787.
2. E. P. 305515; abst. J. S. C. I. 1929, **48**, 290-B.
3. U. S. P. 1563205; abst. C. A. 1926, **20**, 465.

carbon material of high boiling point and non-conductive character, as indicated by the following example:

600 parts of water-insoluble ethylcellulose or benzylcellulose are mixed with 400 parts benzylcresyl ether and *m*-dixylylethane, and dissolved in 1800 parts benzene or toluene and 200 parts ethyl alcohol, then kneaded in a vacuum kneading machine for 2 hrs. at 60-80°. Subsequently about half of the solvent is evaporated, and the mass either calendered, rolled out, dried and pressed, or else applied to wires or cables by means of suitable machinery. In the first instance, a laminiform insulating material is produced, and in the latter instance, a wire or cable covered with a flexible insulating sheath is produced.

The A. Mentzel insulator for electric conductors is made from ethylcellulose or benzylcellulose varnishes, alone or mixed with fillers such as powdered asbestos[1], or[2], a conducting material as carbon, may be mixed with a phenol-aldehyde condensate and a cellulose derivative to form electric resistances. A condensation product of urea and formaldehyde associated with a cellulose ether forms the basis of another electric conductor composition[3]. E. Kiefer[4] has described an electrically conductive article prepared by incorporating graphite with a cellulose ether, a blend of three parts of powdered copper and one part powdered graphite being the proportion used with the binding agent.

The electrical insulating material of Non-Inflammable Film Co. and V. Yarsley[5] involves the use of a mixture of benzylcellulose with a relative high percentage of plasticizers (20-30% of tricresyl phosphate and ethyl tartrate or phthalate with a glycerol ester as triacetin). The following example indicates the working of the process:

100 parts benzylcellulose are added to a mixture of 250 parts benzene and 210 parts acetone in the usual type

1. F. P. 712727; abst. C. A. 1932, **26**, 1684.
2. Naamlooze Vennootschap Philips' Gloeilampen-fabrieken, F. P. 653880; abst. C. A. 1929, **23**, 3636.
3. C. Newbauer, Can. P. 272494; abst. C. A. 1927, **21**, 3718.
4. U. S. P. 1774381; abst. Brit. Plastics, 1931, **13**, #25, 37.
5. E. P. 355654; abst. J. S. C. I. 1931, **50**, 1016-B.

of kneading machine and 22 parts dibutyl phthalate added with stirring. The product is a clear viscous mass of about the consistency of molasses, from which films may be made by casting on moving supports, the film after drying by being pressed through a heated chamber, is rolled up for use.

In metallically coating electrically non-conducting bases[1], a film to be coated with a silver-foil is immersed in a 6-8% pyrogallol-alcohol solution, well dried, and then dipped in a bath of 2% silver nitrate. Immediately firmly adhering metallic silver is separated. According to the invention, any convenient material may be coated with metal by coating the base with a firmly adhering layer of cellulose ethers, and subsequently treating this coating as above outlined. E. Pfiffner[2] chemically coats sheets of cellulose esters with metal for insulating purposes when a silver or copper salt in solution is contacted with the cellulose derivative to cause precipitation of the reduced metal[3].

An insulating material for electric purposes originated in Germany[4], it having been found that the most suitable material for insulation purposes is methyl-, ethyl-, propyl- or butyl-cellulose. The ether may be used alone or dissolved with bitumen in the form of a lacquer or plastic mass, to which natural or synthetic oily or fatty substances may be added. The plastic material may either be applied directly in a heated condition to the surface to be insulated, or may be wound onto conductors in the form of a band, the edges of which are subsequently fused together. It is preferably tempered by heating to 35-50° either before or after molding. The ethers may contain only one radical (mono-, di- or tri-ethylcellulose being specified) of the same

1. M. Ow-Eschingen, E. P. 281663; abst. C. A. 1928, **22**, 3528; J. S. C. I. 1928, **47**, 824-B. E. P. 330677; abst. C. A. 1930, **24**, 6014.
2. U. S. P. 1529712; abst. C. A. 1925, **19**, 1629; J. S. C. I. 1925, **44**, 351-B.
3. S. Wein, U. S. P. 1601607; abst. C. A. 1926, **20**, 3654. E. Pfiffner, U. S. P. 1744281; abst. C. A. 1930, **24**, 1508.
4. Siemens-Schuckertwerke, E. P. 157120; abst. C. A. 1921, **15**, 1954. E. P. 156527; abst. C. A. 1921, **15**, 1772. E. P. 281333. Swiss P. 97643; abst. Chem. Zentr. 1923, IV, 424.

kind or of different kinds as benzylcellulose. Mixtures of different ethers may be used, an example being monoethyldibenzylcellulose or diethylbenzylcellulose.

H. Bartel[1] has called attention to the well known fact that condensers of high capacity consistent with small volume may be manufactured by coating the metal condenser conductors with a dielectric in fluid form. This coating is usually allowed to dry, after which the conducting layers are brought into their final shape by rolling or forming. In a condenser manufactured in this manner there is a possibility of moisture penetrating into the interior of the roll, and in addition, a special binder for holding the roll must be provided. Bartel overcomes these objections by coating the conducting layers of a condenser with a cellulose ether, and in rolling the whole into a rigid mass before the coating becomes solid. This causes the various layers of the roll to become intimately connected and thus form a non-hygroscopic, completely enclosed mass which can only be severed by damaging the parts, and consequently the penetration of moisture into the interior of the roll is effectively prevented.

The process of manufacture is illustrated diagrammatically in Fig. 11, the rolls *2* and *3* representing the source of supply of the condenser element material, which is drawn through a container *4* of cellulose ether solution as it is wound on an arbor *5*. When sufficient of the condenser material has been wound upon the arbor to produce a condenser of the desired capacity the condenser is simply torn off, removed from the arbor and compressed.

In operations such as the manufacture of high-tension cables[2], the insulation is dried and exhausted, and, before impregnation, residual air is replaced by the vapor of a substance which vaporizes under the temperature and low pressure conditions prevailing in the impregnating vessel.

1. U. S. P. 1842648; abst. C. A. 1932, **26**, 1523.
2. Standard Telephones & Cables, Ltd., T. Scott and T. Riley, E. P. 339990; abst. C. A. 1931, **25**, 2787.

and which is condensed to a liquid or solid under the conditions of temperature and pressure. Among the materials specified as suitable for impregnation is cellulose acetate.

The electric insulation board of D. Sutherland[1] comprises 40% cellulose, 15% oil, 2% acaroid resin and 43% gilsonite, over which flows a cellulose acetate lacquer.

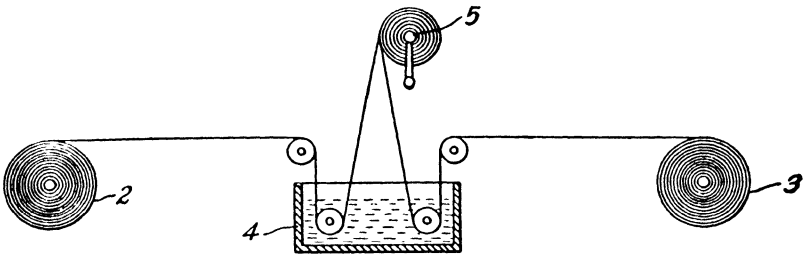


Fig. 11. The Bartel Method of Insulating.

Cellulose Ethers in Pharmacy. The inorganic cellulose esters (nitrocelluloses) have been used pharmaceutically as a protective coating since the early days of pyroxylin exploitation, "ether glue" and "sticking plaster" being familiar names for the various contractile collodions of the Pharmacopea. On account of the blandness, neutrality, and stability to acids and alkalis, the cellulose ether "collodions" should be especially applicable for use on the hands of workmen in chemical plants and elsewhere, especially as it has been found, due to the increased number of solvents available for the cellulose ethers over the cellulose nitrates and acetates, that medicaments of various kinds, especially for topical application, may readily be dissolved in the cellulose ether solvent used. Phenol, cresols, creosote, guaiacol, and other antiseptics, deodorants, fungicides and bactericides are dissolvable with the cellulose ethers to produce water-resistant coatings. The pharmacopeal collodion of nitrocellulose 4, ether 75 and ethyl alcohol 25, might be improved upon by the formula, ethylcellulose 4, acetone 85, methylethyl ketone 15, and the flexible collodion formula

1. U. S. P. 1636491. See U. S. P. 1485894.

of adding 2% camphor and 3% castor oil to ordinary collodion, might be improved upon by the use of ethylcellulose collodion with the addition thereto of 3% ethyleneglycol or ethyleneglycol acetate and 3% castor oil.

The "corn collodions," being pyroxylin in solution to which salicylic acid, salicylates, Indian hemp (Cannabis Indica) and others, may be replaced equally well by ethylcellulose or benzylcellulose solutions of greater stability. If a corn cure of the "freezone" type is desired, addition of ethyl chloride or other low boiling liquid is indicated. Ferric chloride is an astringent, thymol as an antiseptic and deodorant, iodol, iodoform, aristol, paraform, ichthyol, pyrogallol, chrysarobin, mercury salts, and oils of cade, mezereon and savin, having all been used as hemostatic, styptic, and cutaneous applications, in which the dissolved cellulose ethers are recommended as a desirable vehicle for application. As a rubifacient, vesicant and cutaneous escharotic, ethylcellulose solutions containing capsicum, capsicin, croton oil, oil of mustard, sinapin, oil of black pepper, and especially the Spanish fly preparations, cantharides and cantharidin, all are compatible with the dissolved cellulose ethers, of which there is a wide choice of harmoniously acting solvents and diluents.

Bromocoll, euresol, iodized uric acid dissolved in cellulose ether combinations are indicated for the treatment of chilblains. The alkaloids morphine, aconitine, cocaine and veratrine are often best applied cutaneously, and for this purpose solution in a cellulose ether mixture offers localized application without the danger of spreading. Belladonna in ethylcellulose solutions constitutes an acceptable mydriatic for applications in ophthalmological technique.

L. Lilienfeld has described the preparation of a remedy for malignant tumors[1], by using metallic selenides and tellurides, which are claimed to produce a curative effect without causing troublesome toxic symptoms, and prepared

1. U. S. P. 1555016. E. P. 173507.

by adding to 200 parts of a 2-10% solution of a water-soluble methylcellulose or ethylcellulose, or methyl starch or ethyl starch, 300-700 parts of a solution of auric chloride or other soluble gold salt, of which 100 parts of the solution contains 1 part by weight of metallic gold. Into this mixture is introduced hydrogen selenide in aqueous solution, in amount calculated on the amount of gold in solution. A dark olive brown precipitate of gold selenide is formed, the solution being then warmed to 50-80°, whereby the cellulose ether is precipitated carrying the gold selenide with it. Iridium, palladium, osmium, platinum, mercury, silver, copper and tin tellurides or selenides may be produced in the same manner. This medicinal suspension is preferably administered by intravenous, subcutaneous or intratumoral injection.

He has also detailed methods for producing emulsions, suspensions and solutions[1] for pharmaceutical uses, obtained from cellulose ethers and having distinct bactericidal properties, his process being indicated by the following examples:

1. 200 parts of 5-10% solution of methyl- or ethyl-cellulose or methyl or ethyl starch soluble in water are mixed with a solution of 5-7 parts silver nitrate in an equal weight of water. Then 250 parts of 10% ammonia solution and 200-250 parts ammonium formate solution are combined and the mixture heated until the silver is reduced to elemental form. The solution is then cooled, dialyzed, and either vacuum evaporated or precipitated by alcohol or ether-alcohol, and the precipitated hydrosol dried.

2. 15 parts ethylcellulose or ethyl starch soluble in cold water are dissolved in 300-500 parts of water, 5-8 parts solid pyrogallol added and kneaded with the solution. To this mass is then added, a drop at a time, a solution of 15-16 gms. mercuric chloride in 200 gms. water with stir-

1. L. Lilienfeld, U. S. P. 1444257; abst. C. A. 1923, **17**, 1310; J. S. C. I. 1923, **42**, 292-A; Chem. Zentr. 1923, IV, 436. Aust. P. 89859; abst. Chem. Zentr. 1924, I, 2450. Aust. P. 92914, Addn. to Aust. P. 89859; abst. Chem. Zentr. 1924, I, 2450.

ring. The colloidal solution resulting is then mixed with alcohol until a precipitate forms, 5-10 gms. NaOH are then added, and the formed precipitate washed with water until free from reactants, then dried. The black-brown body formed contains 26% mercury.

3. 50 parts phenol or cresol are dissolved in 500 parts of an oil, and this solution emulsified with 500-1000 parts of 5-10% aqueous solution of methyl- or ethyl-cellulose.

4. There is prepared a 5-10% solution of ethyl- or benzyl-cellulose, ethyl starch or benzyl starch soluble in oil, and 100 parts of this solution are dissolved in 10 parts by weight of *b*-naphthol. Then this solution is emulsified with 50-70 parts of 5% ethyl- or methyl-cellulose. In a similar manner colloidal gold solutions remaining indefinitely in suspension are produced by mixing a soluble gold salt with an aqueous methylcellulose solution, adding hydrazine hydrate or hydroxylamine chlorhydrate to precipitate the gold to the elemental form. The products above are said to be especially indicated for gonorrhoeal and syphilitic affections. Instead of gold, there may be used colloidal suspensions of sulfur, selenium or tellurium with the aid of aqueous alkylcelluloses.

Collapsible tubes for cellulose ethers and esters, suitable for pomades, salves and similar proprietary preparations, may be forced, according to the L. Rado process[1], by winding foil of cellulose derivatives, and then applying a cellulose ester or resin waterproofing varnish for purposes of strengthening, the layers being cemented together by means of any suitable adhesive. The pomade of K. Matuura and K. Takagi[2] comprises a mixture of cellulose derivatives as ethylcellulose or nitrocellulose with a solvent, and emulsified with suitable fats, oils and esters to form a salve-like mass. Products which combine antisepsis with solvency for cellulose ethers as guaiacol acetate[3] are excellent

1. E. P. 327212; abst. C. A. 1930, **24**, 5157.
2. Jap. P. 91885; abst. C. A. 1932, **26**, 1716.
3. H. Smith, U. S. P. 1858285.

products to incorporate in collodions for external application with a cellulose ether base.

In the preparation of surgical dressings, bandages and similar materials requiring a textile material relatively non-absorbent with respect to blood and pus, may be prepared from staple fiber, yarns or fabrics composed of cellulose ethers or esters, on account of their relatively low absorptive capacity for these fluids and excretions. The bandage or dressing may be made with a filling comprising fluffed filaments of yarns of cellulose ethers[1], enclosed in a fabric made of yarns of the same or similar material. Or, the dressing may be built up in a composite manner, by means of alternate layers of gauze and cellulose ether or ester filaments or fluff.

The I. G. Farbenindustrie[2] has described a method for the manufacture of ampoules, in which the preferred form is constructed of a small, blunt-edged tube open at both ends which are sealed with a chemically inactive material such as a cellulose ether, wax, paraffin or ceresin. By perforating these seals by means of a needle, the contents of the ampoule may be withdrawn drop-by-drop, as desired. In order to more conveniently regulate the number of drops extruded, a rubber cap or bulb is provided on one end after perforating that end. The ampoule can be used in ophthalmic practice as a pipette, and in the obstetric art for dropping silver nitrate solution into the eyes of newly born infants.

It is claimed that soaps undergo an improvement by addition of cellulose ethers thereto, especially soaps intended for medicinal uses by virtue of medicaments contained therein. The alkylcellulose, preferably water-soluble, or the water-insoluble for tinctures of soap, as the green soap of the Pharmacopea, may be added directly to a soap solution and the soap concentrated by evaporation, or may be in-

1. British Celanese, Ltd., E. P. 307459; abst. C. A. 1929, **23**, 5276; J. S. C. I. 1930, **49**, 441-B. Can. P. 315580.

2. I. G. Farbenindustrie, A.-G., E. P. 283952; abst. C. A. 1928, **22**, 4204.

corporated with the solid soap in the crutching operation preliminary to cake formation[1]. Or, on account of the high resistance of the cellulose ethers to alkalis, the etherized cellulose may be mixed with the fats before saponification. Methylcellulose and ethylcellulose are soluble in melted fatty compounds without the aid of a volatile solvent. It is claimed that 25-40% of methyl- or ethyl-cellulose may be added directly to soap, either for the production of a solid soap or the liquid soaps of the Pharmacopea.

According to J. Eder[2], instead of using preparations such as quinine sulfate or aesculin for the protection of the skin against the action of light of short wave length, better results are obtainable by the employment of certain naphthalene derivatives that display a blue fluorescence as naphtholsulfonic or naphthylaminesulfonic acids or their salts, or the homologous anthracene compounds. Not only for the protection of the skin against sunburn, but also for producing photographic or fluorescent layers as stabilizers or exciters or for ultra-violet filters are these compounds of technical value. For instance, sodium 2-naphthol-6.8-disulfonate in concentrated aqueous solution is made into a paste or salve by means of a cellulose ether, such as water-soluble methyl- or ethyl-cellulose, which may also contain different vehicles and medicaments, and this is applied to those parts of the body it is sought to protect.

These mixtures, with an alkylcellulose as the vehicle for topical application and containing the naphthol-, naphthylamine- or anthracene-sulfonic acids or their alkali salts are indicated for cutaneous application for the prevention of such pathologic conditions as erythema solare, glacier burn, pigmentations, tanned complexion, freckles, summer prurigo, hydroaestivale, xeroderma, pigmentosum, pellagra and beriberi.

1. L. Lilienfeld, Aust. P. 87803; abst. Chem. Zentr. 1922, IV, 904.

2. U. S. P. 1511874. The preparations are said to show the advantage of a more complete absorption of the ultra-violet rays, offering specific protection of the human organism against damages caused by the light, while being harmless for the organism.

Emulsification. In preparing emulsifying agents of a high degree of permanency and of unusual uniformity, the lower etherified methyl- and ethyl-celluloses have recently come into prominence, especially in association with certain aromatic or hydroaromatic sulfonic acids, preferably in the form of their alkyl, aryl or aralkyl esters[1]. The carrying out of the process is indicated in the following example:

2.5 parts dimethylcellulose and 2.5 parts sodium *iso*-propylnaphthalenesulfonate are dissolved in about 300 parts water. Into this mixture are run 80 parts olein, while continually stirring until an entirely homogeneous emulsion is formed. The oiling preparation so obtained is then applied in the usual manner for the impregnation of cotton, wool or other fibers. Instead of using the above salt, sodium butyl-(or benzyl)naphthalenesulfonate or propyl-(or benzyl or butyl)naphthalenesulfonic acid may be employed with analogous results.

Artificial materials of any desired shape which are insoluble in water and organic media are made by mixing a solution in an organic solvent of a cellulose ester[2], which is insoluble in and does not swell in water, with a cellulose ether as methyl- or ethyl-cellulose, dissolved in or swelled by water, and desiccating the emulsion so obtained. *iso*-Propyl or *n*-butyl sulforicinoleate or sulfo-oleate may also be combined with the lower alkylated celluloses as methyl- or ethyl-cellulose[3].

Water-soluble sulfonation products suitable for incorporation with the lower methyl- or ethyl-celluloses in the formation of substantially permanent emulsions are formed

1. I. G. Farbenindustrie, A.-G., E. P. 268387; abst. J. S. C. I. 1928, **47**, 152-B. See E. P. 258551; abst. C. A. 1927, **21**, 3095.
2. *Ibid.* E. P. 285355; abst. C. A. 1928, **22**, 4815; Chem. Zentr. 1928, I, 3016. See E. P. 252176.
3. H. T. Boehm, A.-G., E. P. 313966; abst. C. A. 1930, **24**, 1247; Chem. Zentr. 1929, II, 2108. F. P. 679185, 679186; abst. C. A. 1930, **24**, 3911. F. P. 685994; abst. C. A. 1930, **24**, 6035. See E. P. 306116.

by condensing furfural, methylfurfural or furfuramide with carbocyclic or heterocyclic compounds such as naphthalene, anthracene, carbazole or halogenated aromatic sulfonic acids[1], and if desirable, the product then sulfonated. Dispersing agents are thereby obtained applicable for use in the dyeing of cellulose ethers.

To avoid the high cost of the "vehicle" in the production of cellulose ester enamels, emulsions of the ester of the water-in-oil type, which give tough and transparent films[2], may be prepared by dispersing water, to an extent such that it is substantially absorbed in the emulsion, in a solution of the ester in small quantities of a solvent (cyclohexanone, methylcyclohexanone) which is only slightly miscible with water, is sufficiently volatile to prevent undue prolongation of the drying period, and, under the conditions of drying, is less volatile than water, so that excess of solvent is present during drying of the film. The process is said to be equally applicable to cellulose ether enamels and lacquers.

Aqueous emulsions of cellulose ethers applicable as spraying enamels[3] are prepared by dispersing in water in a colloid mill, with the aid of a suitable emulsifying agent, a solution of a cellulose ether or ester in a solvent which (a) is miscible but slightly or immiscible with water and not freely soluble therein, (b) produces a cellulose ether solution of low interfacial tension against the water phase, and (c) is sufficiently non-volatile to prevent precipitation of the cellulose compound during the drying of the film, even though the ratio of solvent to water is low and yet sufficiently volatile to avoid unduly increasing the period

1. British Celanese, Ltd., G. Ellis, H. Olpin and E. Kirk, E. P. 322737; abst. C. A. 1930, **24**, 2900; J. S. C. I. 1930, **49**, 361-B. See E. P. 224925, 242393, 273819.

2. G. Davies, W. Jenkins and Imperial Chemical Industries, Ltd., E. P. 328657; abst. C. A. 1930, **24**, 5517; J. S. C. I. 1930, **49**, 655-B; Brit. Plastics, 1930, **2**, #15, 75. F. P. 679440; abst. C. A. 1930, **24**, 3901. Can. P. 314397. Australian P. 23003.

3. *Ibid.* E. P. 328934; abst. C. A. 1930, **24**, 5517; J. S. C. I. 1930, **49**, 760-B; Brit. Plastics, 1930, **2**, #17, 101. Can. P. 314396, 314397.

of drying. Suitable solvents include cyclohexanone and cyclohexanyl acetate or butyl propionate, and as emulsifying agents may be used gelatin, casein or soap, preferably prepared from oleic acid in the non-aqueous phase and caustic soda in the aqueous phase, for unpigmented emulsions.

Water-insoluble cellulose derivatives are finely dispersed mechanically[1] in water and mixed with aqueous emulsions of assistants acting as dissolving, softening or gelatinizing agents, in amounts insufficient for homogenizing the mixture. The assistant emulsions are preferably prepared with the use of methylcellulose with alkylnaphthalenesulfonic acid salts as wetting or emulsifying agents. The process may be practically carried out as indicated in the following examples:

1. A mass obtained from 50 parts nitrocellulose, 100 parts water and 20 parts Lithol Fast Scarlet RN paste, by rolling with friction rollers and subsequent grinding in a mill, is mixed with an emulsion of 30 parts butyl stearate and 15 parts dibutyl phthalate, and if desired from 2-5 parts of a resin prepared by polymerizing cyclohexanone with alkali, in a mixture of 5 parts methylcellulose in 50-100 parts water, and applied preferably three times to chrome-tanned leather after further dilution with water. After drying, the leather is sprayed over with ethyl acetate and then hot calendered. The coating obtained is said to be permanent, and may be burnished.

2. 50 parts 25-30% aqueous nitrocellulose paste prepared by rolling with friction rollers and subsequently grinding, are mixed with 15 parts chalk, 15 of lithopone, 30 slate meal, 15 talc or graphite, and further with 25 parts of an emulsion of 0.8 part sodium butylnaphthalenesulfonate, 0.8 part methylcellulose, 40 parts water, 19.5 parts each butyl stearate, dibutyl phthalate and a synthetic resin of cyclohexanone with alkali. A thick paste is ob-

1. I. G. Farbenindustrie, A.-G., E. P. 330897; abst. J. S. C. I. 1930, **49**, 828-B. See E. P. 330957.

tained, which after dilution with water, may be used as a priming composition for filling the pores of wood.

In the formation of plastic masses, films, artificial fibers or lacquers[1], methylcellulose which is water-insoluble at 16° or over, may be incorporated with ethyl-, acetyl- or nitro-cellulose, and the mixture thereby entirely loses its water-solubility. The application of this discovery is indicated as follows:

1. 75 parts methylcellulose are treated with such an amount of alcohol that complete gelatinization just takes place, and is then well mixed with 25 parts acetylcellulose gelatinized with aqueous acetone, whereupon the solvent is evaporated. There results a water-insoluble product suitable for plastic mass formation, the product not even swelling in water.

2. A 10% aqueous solution of methylcellulose is able to dissolve water-insoluble ethylcellulose up to 2% of its weight, and from this, plastic masses may be fabricated. Or, 50 parts methylcellulose with 50 parts water, worked up in a kneading machine to a homogeneous mass, to which is then added 50 parts ethylcellulose swollen by means of alcohol, and this worked up to an indistinguishable mass. The two are mixed and the solvent removed by evaporation, plastifying bodies being added if desired, before or after solvent expulsion.

3. 25 parts methylcellulose are homogenized with 20 parts water and the paste thus formed worked up with 50 parts nitrocellulose swollen by ethyl acetate, acetone and butyl acetate. Plastifiers, dyes or pigments may also be incorporated.

In order to obtain stable emulsions of nitrocellulose, celluloid or acetylcellulose by means of the presence of methylcellulose in combination therewith[2], which emulsions are entirely insoluble in water after having once been evap-

1. I. G. Farbendind., A.-G., D. R. P. 534852. F. P. 615876.
2. H. Persiel, G. Balle and K. Sponsel, D. R. P. 540872; abst. Chem. Zentr. 1932, I, 1316.

orated to dryness, the following method may be used, as indicated by the following quantitative formulas:

1. 50 parts of nitrocellulose dissolved in 30% butyl acetate, 40% butyl alcohol, and 25% benzene are mixed with 50 parts 5% aqeous methylcellulose, whereby an emulsion is formed of excellent stability. After drying, there results a sticky, elastic, transparent mass, soluble either in water, benzene, benzine, alcohol or ethyl or butyl acetates.

2. 7 parts of 6% celluloid solution prepared from 6 parts cellluoid scrap, 12 parts ethyl acetylglycollate, 18 parts butyl acetate, 45 parts butyl alcohol, 10 parts xylene and 8 parts light benzine (ligroin) are emulsified with 8 parts of 5% aqueous methylcellulose and brought onto cardboard. The coating protects the paper from wetting and dampness, can be readily soaped and washed, and also be provided with stampings.

3. 20 parts nitrocellulose solution consisting of 14 parts nitrocellulose moistened with butyl alcohol (65% content dry nitrocellulose) are mixed with 100 parts ethyl acetylglycollate, 10 parts benzyl alcohol, 50 parts ethyl acetate and 42 parts methyl acetate, and to this is added 50 parts of 5% aqueous oxyethylmethylcellulose. There results a thick, whitish emulsion which is very stable. On drying in thin layers it leaves behind a transparent film, insoluble in water and organic solvents, and is distinguished by great mechanical strength and resistance to cold.

4. 30 parts of 8% acetylcellulose solution consisting of acetylcellulose 8, benzyl alcohol 10, ethyl acetylglycollate 40, cyclohexanone 10 and methyl acetate 32, are emulsified with 50 parts of 5% aqueous, water-soluble ethylcellulose. On drying this emulsion leaves behind a flexible, sticky film, non-inflammable, and unaffected by water or organic solvents.

In an analogous manner, emulsions of methylcellulose with linseed or other oils may be prepared of substantial stability[1]. A substitute for egg yolk for the tanning of

1. I. G. Farbenindustrie, F. P. 35939, Addn. to F. P. 615876.

leather has been described by O. Röhm[1], who treats hides with 10% of their weight of a tanning liquid comprising 20 parts oil, 5 parts sodium glycerophosphate, or a salt of one or more di- or poly-hydric alcohols with phosphoric acid (sodium glycerophosphate), except lecithins or phosphatides, with methylcellulose as an emulsifying agent.

Water-insoluble binding agents as the cellulose ethers and cellulose esters, or natural or artificial resins[2] may be formed without the aid of plasticizers or solvents. The binding agents for this purpose are dispersed in aqueous media as a paste, emulsion or suspension. The application of the process is indicated by the following examples:

1. 100 parts nitrocellulose are intimately kneaded with 100 parts each water and methylcellulose until a putty-like mass results. Through further kneading or grinding with 100-500 parts of filler (wood flour, kieselguhr or chalk), previously wetted with water, a stiff mass is obtained. The mass can be now applied as such or thinned with water or volatile solvent, as a filler for wood or other porous surfaces. Upon placing a coating of cellulose ether or ester lacquers upon a surface so filled, the lacquer solvents penetrate and dissolve the filler coating, forming a unitary-appearing coating, coherent and of high adhesiveness.

2. 100 parts water-insoluble ethylcellulose are rubbed into a paste with a solution of 1 part sodium butylnaphthylenesulfonate in 50 parts water and with 150 parts ultramarine blue. After dilution with water to painting consistency, in order to prevent settling out, a solution of starch or glue may be added, the paint thus obtained being useful for application to concrete. The dry coating is sprayed over with a mixture of 60 parts alcohol until the surface is thoroughly wetted. After volatilization of the solvent, there remains a coherent, highly adhesive protective color.

1. E. P. 337524; abst. J. S. C. I. 1931, **50**, 131-B.
2. I. G. Farbenindustrie, A.-G., Swiss P. 145463; abst. Nitrocellulose, 1931, **2**, #8, 167.

3. 100 parts linseed oil varnish are well mixed with a solution of 28 parts methylcellulose in 252 parts water and ground with sufficient wood flour to form a paste. The mixture is rolled upon a fabric or upon pasteboard in a thin layer, and after drying, painted over or coated with a mineral oil lacquer, the thinner of which on penetrating into the lacquer dissolves the oil particles and brings about their coalescence to a coherent film. On drying in air the mass hardens to an elastic layer. By the use of a plurality of coats, a flooring material may be produced.

The I. G. Farbenindustrie have found that by incorporating in an aqueous solution of an alkylcellulose as methylcellulose[1], a colloidal substance in solution or emulsion, such as an oxidized or drying oil, hydroxybenzyl alcohol or a synthetic resin, may be obtained, as indicated in the following two examples:

1. 1000 parts of 10% aqueous methylcellulose solution and 5 parts linseed oil are intimately mixed until the oil is dispersed uniformly throughout the mixture in a fine state of subdivision, and the preparation is then worked up into a film, which after removal of solvent by evaporation is still soluble in water, but completely loses this property if heated at 100-110° for 4 hrs. in presence of air. The linseed oil is converted into linoxyn, insoluble or only sparingly soluble in the usual solvents, and when the film is brought into contact with water, prevents access of water to the methylcellulose particles. The duration of the heating operation may be shortened if there is added to the linseed oil a siccative. Conversion of the film to the insoluble state may also be brought about at ordinary temperature, but the operation requires a longer time.

2. 15 parts of formaldehyde-urea condensate insoluble in but capable of forming an emulsion with water, are intimately mixed with 1000 parts 15% aqueous ethylcellulose solution, until the condensate is uniformly dispersed

1. I. G. Farbenindustrie, A.-G., E. P. 308284; abst. C. A. 1930, **24**, 239; J. S. C. I. 1929, **48**, 595-B; Brit. Plastics, 1929, **1**, #3, 113; Chem. Zentr. 1929, II, 1103.

throughout the mass in a fine state of subdivision. A sheet or film made from the preparation so obtained becomes completely insoluble in water when heated 2 hrs. at 80-100°.

Cellulose Ether Ultra-Filters. Nitrated cloth has been used to a limited extent for the clarification of products of strongly acid reaction[1], details of which are found in the disclosures of O. Hering[2], C. Claessen[3], F. Erban[4], Farbenfabriken vorm. F. Bayer & Co.[5], H. Warren[6], E. Cramer[7], D. Bachrach[8], and D. Field[9]. In bacteriological work for osmosis, dialysis and other physical experiments, collodion membranes have been used for some time, and their preparation and utility have been described by A. Fick[10], W. Schumacher[11], J. Baranetsky[12], Gorsline[13], G. Malfitano[14], H. Bierry and J. Giaja[15], E. Gripon[16],

1. R. Böttger, Ann. 1860, **114**, 111; abst. Poly. Notiz. 1860, **15**, 97; Dingl. Poly. 1860, **155**, 463; J. prakt. Chem. 1860, **79**, 384; Jahr. Chem. 1860, **13**, 680; Poly. Centr. 1860, **26**, 863.
2. Farbenfabr. vorm. F. Bayer & Co., D. R. P. 72969, 1892; abst. Chem. Ind. 1894, **17**, 464; Ber. 1894, **27**, 179-R; Zts. ang. Chem. 1893, **6**, 371; Mon. Sci. 1894, **44**, 65. Farbenfabriken vorm. F. Bayer & Co., Zts. ang. Chem. 1907, **20**, 571; abst. Wag. Jahr. 1907, **53**, I, 584.
3. D. R. P. 58133; abst. Zts. ang. Chem. 1891, **4**, 721; Wag. Jahr. 1891, **37**, 385; Ber. 1892, **25**, 180-R. Eschellmann, D. R. P. 107050; abst. Wag. Jahr. 1900, **46**, I, 345. D. R. P. 88681; abst. Wag. Jahr. 1896, **42**, 262. Zts. ang. Chem. 1907, **20**, 318; abst. C. A. 1907, **1**, 1462.
4. Zts. Schiess. Spreng. 1906, **1**, 433; abst. Chem. Zentr. 1907, I, 382.
5. Zts. ang. Chem. 1907, **20**, 317; abst. Wag. Jahr. 1907, **53**, I, 583; J. Soc. Dyers & Col. 1907, **23**, 175; C. A. 1907, **1**, 1169.
6. Chem. News, 1895, **71**, 165; abst. Jahr. Chem. 1895, **48**, 1360; Bull. Soc. Chim. 1895, **14**, 914; Chem. Zentr. 1895, I, 1036.
7. Zts. ang. Chem. 1894, **7**, 269; abst. J. S. C. I. 1894, **13**, 833; Proc. Amer. Pharm. Assoc. 1895, **43**, 493; Jahr. Chem. 1894, **47**, 350.
8. U. S. P. 692102; abst. Chem. Ztg. 1902, **26**, 165; J. A. C. S. 1902, **24**, 381.
9. E. P. 17472, 1912; abst. C. A. 1914, **8**, 274; J. S. C. I. 1913, **32**, 882.
10. Pogg. Ann. 1855, **94**, 59; abst. Ann. 1857, **102**, 97.
11. Pogg. Ann. 1860, **110**, 337.
12. Pogg. Ann. 1872, **147**, 195; abst. J. C. S. 1873, **26**, 346; Jahr. Chem. 1872, **26**, 28.
13. "Contributions to Medical Research," 1903, 390.
14. Compt. rend. 1905 **140**, 1245; **141**, 660; abst. Chem. News, 1905, **91**, 261, **92**, 237; 1906, **94**, 36; J. C. S. 1905, **88**, ii, 459; 1906, **90**, ii, 33; Chem. Zentr. 1905, II, 20, 1660, 1778.
15. Compt. rend. soc. Biol. 1907, **62**, 432.
16. Compt. rend. 1875. **80**. 882; abst. J. C. S. 1875. **28**. 726.

J. Matthews[1], S. Bigelow[2], S. Bigelow and A. Gemberling[3], A. Porter[4], A. Schoep[5], H. Bechhold[6] and E. Hatschek[7].

Collodion membranes, however, have their limitations when used with alkaline solutions or with sulfides which either de-esterify the nitrocellulose, or acetylcellulose if this ester has been used, or else the sulfide denitrates the cellulose nitrate. To overcome these objections, H. Fink and R. Stahn[8] have described the preparation of cellulose ether ultra-filters with pore sizes capable of being graded within wide limits, and of high resistance to both weak and strong alkalis, acids, alkaline sulfides and even high concentration ammonia. The use of aromatic-aliphatic cellulose ethers as cellulose phenylurethane may also be employed[9] as likewise the cellulose methylphenylthiocarbamides.

The degree of decomposition of the cellulose ethers used as measured by the viscosity of their solutions determines to a certain extent the porosity of the ultra-filters obtained therefrom, the porosity of the filter, under otherwise similar methods of manufacture, increases with decreasing viscosity of the initial material. According to the invention, the average pore size of the ultra-filter may be

1. J. Phys. Chem. 1910, **14**, 281; abst. Jahr. Chem. 1910, **63**, I, 45. J. Duclaux, F. P. 461785; abst. C. A. 1914, **8**, 2484.
2. J. A. C. S. 1907, **29**, 1675; abst. Chem. Zentr. 1908, I, 1132; C. A. 1908, **2**, 750; J. C. S. 1908, **27**, ii, 88; J. S. C. I. 1908, **27**, 93; Bull. Soc. Chim. 1908, **4**, 962; Jahr. Chem. 1905-8, I, 167.
3. J. A. C. S. 1907, **29**, 1576; abst. Chem. Zentr. 1908, I, 322; C. A. 1908, **2**, 618.
4. Biochem. Zts. 1910, **25**, 301. Cf. H. Bechhold, Zts. physik. Chem. 1907, **60**, 257.
5. Bull. Soc. Chim. Belg. 1910, **24**, 278; abst. J. S. C. I. 1910, **29**, 1041; C. A. 1911, **5**, 1240, 2350.
6. Zts. Chem. und Ind. der Kolloide, 1906, **1**, 107; Biochem. Zts. 1907, **6**, 379; Elektrochem. 1907, **13**, 527; abst. C. A. 1907, **1**, 2762; 1908, **2**, 1155, 1225, 3183; J. C. S. 1908, **94**, ii, 24, 823; J. S. C. I. 1907, **26**, 993; Bull. Soc. Chim. 1908, **4**, 1032; Chem. Zentr. 1907, II, 1374; 1908, I, 193; Jahr. Chem. 1905-8, I, 264, 265, 267; Zts. physik. Chem. 1907, **60**, 257; 1908, **64**, 328.
7. J. S. C. I. 1910, **29**, 125; abst. C. A. 1910, **4**, 1121.
8. D. R. P. 542063.
9. L. Lilienfeld, D. R. P. 455589; abst. Chem. Zentr. 1928, I, 1732.

graded as finely as desired in that to the solution of the cellulose ether in a volatile solvent, there is added a second material before the evaporation of the solvent, which shows the properties of (1) being practically non-volatile, (2) forms a transparent pellicle with the cellulose ether after evaporation of solvent, and (3) must be soluble in water. The usual solvents as pyridine, chloroform-methanol, dioxane or methyl acetate may be used, the water-soluble body being such compounds as glyceryl *a*-chlorhydrin, diethyl tartrate, triethanolamine, dimethyl ether, polyglycol as ethyleneglycol. According to the degree of porosity desired in the filter, there is added 200-500% of the water-soluble component. With the use of higher amounts of addition agents, more highly viscous cellulose ethers are employed.

In the following examples, the relative viscosities tabulated are the out-flow period of the solutions in an out-flow viscosimeter, as compared to the out-flow of the solvent, a 2% solution being used in each case. As solvent for the pure cellulose ether, pyridine alone was used, and for the cellulose thiourethanes, a mixture of pyridine-water (9:1). In the following examples, the porosity of the ultra-filter signifies the number of cc. of water passing through a filter surface of 42 sq. cm. in 10 min., with a vacuum of 12 mm.

1. An ethylcellulose (45% ethoxyl) and relative viscosity 17.5 sec., is dissolved to a 3.3% solution in anhydrous pyridine, and to the solution is added 150-350% of the weight of ethylcellulose of glyceryl *a*-chlorhydrin, the solution being then poured out in a thin layer. After evaporation of the pyridine (about 20 hrs.), there remains a glassy, sticky film, which is then immersed in water and washed. The following porosities were obtained: hydrin, 200%, 250%, 300%, 350%, porosity 0.8, 2.6, 3.5 and 4.8 respectively.

2. Ethylcellulose (43% ethoxyl), relative viscosity 16.7 sec., is dissolved to 2.5% in dioxane. To the solution

is added 300-400% of the weight of ethylcellulose of diethyl tartrate. Further working as in (1) above. After evaporation of the dioxane, the films are glass-clear with respect to transparency. The ultra-filters gave the following porosities: Diethyl tartrate, 300%, 350%, 400%; porosity, 3.9, 4.8, 9.2 respectively.

3. To ethylcellulose phenylthiourethane (25.5% ethoxyl, 1.53% N), with relative viscosity of 25.9 sec., in a 3% solution in pyridine-methanol (4:1), was treated with 250-500% hydrin as before, the following porosities being obtained: Hydrin, 250%, 300%, 400%, 500%; porosity, 1.1, 1.6, 8.4 and 28.0 respectively.

4. Ethylcellulose phenylthiourethane (28.62% ethoxyl, 1.54% N), relative viscosity 10.16, is dissolved up to 4% in pure pyridine and treated with the amounts of dimethyltriethanolamine (triethanolamine dimethyl ether) given below. The film remaining after evaporation of the pyridine is weakly opalescent by reflected light and gave the following results: Amine, 150%, 200%, 300%; porosity, 0.0, 4.2 and 23.5 respectively.

Another process[1] basically similar, has also been described.

Cellulose Ethers in Leather Industry. The formation of artificial leather coatings by the application of a textile backing was one of the early successful applications of pyroxylin in the arts, and is the basis of an extensive and growing industry. The automobile manufacturer consumes large quantities, and considerable amounts are used in furniture manufacture. The application of cellulose acetate in the production of imitation leather coatings has not reached commercial prominence for the reason that up to the present time, the nitrocellulose coatings are much less expensive, especially as considerable waste moving picture scrap is being used for this purpose. Likewise, up to the present, the cellulose ethers are unable to compete in cost

1. I. G. Farbenindustrie, A.-G., D. R. P. 535337; abst. C. A. 1932, **26**, 1120; Chem. Zentr. 1932, I, 111.

with the pyroxylins in this industry, but several methods have been proposed for the utilization of cellulose ethers in the various ramifications of this art, which merit careful attention on account of their potentialities, if the price factor should become more nearly equalized.

The Imperial Chemical Industries have laid claim to the use of the cellulose ethers in this connection[1], in association with synthetic resins of the glyptal type, and glyceryl phthalate resins (Rezyls) have been advocated for the same purpose in connection with the cellulose esters, especially on account of their resistance to deterioration by ultra-violet light[2]. The resulting leather cannot be glazed. The artificial leather composition of R. Clavel[3] makes use of cellulose alkyl ethers either alone or in association with cellulose acetate.

The C. Simpson imitation suede leather[4] is prepared by coating the smooth side of velour cloth of fine texture with a solution of an organic cellulose derivative to form a flexible backing. The Langverte & Co. fabric is similar[5]. W. Stelkens[6] glues leather and similar materials by reducing the cellulose ether or ester to a fine powder, sprinkling it on the surface and between the layers to be glued, then applies simultaneously heat and pressure. The cellulose ether contains therein, preferably a large amount of plastifiant.

In protecting leathers, skins, fabrics and similar articles in the manufacture of fancy goods[7], during their various transformations and manipulations and their shaping

1. F. P. 686381; abst. C. A. 1931, **25**, 616. F. P. 669612.
2. M. Lamb and J. Gilman, Cuir tech. 1932, **21**, 138; abst. C. A. 1932, **26**, 3404.
3. U. S. P. 1727862; abst. C. A. 1929, **23**, 5349. E. P. 252661; abst. C. A. 1927, **21**, 2397. F. P. 611401; abst. J. S. C. I. 1927, **46**, 362-B. D. R. P. 509400; abst. C. A. 1931, **25**, 840. Can. P. 275369, 292887.
4. E. P. 306693; abst. C. A. 1929, **23**, 5349. See E. P. 291890.
5. E. P. 298982; abst. C. A. 1929, **23**, 3111.
6. E. P. 314867; abst. C. A. 1930, **24**, 1542; J. S. C. I. 1930, **49**, 1081-B.
7. Etabl. R. Schneider and A. Poelman, E. P. 344453; abst. J. S. C. I. 1931, **50**, 601-B.

by machine or by hand, dirt, deterioration and markings show which it is almost impossible to avoid. This drawback is particularly conspicuous in the case of leathers, skins and fabrics of light color or white, which, whatever subsequent steps may be taken, cannot entirely recover their pristine appearance. This may be obviated, according to the patentees, by covering the goods with a thin adherent film of benzylcellulose while the article is passing through the various steps of fashionings, the cellulose ether being rendered plastic to allow of distortion during the shaping of the material. Adhesion is obtained either by a partial solution of the plastic material and calendering, or by hot calendering, or by direct pouring of a film, precautions being taken lest it be too adhesive. For instance, the surface of the article may first be moistened with a non-aqueous liquid which is not a solvent for the cellulose ether, as benzine, or with a body precipitating the solution when the film is subsequently applied. The lacquer or film is ,of course, applied to the top or face side of the leather or fabric to be protected, that is, upon the face which will be seen when the article is finished.

In the production of imitation leather according to directions as laid down by L. Lilienfeld[1], cellulose ethers are combined with an oil obtained by treating crude aromatic hydrocarbons with a dehydrating, condensing and polymerizing agent, the product being especially applicable for the preparation of imitation leathers, as indicated in the two following examples:

1. In a mixture of 60 parts benzene and 30 parts alcohol, or 90 parts benzene only, 10-15 parts ethylcellulose are dissolved, and this solution mixed with 7.5-15 parts of polymerized aromatic hydrocarbon oil. Then a pigment or lake is added to the solution, and the latter spread in one or several layers on a suitable textile fabric or on paper. If several layers are used, it is possible to calender or press

1. U. S. P. 1625416. See U. S. P. 1563203, 1563204.

the several layers. The artificial leather may be provided with any grain or pattern by heat embossing.

2. Benzylcellulose or ethylcellulose 30 parts are mixed with 20-35 parts by weight of a polymerized oil as above, preferably while warm, until a uniform paste or solution results. With this solution, a pigment as lampblack is added, after which the paste is friction calendered onto a suitable surface as fabric or paper. It is also possible to mix the cellulose ether with the oil in the presence of a very small quantity of a suitable solvent as benzene or benzene-alcohol.

In the production of artificial leather by another process, the base or ground coat as applied to the paper or textile backing[1] is recommended to be made of dissolved ethylcellulose. In the coating composition for treating surfaces as devised by British Celanese, Ltd.[2], a cellulose ether is precipitated on a textile, wood, metal or glass surface by evaporation of a solution in a mixed solvent which has a predominating portion of high boilers as methylcellulose, toluene or amyl alcohol, clouded or opaque effects being produced. In the formation of imitation leather from cellulose ethers according to another method[3], the basic fibrous material or the tips of its fibers, are impregnated superficially with a thin layer of either the cellulose ether or with a solvent only for the same, the plastic cellulose ether being subsequently applied before all the solvent has been evaporated. The upper layer of material may also be previously impregnated with a liquid softening agent as ethyl phthalate, or with a gelatinizing agent.

Or, a thin layer of cellulose ether may be rolled out in

1. Compagnie Francaise D'Exploitation Des Procedes Plinatus, F. P. 664888; abst. Kunst. 1931, **21**, 213.

2. E. P. 346269; abst. J. S. C. I. 1931, **50**, 685-B; Brit. Plastics, 1931, **3**, #30, 84.

3. Compagnie Francaise D'Exploitation Des Procedes Plinatus, E. P. 317824; abst. J. S. C. I. 1930, **49**, 985-B; Brit. Plastics, 1930, **2**, #18, 279.

the semi-solid state[1], attached to the base, and then by means of heat and pressure, made into a unitary appearing mass. This is said to be especially applicable when impressing a cellulose ether film into a textile backing. Impression and embossing may be made a single operation.

In producing imitation of the so-called Spanish or antique leather, E. Katz[2] induces a mottled or blurred effect indicative of old age, by mechanically or manually applying several stippled coats of dyes, that is, by stippling on the dye by means of sponges or sponge-rollers, or by squirting on the coats. After the first dye or paint is applied the fabric is dried, and subsequently a second or plurality of coats are applied either of the same or a different color. The cellulose ethers have been described as desirable materials for the manufacture of book cloth[3]. R. Ditmar[4] has described the various methods appearing in the literature for rendering leather and artificial leather impermeable, and M. Deschiens[5] a review of the patents and their application for the use of cellulose acetate in the manufacture of artificial leather.

Cellulose Ethers and Tannin. In order to insolubilize those cellulose ethers which have not been etherified to the maximum and which are either soluble in or swollen by water, especially the lower alkylated methyl- and ethyl-celluloses, L. Lilienfeld[6] treats the ether with albumin-precipitating agents, especially tannin or tanning agents, trichloracetic acid, phosphotungstic acid, chrome alum, potash alum or aluminum sulfate. The process appears suited not only to those alkylcelluloses which are soluble in water,

1. W. Plinatus, E. P. 301759; abst. C. A. 1929, **23**, 4369; J. S. C. I. 1930, **49**, 319-B; Chem. Zentr. 1929, I, 1875. See E. P. 317824.
2. U. S. P. 1858859.
3. L. Lilienfeld, U. S. P. 1505043; abst. C. A. 1924, **18**, 3272.
4. Caout. et Gutta. 1932, **29**, 15, 914; abst. C. A. 1932, **26**, 3403.
5. M. Deschiens, Cuir, 1923, **12**, 58; abst. C. A. 1923, **17**, 1731.
6. U. S. P. 1505044. E. P. 7137, 1914; 181392, 181393. F. P. 447974, 451875, 451876, 552770. D. R. P. 207743, 260379, 262558, 265415, 265855, 285772, 291457, 292531, 293640, 293693, 331523, Aust. P. 94837. Can. P. 249775.

but also those ethers which do not dissolve at room temperatures but which swell in water below 16°, and particularly in water below 10°.

In the execution of the process, solutions or jellies of the alkylcellulose are treated with either natural or synthetic tannins (see p. 85, n. 3) dissolved in such solvents as glacial acetic acid, benzene-alcohol mixtures, chloroform or chloroform-alcohol, and then dried. The process may be carried out commercially as follows:

1. To a 5% solution of an ethyl- or methyl-cellulose soluble in water, a 10-30% solution of tannin in water is added with stirring, until precipitation ceases. Excess of tannin is not harmful. The fibrous, flocculent precipitate is collected on a filter and washed with water. Then it is either dried or dissolved in an organic solvent as glacial acetic acid, and this solution used for the production of films, filaments or plastic masses.

2. A film made from a methyl- or ethyl-cellulose soluble in water or artificial filaments made from such cellulose ethers, is immersed 5 min. or longer in a 3-30% aqueous tannin solution, cold or hot, then the precipitate formed is washed and dried, when it may be used as such in the arts, or redissolved and employed for other purposes (see p. 1426).

The tanning agent of A. Schmidt[1] comprises emulsions prepared from aqueous solutions of water-soluble alkylcelluloses, particularly methylcellulose and ethylcellulose, by incorporation therewith of fatty substances as train oil, rape oil, bone oil, neatsfoot oil, wool fat, tallow, vaseline or paraffin oil. The emulsions so formed may be employed either for tanning agents in chamoising, or to serve as a fat-liquor for leathers tanned with vegetable or mineral tanning agents, and also for leathers obtained by means of a synthetic tanning material. The application of the process is indicated by the following examples:

1. U. S. P. 1780983; abst. C. A. 1931, **25**, 231. E. P. 318070.

1. An emulsion of 100 parts train oil in 100 parts of 5% aqueous methylcellulose solution of low viscosity is used for chamoising, by uniformly impregnating the unhaired skin with this emulsion. The skin is then dried in the air and the train oil allowed to oxidize, the leather then being worked up in the usual manner by washing in an alkaline solution. Owing to the protective effect of the dimethylcellulose solution the oxidation of the train oil takes place slower than when no dimethylcellulose is used, but is much more uniform, and the plumpness of the leather is considerably increased.

2. 100 parts of 5% aqueous dimethylcellulose solution, and which does not coagulate unless heated to 60-70°, are stirred with 100 parts of neatsfoot oil until emulsification is complete. The leather is then stuffed with this mixture at about 60°.

3. Three parts of a wetting agent, as sodium dibutylnaphthalenesulfonate dissolved in 20 parts water, are added to 100 parts 5% aqueous dimethylcellulose solution, and 80 parts mineral oil are then run with stirring, into the mixture thus obtained. An emulsion is immediately produced which can be used for stuffing leather. Instead of the mineral oil, there may be advantageonsly used a mixture of mineral oil 20 and bone oil 60.

K. Daimler, K. Sponsel and G. Balle[1] have described a process for the manufacture of transparent structures insoluble in water and not materially swelling therein, by the use of water-soluble methyl- and ethyl-celluloses, whereby water-insoluble coatings result by the use of tannin precipitating agents. Unless the manipulation is carried on with great care, and with the precipitating agents at certain concentration, the cellulose ether precipitates out in flocks and thus makes the structure non-transparent. It has been found that by the addition of ammonia or its liquid organic derivatives to a weakly acid albuminous precipitating agent, these disadvantages are overcome. After

1. D. R. P. 508930. See D. R. P. 511205.

evaporation of the solvent and the liquid base, water-insoluble, but nevertheless transparent, flexible and lustrous structures are obtained. A further advantage of the process is said to lie in the fact that the use of organic solvents is avoided.

The practical carrying out of the process is indicated in the following examples:

1. 100 gms. of a 10% aqueous solution of methylcellulose are treated with a solution containing 10 gms. tannin, 5 gms. ammonia and 85 gms. water, and the mixture poured on a glass plate. After evaporation of the solvents there remains a clear, transparent insoluble film.

2. 10 gms. methylcellulose and 1 gm. sulfonated diphenylmethylene ether[1] are dissolved in 100 gms. 2% ammonia, filtered, and poured out on glass. After drying, a thin layer is obtained which is capable of swelling in water with difficulty.

3. 100 gms. 10% aqueous ethylcellulose are treated with a solution of 10 gms. tannin and about 5 gms. ethylamine in 95 cc. water. After spraying the mixture through a fine opening there remains a thread, which after drying in a stream of warm air, has become completely insoluble in water.

It has also been found that alkylcelluloses which are soluble in water or swelled thereby[2] may be brought into solution or kept in solution after treatment with tannin or tanning materials, by mixing an organic solvent, which must be soluble in water, with a considerable proportion of water and adding thereto. It is preferable to dissolve the water-soluble alkylcellulose in the organic solvent and then add the tanning material. Should these additions not be clearly soluble in the solution mixture of the finished solution, they are precipitated in finely divided form in the manufacturing, without affecting the solubility of the alkyl-

1. A. Steindorff, K. Daimler and G. Balle, D. R. P. 445569; abst. Chem. Zentr. 1927, II, 1000.

2. H. Persiel, D. R. P. 509067; abst. C. A. 1931, **25**, 1083. See E. P. 181392. F. P. 447974, 686598. D. R. P. 406081.

cellulose-tannin compound. The following examples are illustrative:

1. There are mixed together equal parts by weight of methylcellulose in water (10% strength) on the one hand, and a 10% alcoholic solution of tannin on the other. The clear solution leaves behind on drying, insoluble tanned methylcellulose.

2. In a solution of 3 parts by weight of tannin in 12 parts of water, and 14 parts by weight of *n*-propanol, there are dissolved 4 parts methylcellulose. The solution is less viscous than an aqueous solution of methylcellulose of the same concentration.

3. In the organic solvents used other suitable cellulose derivatives may be dissolved and thus introduced into the total solution as a further ingredient. Thus, I part tannin and 1 part water-insoluble ethylcellulose are dissolved in 4 parts ethyl alcohol and 4 parts ethylglycol, and this solution combined with 10 parts 10% aqueous methylcellulose solution.

In the preparation of filaments, and especially films from water-soluble methylcellulose[1], or a mixture of water-soluble methyl- and ethyl-cellulose, it has been found that if such solutions be extruded through circular orifices or slits into hot water as a setting bath, transparent products result. The following example indicates the practical carrying out of the process:

1. A 20% solution of methylcellulose is prepared in cold water by stirring with an amount of cold water insufficient to produce a 20% solution, and slowly, as the dissolving process progresses, adding such an amount of ice that at the end the solution has a 20% content of alkylcellulose at 0-10°, or else the solution is taken up in a vessel equipped with stirrer and cooling jacket, in the proportionate amount necessary, or else a paste is made of the methylcellulose with the calculated amount of water at 60-80°,

1. K. Sponsel and G. Balle, D. R. P. 509304; abst. C. 9. 1931, **25**, 1083.

and the mass slowly cooled with stirring to 10-15°, whereby a homogeneous solution results. A methylcellulose prepared in this manner is extruded through a slit opening of 0.5 mm. diameter under pressure into a bath of water at 80-90°, the methylcellulose ribbon coagulating at once, and from the water bath is led to a suitable drying apparatus. A clear, elastic film of about 0.1 mm. thickness results.

Cellulose Ethers in Explosive Industry. The etherified celluloses have but few applications in connection with the explosive art, but the several uses indicated appear to be more than of passing importance. The Imperial Chemical Industries, Ltd.[1], have described a method for the treatment of gun powder and other propellent explosives in granular form in order to modify the brisance, increase the water-proofing qualities, and modify the speed of combustion, in which ethyl- and benzyl-cellulose are used.

The object of the invention is the treatment of explosives in granular form so as to effectually control its burning speed, the treatment of black powder in order to diminish its hydroscopicity and render it more desirable for use in a safety fuse, the treatment of explosives to retard combustion without affecting its dependability, and to provide a slow burning powder which will enable the user to economize on length. Efforts have been made from time to time to slow down powder by mixing with it inert materials as clay, brickdust, rosin, starch, graphite and wax. The difficulty encountered in this method appears to be chiefly due to the fact that when a small amount is added, the powder grains lie contiguous to each other, and though there are not as many grains in a given area, the rate of flame propagation is but little retarded, while if a sufficient amount of inert material is added to produce a marked effect in the burning speed, the powder grains are sometimes separated from each other by grains of inert material, and at once, irregularities in speed occur.

1. E. P. 300611; abst. J. S. C. I. 1929, **48**, 912-B.

These difficulties are said to be obviated by treating a well-balanced powder with a solution of ethylcellulose or benzylcellulose of the proper viscosity and dilution, and then drying the powder. There remains deposited or coated upon the grains or penetrated into their minute interstices a film or residue which does not materially check the progress of burning of the powder, but does render it waterproof.

The W. Dickson percussion cap[1] and similar types of primers and igniters, as used for ignition of propulsive powder charges in cartridges, may have the exposed surface of the priming composition protected from moisture and from damage during insertion into the cartridge, by being coated with a benzylcellulose lacquer, prepared, for example, by dissolving 2.7 gms. benzylcellulose in acetone 80 cc. and ethyl lactate 20 cc., to which is added 0.3 gm. dibutyl phosphate. The application of the varnish to the caps is carried out in the usual way by picking up drops of the varnish on a series of metal pegs and touching the surface of the caps with the drop hanging to the peg.

In protecting the paper tubes of shot gun cartridges and cartridges from the damaging effects of moisture or water[2], F. Griffiths coats the tubes with a mixture of cellulose ethers or esters or a mixture of cellulose ethers with cellulose esters, to which resins and a drying oil may be added. The solvents used are toluene, butyl acetate, methylethyl ketone and industrial spirit, with such plasticizers as dibutyl phthalate or tricresyl phosphate.

Shoe Stiffener.[3] In the manufacture of shoes and boots with thermoplastic toe stiffeners, it is essential that the stiffening composition shall not soften at atmospheric heat extremes, shall be substantially unaffected by moisture,

1. E. P. 307560; abst. C. A. 1929, **23**, 5319; J. S. C. I. 1929, **48**, 418-B. F. P. 671683; abst. C. A. 1930, **24**, 2297.

2. F. Griffiths, J. Shufflebotham and Imperial Chemical Industries, Ltd., E. P. 327429; abst. C. A. 1930, **24**, 5159.

3. For general manufacture of shoe stiffening compositions, see U. S. P. 1209661, 1215875, 1215876, 1283391, 1316650, 1365607, 1426538, 1429237, 1517520.

solid under normal conditions, yet capable of being softened by a degree of heat not injurious to leather. Celluloid has long been used in this art for the manufacture of shoe tips[1], insoles[2], foot-arch supports[3], heels[4], shoe lasts[5], shoe tips[6], boot uppers[7], lacing tips[8] and strips[9], shoe enamels[10], shoe patches[11], shoe hook caps[12], shoe stiffeners[13], shoe bottom fillers[14]. The processes of W. Carpenter[15], D. Heinsohn[16], L. Levy[17], T. Clarke[18], F. Oliver[19], P. Vorsteher[20] and S. Lovell[21] are similar. Cellulose and resin[22], and celluloid and copal, the latter with alcohol and ethyl acetate as solvents[23], combine high thermoplasticity and insolubility with the necessary rigidity when cold. Starch paste with diethylene glycol[24], zein[25], cellulose acetate[26], phenolic condensation products[27] and resinoids have also been advocated.

The shoe stiffening composition of Atlas Ago Chemische Fabrik[28] employs the cellulose ethers, which are indicated as desirable for this purpose on account of their ready solubility in a wide range of readily obtainable solvents, insolubility in water, extreme stability, especially in the

1. J. Hyatt, U. S. P. 203834.
2. U. S. P. 219484, 1018132.
3. S. Korn, E. P. 10988, 1912.
4. E. Stoe**1**er, U. S. P. 675451.
5. A. Lorant, E. P. 25939, 1902.
6. K. Schilling, D. R. P. 178438.
7. J. and A. Thierry, E. P. 2134, 1885; 3247, 1899.
8. M. Bortree, U. S. P. 575387.
9. D. Berry, E. P. 1377,1902.
10. C. Orcutt, U. S. P. 114470.
11. Deutsche Gummiwaren-Industrie Schlappig & Co. and O. Schlappig, E. P. 25541, 1911.
12. F. Mostert, D. R. P. 228381; abst. Kunst. 1911, **1**, 17.
13. K. Lengfellner, E. P. 25726, 26033, 1908. Swiss P. 43470, 1908. D. R. P. 206223. F. P. 396814.
14. Livingston & Doughty, Ltd., E. P. 4402, 1910. See also Thomas, E. P. 17667, 1906.
15. U. S. P. 256198.
16. E. P. 12016, 1906.
17. E. P. 16632, 1904.
18. E. P. 24806, 1908.
19. E. P. 10104, 1896.
20. E. P. 13225, 1912.
21. U. S. P. 1843687; abst. C. A. 1932, **26**, 1735. See U. S. P. 1711956; abst. C. A. 1929, **23**, 3316.
22. I. McClellan, U. S. P. 1408816.
23. *Ibid.* U. S. P. 1353968.
24. W. Lund, U. S. P. 1852018.
25. C. Swett, U. S. P. 1348968.
26. W. Lund and L. Mellerio, U. S. P. 1720243; abst. C. A. 1929, **23**, 4310.
27. *Ibid.* U. S. P. 1846346; abst. C. A. 1932, **26**, 2562.
28. E. P. 339394. See E. P. 320488.

presence of perspiration and alkaline solutions, and their thermoplastic nature. Canvas, felt, pasteboard or fabrics are impregnated with the cellulose ether in solution, either as a unitary coating or a plurality of impregnations, the solvent allowed to dissipate, and then by combined heat and pressure formed to the contour and size required. The stiffener is placed on the last with its adhesive side against the lining, through which the impregnant permeates.

The F. Woodruff box toe blank comprises a porous waterlaid sheet of fibers, at least partially coated with a previously gelatinized cellulose derivative as benzylcellulose[1] existing as a discontinuous phase and capable of being again gelatinized by a volatile solvent, and of rendering the blank stiff upon the expulsion of solvent. The amount of cellulose compound deposited is about equal to the weight of the fiber.

A stiffener for toes[2], and a shoe heel lacquer[3], both utilizing cellulose derivatives as cellulose acetate or cellulose ether, have been described. Or[4], the toe or other part of a shoe may be stiffened and reinforced by incorporation with a fibrous material of a cellulose acetate lacquer, gelatinized with acetone and the material then dried.

For the blackening of colored shoes[5], G. Steimmig recommends dissolving 50 parts alcohol-soluble Nigrosine (Schultz-Julius No. 698) dissolved in 200 parts ethylene glycol mono-cresyl ether alone or admixed with ethyleneglycol mono-propyl formate, while slightly heating and diluting with 150 parts ethyl alcohol-benzine. Russian leather oil may be added as a perfume. The glycerol-glue-formalin mixtures are non-thermoplastic[6].

1. Can. P. 319439.
2. H. Dover, E. P. 298371.
3. F. Edbrook, E. P. 202154; abst. C. A. 1924, **18**, 335. U. S. P. 1607516; abst. C. A. 1927, **11**, 333; J. S. C. I. 1927, **46**, 85-B. Can. P. 238217.
4. E. P. 289496; abst. C. A. 1929, **23**, 720.
5. G. Steimmig, U. S. P. 1788781; abst. C. A. 1931, **25**, 1083.
6. F. Beckwith, U. S. P. 1834999; abst. C. A. 1932, **26**, 1080.

Cellulose Ether Inks. Special inks for writing and printing on cellulose have been evolved and described in detail by A. Graf[1], M. Lefferts and J. Stevens[2], J. McClosky and C. Farwell[3] and W. Kuwert and C. Buschler[4]. They for the most part comprise a basic dyestuff or lake soluble in solvents in conjunction with a small proportion of active solvent or low boiling as acetone or methyl or ethyl acetate, together with a high-boiling, slow evaporating solvent or colloidant as triacetin, dibutyl phthalate or dibutyl lactate. In the M. Krümmling method, wrappers of canvas or pasteboard are printed upon by means of an ink comprising cellulose acetate dissolved in glycol diacetate or triacetin, or similar solvents which act in the cold on partially hydrated acetylcellulose. Any suitable dye dissolvable in acetone or other volatile solvent which is preferably a solvent for the cellulose derivative may be used[5].

The manufacture of a new class of inks especially adapted for printing purposes has recently been described, containing the water-soluble or water-insoluble cellulose ethers as a basis together with charcoal, graphitic carbon or soluble dyestuffs to impart the desired color. In the J. Scheiber process[6] esters of octadecadien(9.11)acid(1) of polyalcohols are combined with colored pigments or dyestuffs as a printing ink base, and in a subsequent improvement on the process[7], the triglyceride of octadecadien(9.11)-acid(1), which is a solvent of the cellulose ethers is combined therewith, to which natural or artificial resins may be added to increase the viscosity.

1. Swiss P. 62354; abst. C. A. 1914, **8**, 2270. Eder's Jahr. 1897, 500. Pharm. Centr. 1901, **42**, 661; Seifenfabr. 1901, **21**, 745. Cosmos, 1907, **56**, 138.
2. U. S. P. 380654.
3. U. S. P. 422430.
4. Erfind. Erfahr. 1896, **23**, 304. Rev. Gen. Pharm. **10**, 727; abst. Year Book of Pharmacy, 1903, 333.
5. M. Kruemmling, E. P. 10578, 1909. See E. P. 14483, 1903; 4957, 26502, 1906. W. Brueckner, D. R. P. 238361, 241781, 1909; abst. C. A. 1911, **5**, 2960; 1912, **6**, 2180; J. S. C. I. 1912, **31**, 227.
6. D. R. P. 522486; abst. Chem. Zentr. 1931, I, 3618.
7. J. Scheiber, D. R. P. 544697, Addn. to D. R. P. 522486; abst. Chem. Zentr. 1932, I, 2242.

H. Arzt[1] claims that hitherto there has been lacking in the textile finishing industry an ink, which by writing or stamping would show a high resistance towards chemical and mechanical influences, all previously prepared inks of this nature being deficient either on account of their chemical aggressiveness or because they act injuriously on the goods to which they are applied, if satisfactory otherwise. He claims to have overcome these disadvantages by the use of a cellulose ether solution carrying a single organic solvent and suspended pigment. The advantages claimed for an ink of this nature is that it is neutral, simple to use, capable of being stored indefinitely without deterioration and has good covering power. Writings made with the ink are said to stand on vegetable fibers steeping with 3° Be. NaOH solution at 2-3 atms. pressure for 16 hrs., or mercerizing with 40° Be. NaOH solution or chlorine bleach. The ink is prepared by mixing 130 gms. benzene and 13 gms. alcohol into which is dissolved 10 gms. ethylcellulose. When the solution has been stirred until homogenous, 5 gms. pure, dry lampblack are introduced, and after vigorous stirring the preparation is filtered through a fine mesh sieve and is ready for use. Before use, it is shaken to insure proper and uniform suspension.

The ink for cellulose esters or ethers as devised by J. Clewell[2], and which is said to remain permanent against abrasion, and the attack of photographic developing solutions, and not to have a deleterious effect on a sensitized photographic emulsion, is obtained by dissolving 2 parts National nigrosine base N in a mixture of 20 parts diacetone alcohol to which has been added 8 parts orange shellac. The rate of drying may be increased by addition of acetone or methyl acetone, and diminished by the incorporation of diacetin or triacetin. Other compatible solvents are ethyl lactate or diethylene glycol.

1. D. R. P. 540997.
2. U. S. P. 1806965; abst. Chem. Zentr. 1931, II, 2820.

Pigmentation of Cellulose Ethers. In the pigmentation of cellulose ethers and cellulose esters by inorganic chemicals by double decomposition[1], M. Theumann has pointed out several methods which are applicable. In general, in coloring by this method, the salts or chemicals used shall either be soluble in a solvent of the cellulose compound, or else they shall be used in such small proportions that incipient precipitation of the cellulose ether or ester is avoided. When the color desired has been obtained by double decomposition of the salts, it is usual to precipitate the cellulose ester or ether by a liquid in which the formed color is insoluble, and then evaporate to dryness. For instance, the cellulose derivative may be dissolved in acetone and a small quantity of aqueous solution of potassium ferrocyanide added and a concentrated solution of ferric chloride added. Prussian blue in an extremely divided state is formed. At the completion of the reaction, the product is poured into water, the blue colored cellulose compound washed, and dried.

Or, cadmium sulfate and sodium sulfide gives the yellow cadmium sulfide nickel nitrate with a soluble oxalate, green nickel oxalate; manganous nitrate with an alkaline sulfide, a pink manganous sulfide; antimony chloride with a sulfide, orange antimony sulfide; and about every color of the spectrum is producible in this manner by coupling the usual decompositions used in inorganic qualitative analysis.

L. Clement and C. Riviere[2] have disclosed a process for the pigmentation of cellulose ethers which are water-insoluble, the invention being characterized by the feature that the ether to be pigmented as well as the pigment be previously reduced to powder form, and then stirred together in a liquid medium comprising a solvent for the cel-

1. U. S. P. 1789121; abst. C. A. 1931, **25**, 1101; Plastics, 1931, **7**, #5, 277; Chim. et Ind. 1931, **25**, 956. Can. P. 278978; abst. C. A. 1928, **22**, 2839.

2. E. P. 350924; abst. J. S. C. I. 1931, **50**, 877-B; Textile Mfr. 1931, **57**, 422. F. P. 704499; abst. C. A. 1931, **25**, 4705. F. P. 710345.

lulose ether with an equal volume of water, so that the ester is slightly attacked and swollen by the solvent-water mixture. After a few hours a large quantity of the pigment is found to have been fixed in the cellulose derivative substance, being either of a chemical or physical order of fixation, depending upon the nature of the pigment. The product is then precipitated, washed, and dried, when it may be dissolved in organic solvents to a colored solution of a high degree of permanency. To such a solution of cellulose ether titanium oxide may be added, or prussian blue or similar colored pigments. The process is said to be especially applicable to the incorporation of bronzes therein, which may be fixed directly upon the cellulose compound. Films prepared therefrom are claimed as useful for the manufacture of gold tips for cigarettes. Both ethylcellulose and benzylcellulose are specified as suitable. Or[1], an emulsion of soap with the pigment may be made, and this mixed with ethylcellulose and the solution boiled until the major portion of the pigment has been absorbed in the interstices of the cellulose ether, the latter then being precipitated and dried.

In the pigmentation of cellulose ethers, specifically ethylcellulose, according to the E. de Stubner method[2], double decomposition is relied upon as in the M. Theumann method outlined above, methods for producing lead chromate from lead acetate and a bichromate being given, and also the impregnation of the cellulosic material with metallic copper by first soaking in a solution of a water-soluble copper salt as the sulfate, and then treating with a reducing agent as iron filings or zinc dust. Prints obtained from vat dyes with the aid of methylcellulose[3] are fixed without steaming, by means of a salt bath containing alkali and a reducing agent as a hyposulfite.

1. L. Clement and C. Riviere, F. P. 709195.
2. U. S. P. 1795764; abst. C. A. 1931, **25**, 2566. E. P. 277949; abst. J. S. C. I. 1929, **48**, 365-B; Chem. Zentr. 1928, I, 266.
3. A. Schmidt and E. Pfeffer, D. R. P. 515305; abst. C. A. 1931, **25**, 2007; Kunst. 1931, **21**, 94. D. R. P. 155415, 193121, 448286.

Insoluble or difficultly soluble dyes may be solubilized by treatment with a small amount of alkylcellulose before reducing the dye to small particles. Thus, a small amount of methylcellulose solution is added to a sodium hydroxide solution of 2-hydroxy-3-naphthoic acid anilid, and the whole added to acetic acid in ice water. A fine suspension results. A diazo solution may then be added[1].

In the preparation of pigments in a high state of dispersion[2], as in the manufacture of covering varnishes, it is customary to use insoluble inorganic and organic pigments, but in order to obtain the desired opacity and hence maximum covering power, it is necessary that the pigments be in an exceedingly fine state of subdivision, and in intimate association with the lacquer vehicle. This is accomplished according to a patent granted the I. G. Farbenindustrie, by preparing the pigments in a highly dispersed form before incorporation into the varnish mass, and by the use of water-soluble alkylcelluloses as colloiding agents. The working of the process is clarified by means of the following three examples:

1. A solution of 10 gms. ferric ammonium sulfate in 100 cc. water is stirred with 75 gms. of a 5% aqueous methylcellulose solution, and further mixed with constant stirring, with a solution of 5.5 gms. potassium ferrocyanide in 60 cc. water. The intensely blue solution thus obtained is coagulated by heating on the water bath, and the coagulum washed with boiling water until free from water-soluble salts.

2. 90 gms. dry methylcellulose are dissolved in a solution of 125 gms. crystallized cadmium sulfate in 1600 gms. water, and then mixed with stirring with 250 cc. ammonium thiocyanate solution of 9% strength. The coagulum is treated as in Ex. 1.

3. A cold, saturated solution of 34.2 gms. crystallized sodium chromate (about 100 gms. water) is mixed with

1. F. Risse and E. Fischer, D. R. P. 523910.
2. I. G. Farbenindustrie, A.-G., E. P. 354696.

100 gms. 4% methylcellulose aqueous solution, and mixed with a cold, saturated solution of 33.1 gms. lead nitrate (requiring about 90 gms. water) mixed with 100 gms. methylcellulose solution as above. By vigorous stirring after mixing, the yellow lead chromate is thrown down in an exceedingly fine state of subdivision. By heating the mixture the methylcellulose is coagulated and encloses the lead chromate. Those ethylcelluloses which coagulate on rise in temperature may substitute the methylcellulose in the above process[1].

A. Martin[2] impregnates cellulose ethers with pigments which are caused to penetrate under pressure, by placing the moistened or swollen cellulose ether or ester in a rapidly revolving centrifuge, and then slowly pouring in the pigment, say a finely precipitated prussian blue. The increased gravity of the pigment aided by the high centrifugal force "throws" the pigment particles against and into the cellulose derivative with the result that, after running the whizzer at maximum speed for 20 or so minutes, the material may be washed with hot water if desired, without removal of substantial amounts of blue color. The process of Kali-Chemie A. G. and W. Lambrecht is basically analogous[3].

The Celluloid Corporation[4] have found that if a spray of finely divided metal be impinged with sufficient force on a cellulose ether plastic, particles of the metal will "stick" thereto and be imbedded therein, and firmly adhering metallic deposits may be produced. As a wide variety of metals are readily converted into spray form, it is thus possible to produce on cellulose derivatives a wide variety of ornamental effects of highly decorative value. One way of producing the metallic spray is by feeding a metallic rod into an oxyacetylene flame and blowing the fused metal into spray. Any metal may be used for this purpose as zinc, tin,

1. I. G. Farbenind., A.-G., E. P. 354696; abst. C. A. 1932, **26**, 3942.
2. E. P. 354784; abst. C. A. 1932, **26**, 3942; J. S. C. I. 1931, **50**, 1019-B.
3. D. R. P. 541201; abst. C. A. 1932, **26**, 2065.
4. E. P. 369309; abst. J. S. C. I. 1932, **51**, 503-B.

pewter, brass, copper, bronze, silver, gold or platinum, but probably not much of the latter two are used in practice.

In preparing a filler or primer for the coating of surfaces that are not smooth, in order to prepare the surface for the application of lacquers thereon, especially wood surfaces, W. Moss[1] utilizes methyl-, ethyl- and benzylcellulose solutions in conjunction with a non-drying oil as cocoanut oil or the fatty acids obtained therefrom. Plastifiers may be added, and pigments acting as fillers (China clay, silex) incorporated with the cellulose derivative placed in solution by means of a volatile solvent combination.

In order to produce pigmented lacquers and enamels, one method advocated is to swell artificial threads of cellulose ethers or esters by means of a solvent, then bringing the intumesced cellulose derivative in contact with the mineral or pigment, also in suspension in a liquid composition which exerts a solvent or swelling action on the cellulose ether[2].

Solid Alcohol. The production of "travelers spirits," "alcohol cubes," "solid spirit" with nitrocellulose as a base is a common article of commerce, being sold under such names as Alcoheat, Alcofuel, Sterno, Solol, Theroz, Solid Sunbeams and Solakol. The imprisoning physically of alcohol for facility of transportation has also been accomplished by the use of soap[3], paraffin[4] or wax[5]. F. Bayer & Co. disclosed a method in which cellulose acetate was used to diminish the inflammability without, at the same time, materially diminishing the speed of burning[6].

1. U. S. P. 1857161. Can. P. 306829.
2. L. Clement and C. Riviere, F. P. 710345; abst. C. A. 1932, **26**, 1134; Chem. Zentr. 1931, II, 3061.
3. R. Wild, E. P. 5405, 1901; abst. J. S. C. I. 1902, **21**, 244, 1226.
4. L. Denayrouze, E. P. 17687, 1900; abst. J. S. C. I. 1901, **20**, 976. F. P. 296132, Addn. F. P. 3962; abst. J. S. C. I. 1905. **24**, 429. G. le Fortier, Belg. P. 195098. See Bull. de la Soc. Fran. de Phot. 1881, **27**, 121. V. Perelzveich and G. Rosenbusch, U. S. P. 919759. E. P. 26915, 1907. F. P. 397092.
5. J. Schaub, U. S. P. 1262267, 1262268; abst. J. S. C. I. 1918, **37**, 330-A. F. Poulton, U. S. P. 1299408; abst. C. A. 1919, **13**, 1759. C. Wagner, U. S. P. 1317950; abst. C. A. 1919, **13**, 3309.
6. F. Bayer & Co., D. R. P. 134721; abst. Wag. Jahr. 1902, **48**, II, 456.

In 1932 appeared the process for the manufacture of solid alcohols of R. Geller[1], in which pharmaceuticals and medicaments are incorporated, he having discovered that the sodium salts of benzoic, salicylic and phthalic acids either singly or in mixture are particularly suitable for solidifying alcohols, especially in combination with relatively small amounts of dimethylcellulose or trimethylcellulose. The solidifying or hardening process may be used for all purposes in which solid alcohols are required, as in the preparation of solid alcohol compositions for burning purposes and for cosmetic and therapeutic uses. Due to their great stability from a chemical and mechanical aspect, these solid alcohols are said to be particularly useful for the manufacture of solid alcoholic iodine preparations, such as utilizable in pharmaceutical operations. It is not necessary to add an iodide as a chemical stabilizer for the free iodine. In order to suppress the iodoform formation occurring in the course of time from the action of iodine upon alcohol, one of the acids above mentioned or the corresponding sodium salt may be added.

Airplane and Balloon Fabric Lacquers. There is a well-marked distinction between these two classes of protective coatings. While both seek to render the fabric impervious and impermeable, coatings intended for airplane wings must possess in addition a certain well-defined contractile, astringent and tautening effect upon the canvas so treated, and both should be coated with preparations which are affected by ultra-violet rays to a minimum. The general subject of airplane dopes, more specifically of cellulose acetate base, has been treated in the writings of H. Britton[2], K. Atsuki and R. Shinoda[3], H. Gardner[4], E. Schmidt[5],

1. U. S. P. 1844754.
2. Aviation, 1927, **22**, 991. Ind. Chemist, 1927, **3**, 59; abst. C. A. 1927, **21**, 1555. Ind. Chemist, 1927, **3**, 116; abst. C. A. 1927, **21**, 2070; Chem. and Met. Eng. 1927, **34**, #5, 312.
3. Rept. Aeronautical Research Inst. Tokyo Imp. Univ. 1928, **3**, 49; abst. C. A. 1928, **22**, 2473.
4. Paint Mfr. Assoc. of U. S. Circ. 1926, #274, 61; abst. C. A. 1926, **20**, 2756.
5. Farben-Chem. 1932, **3**, 165, 209; abst. C. A. 1932, **26**, 4188.

G. Esselen[1], P. Drinker[2], M. Deschiens[3], Neocellon, Ltd.[4], W. McCutcheon[5], O. Merz[6], L. Clement and C. Riviere[7], A. Eichengruen[8], J. Ramsbottom[9], G. Young[10], and J. Cochrane[11]. Tautness has been shown to be governed by humidity, temperature, the composition of the dope and by the nature, initial tension and extensibility of the fabric.

Both nitrocellulose[12] and cellulose acetate[13] have been used for the coating of balloon and dirigible fabric, being usually associated with aluminum powder or an iron oxide to minimize the destructive effect of the sun's rays, and also to minimize loss of hydrogen or helium. Zeppelins[14] have the fabric coated one or both sides with a combination of rubber and cellulose derivative in solution, a mixture of cellulose ether and rubber being readily prepared by means of the mutual and inexpensive solvent benzene or toluene. The use of animal skins is then claimed to be unnecessary. The J. McKechnie fabric for aircraft gas bags combines cellulose esters with rubber applied over goldbeaters skin[15], while the Ballonhüllen Ges.[16] prefers a

1. Ind. Eng. Chem. 1918, **10**, 135.
2. Rev. Prod. Chim. 1921, **24**, 716. Paper, 1921, **28**, 29. Ind. Eng. Chem. 1921, **13**, 831; abst. C. A. 1921, **15**, 3910; Chim. et Ind. 1922, **7**, 121; Kunst. 1921, **11**, 189. Kunst. 1922, **12**, 18; abst. Chim. Tech. Uebers, 1922, **46**, 266.
3. J. S. C. I. 1925, **44**, 902-C. & I.; abst. C. A. 1921, **15**, 764. Rev. prod. Chim. 1921, **24**, 3; abst. C. A. 1921, **15**, 1409.
4. Chem. Age (London), 1925, **12**, #309, 480.
5. J. Soc. Automotive Engrs. 1930, **27**, 263; abst. C. A. 1932, **26**, 4485.
6. Farben-Ztg. 1931, **36**, 2156, 2197; abst. C. A. 1931, **25**, 5999.
7. Chim. et Ind. 1920, **3**, 440; abst. J. S. C. I. 1920, **39**, 481-A.
8. Kunst. 1916, **6**, 151.
9. J. Royal Aeronautical Soc.; abst. J. Soc. Auto. Eng. Aug., 1924, 16. Trans. Faraday Soc. 1924, **20**, 295; abst. C. A. 1924, **18**, 2608; J. S. C. I. 1925, **44**, 238-B.
10. Aviation, 1928, 1149.
11. Commonwealth Australia Munitions Supply Board, Tech. Repts. 1921, 20; abst. C. A. 1924, **18**, 584.
12. G. Blenio, U. S. P. 1427941.
13. V. Richmond, U. S. P. 1378804.
14. H. Strobl, U. S. P. 1827213; abst. C. A. 1932, **26**, 606. Luftschiffbau Zeppelin G. m. b. H. and H. Strobl, D. R. P. 483484; abst. C. A. 1930, **24**, 512; Chem. Zentr. 1930, I, 459.
15. U. S. P. 1301955; abst. C. A. 1919, **13**, 1936.
16. D. R. P. 321264; abst. Caout. et Gutta. 1921, **18**, 11158;

30% solution of factis in amyl formate to which zapon varnish is added. I. Jacobsohn and S. Truscott[1] disperse rubber in viscose solution and apply as an aircraft covering. Instead of attaching the fabric to the woodwork of the airplane and then coating, C. Dreyfus[2] obtains a maximum tautening effect by applying an acetylcellulose lacquer to the fabric, and while the coating is still moist, the fabric is tacked onto the aileron frames and allowed to tauten as it dries.

T. Tesse[3] finds "a very fine aesthetic effect" is imparted to airplane cloth or canvas by applying a coating of a cellulose ether dissolved in low and high boilers and plasticizers, and having admixed therewith zinc oxide in very fine degree of suspension[4]. The dope of A. Barr and H. Lazell[5], which tightens, stretches and waterproofs aeronautical envelopes, and at the same time absorbs ultraviolet rays, is obtained by adding to an acetylcellulose dope, a mixture of yellow ochre, ultramarine and zinc oxide. Waxes as beeswax or paraffin may also be added to regulate tensioning[6], or a mixture of acetin and acetanilid may be incorporated[7]. The tautening effect may be heightened, it is claimed[8], by using a combined dope containing both nitro- and acetyl-cellulose.

In the cellulose ether field a number of processes have been proposed and formulas evolved for the utilization of

C. A. 1921, **15**, 1083. Airship Guarantee Co., Ltd., and C. Burney, E. P. 239569; abst. C. A. 1926, **20**, 2254.

1. U. S. P. 1706294; abst. J. S. C. I. 1929, **48**, 554-B.
2. E. P. 100180; abst. J. S. C. I. 1916, **35**, 887. E. P. 131384; abst. J. S. C. I. 1919, **38**, 759-A.
3. E. P. 124763; abst. J. S. C. I. 1919, **38**, 319-A.
4. T. Tesse, E. P. 124844; abst. C. A. 1919, **13**, 1771; J. S. C. I. 1919, **38**, 319-A; Chim. et Ind. 1921, **6**, 89.
5. E. P. 131641; abst. C. A. 1920, **14**, 359; J. S. C. I. 1919, **38**, 834-A; Ann. Rep. Soc. Chem. Ind. 1920, **5**, 324.
6. British Aeroplane Varnish Co. and S. Groves, E. P. 128974; abst. C. A. 1919, **13**, 3028; J. S. C. I. 1919, **38**, 518-A.
7. British Emaillite Co. and J. Goldsmith, E. P. 124515; abst. C. A. 1919, **13**, 1771; J. S. C. I. 1919, **38**, 273-A; Chim. et Ind. 1921, **5**, 572.
8. G. Given and N. Thomson, Can. P. 324954. Imperial Chemical Industries, E. P. 353589; abst. C. A. 1932, **26**, 3686.

the higher etherified celluloses, particularly those ethyl- and benzyl-celluloses which are not soluble in or swollen by water. The high stability of the cellulose ethers over other cellulose derivatives makes them peculiarly applicable for airplane coatings, especially as the fact has been demonstrated that, due to the absence of an acid radical therein, they are least affected by the ultra-violet rays and by direct sunlight.

The dope for aircraft constructions as evolved by S. Groves involves the use of cellulose ethers in conjunction with waxes as beeswax, or a cellulose ester varnish associated with paraffin in solution[1], while M. Hagedorn and A. Jung[2] combine cellulose ethers or esters with highly polymeric albuminous substances, as protein, gelatin, glue or casein. The addition of lanolin with cellulose derivatives has also been advocated[3]. Ethyl cinnamate and diethyl *iso*phthalate[4]; benzyl alcohol, ethyl acetoacetate, eugenol and isoeugenol[5]; and carvacrol or carvol[6] are some of the solvents which have been put forward as especially applicable with cellulose derivatives in airplane coating operations.

Methyl-, ethyl- or benzyl-cellulose lacquers as suitable fabric-proofing agents form the subject matter of an invention granted British Celanese, Ltd., T. Woodman and W. Dickie[7], who plasticize the cellulose ether by admixture with triacetin or the toluene- or xylene-sulfonamides.

1. S. Groves, U. S. P. 1366256; abst. C. A. 1921, **15**, 951; J. S. C. I. 1921, **40**, 154-A.
2. Can. P. 321056. I. G. Farbenindustrie, A.-G., E. P. 371604; J. S. C. I. 1932, **51**, 675-B. F. P. 715130; abst. C. A. 1932, **26**, 1783.
3. C. Dreyfus, E. P. 127615; abst. C. A. 1919, **13**, 2444; J. S. C. I. 1919, **38**, 531-A; Chem. Ztg. 1919, **43**, 581. E. P. 127678; abst. J. S. C. I. 1919, **38**, 531-A.
4. Soc. Nauton Freres et de Marsac and T. Tesse, E. P. 126989; abst. Ann Rep. S. C. I. 1920, **5**, 324; J. S. C. I. 1919, **38**, 531-A. F. P. 492698; abst. Chim. et Ind. 1920, **3**, 352.
5. *Ibid.* E. P. 158521. T. Tesse and L. Jaloustre, F. P. 508975; abst. Caout. et Gutta. 1921, **18**, 10894.
6. T. Tesse, U. S. P. 1521055; abst. C. A. 1925, **19**, 739; J. S. C. I. 1925, **44**, 95-B.
7. E. P. 249946; abst. C. A. 1927, **21**, 1019.

The addition of phenols or oxyacids is recommended as an antiseptic ingredient to prevent depredations by insects[1], whereas R. Wheatley incorporates amber oil for its solvent effect[2], the coating being made more fire-resistant by the addition of magnesium chloride and boric acid[3]. It has been found, however, that the addition of a large quantity of any deliquescent or hydroscopic material such as magnesium chloride, diminished the tautening effect induced by the cellulose derivative. Chinese wood oil in limited quantities appear to be a useful addition[4]. *iso*-Butyl *iso*butyrate, on account of its high boiling point and low solubility in water[5], has been recommended to induce a maximum contractility of the fabric when used as solvent for a cellulose derivative.

In airship construction, where the wings are usually constructed of a light framework over which is stretched a textile fabric, A. Sulzer[6] has shown that water-insoluble ethylcellulose is excellent as the cellulosic ingredient, pointing out that it does not become brittle at high altitudes or in the winter months as do the cellulose acetate dopes when applied for the same purpose. He dissolves 10 parts of ethylcellulose in 33 parts denatured alcohol and 7 parts benzene. This is applied to the airplane wings in the same way that cellulose acetate dopes have been hitherto used. It is advisable to incorporate in the dope 1-2 parts of plastifying ingredients as tricresyl phosphate, triphenyl phosphate, acetin or monochlorbenzene, and when several coatings are applied to the fabric, the initial or skim coat is free from plasticizer to give the maximum anchorage in the interstices of the fabric, and the outer layer having an

1. N. Voznesenskii and M. Chilikin, Russ. P. 4563; abst. C. A. 1928, **22**, 4844.
2. E. P. 112483; abst. C. A. 1918, **12**, 1002; J. S. C. I. 1918, **37**, 120-A.
3. K. Kawashma, U. S. P. 1469829.
4. A. Beck and J. Nicholson & Sons, Ltd., E. P. 134899; abst. Chim. et Ind. 1921, **6**, 816.
5. Cellon, Ltd., Tyrer & Co. and T. Tucker, E. P. 123628; abst. J. S. C. I. 1919, **38**, 207-A.
6. U. S. P. 1552808; abst. C. A. 1925, **10**, 3605.

excess of plasticizer. This is following the usual method of coating fabrics for artificial leather manufacture.

T. Araki and T. Nagamote[1] have found that the benzene-soluble ethylcellulose when dissolved in benzene or toluene furnishes solutions which are or become turbid, but the solution clarifies upon the addition of 3.5% alcohol, and again becomes opalescent upon increasing the alcohol content to 37.5%. Their recommended thinner suitable for the undercoating of airplane fabrics using ethylcellulose is benzene 60, methyl alcohol 13, benzyl alcohol 2 with ethylcellulose 12 (parts by weight). After the above dope has stood for a year and a half, no appreciable change was recognizable, the tensile strength of the film being 5 kgm. per sq. mm. They found that fabric doped with ethylcellulose is less loosened by atmospheric moisture than that with acetylcellulose, pigmented dope being decidedly superior to unpigmented.

A class of cellulose ethers new to this art has been proposed by I. Jacobsohn and S. Truscott[2] who use a lacquer of glycolcellulose (cellulose ether of glycollic acid) as a substitute for goldbeaters skin in the strengthening of fabrics used in gas-retaining fabric. The glycolcellulose is prepared by treating mercerized cotton with 20% NaOH solution for the formation of alkalicellulose. Then a suspension of sodium chloracetate in alcohol is added and the mixture allowed to stand over night. Next morning the entire mass is stirred into a large amount of water and purified by precipitation with alcohol. The purified product when dispersed in the same amount of water is ready for the operations of spreading on balloon cloth, fixing and plasticizing.

Stencil Sheets. In the preparation of stencil paper for mimeographing, neostyle, and duplicating work, where it is desired to make a number of copies in monochrome or polychrome, the typing or drawing on a sheeting of prepared or stencil paper has been found the most rapid and

1. J. S. C. I. (Japan) 1930, **33**, 382-B; abst. C. A. 1931, **25**, 1398; Cellulose, 1930, **1**, 292; J. S. C. I. 1931, **50**, 502-B.
2. U. S. P. 1706294, 1706295; abst. J. S. C. I. 1929, **48**, 554-B.

economical manner, where the maximum number of impressions desired is limited to a few hundred, and the preparation of paper of this nature constitutes a rather large and quite rapidly expanding industry. The stencil sheet fills the gap between the number of legible copies that may be obtained by means of sheets of carbon paper, and a large number of permanent impressions, wherein printing from type is concerned. The preparation of this impressionable sheet appears quite simple. It is but necessary to take a sheet of Japanese, Yoshino or other paper web of high tensile strength and with large interstitial spaces serving as a framework, and flow over or impregnate this sheet with a soft, waxy, impressionable coating comprising a binding agent as a cellulose compound, together with an unctuous tempering agent, the ratio of solvent in the composition being such that upon setting a solid layer results, or the layer becomes solid upon reduction of temperature to that of the room. However, the subject is much broader than this. The coating compound must be sufficiently elastic and plastic so that when such letters as "o" and "e," which have a central portion are cut into the stencil matrix, the center or core will remain in position and clear cut, and possess sufficient strength and body to withstand several hundred contacts of stencil sheet with paper upon which the reproduction is to be made. An immense amount of experimentation and also litigation has involved this subject, especially in connection with the two points as to the most desirable binder for the composition which is placed on the receptive paper matrix, and the nature and composition of the tempering agent applied thereto and used therewith, it being remembered that the tempering agent (a fatty or waxy substance) is seldom a solvent for and is usually incompatible with the binder (a cellulose ester or cellulose ether).

The subject matter of this topic is divided into four subdivisions, (1) Uses of nitrocellulose as a binder, (2) application of the organic cellulose esters (cellulose acetate)

for this purpose, (3) employment of the cellulose ethers, and (4) utilization of other materials for the same purpose, other than touched upon in the three topics preceding.

(1) *Stencil Sheets Containing Nitrocellulose.* Early in the field of producing sheets or compositions which may be applied to sheets, and when so applied are suitable for duplicating purposes, was Paul Campion who described a type-impressionable sheet in a patent application filed in Belgium, December 7, 1920, his composition comprising a base of pharmaceutical collodion (pyroxylin dissolved in alcohol-ether, 3:1) with the addition of solidifiable fats, oils and waxes, the Japanese paper being coated on one side only. Ether, acetone and ethyl acetate are mentioned as acceptable solvents[1].

W. Koreska[2] deposited in Austria October 11, 1922, a resume of his process for producing sheets capable of being used as stencils, in which celluloid or a cellulose ester is combined with natural or synthetic resins, waxes, oils and solid hydrocarbons. Tetra- and deca-hydronaphthalene were added to induce emollient effects. S. Horii[3] dissolves cellulose nitrate in a mixture of ethyl alcohol and acetate, amyl alcohol and acetate, glyceryl naphthenate (naphthenic acid glycerides) and squalene, with a small proportion of olein and stearin, quince oil also being used as a softener[4]. A. De Waele[5] combined ricinoleic acid, as the tempering agent, with nitrocellulose as the ink-resisting medium, or

1. Can. P. 249680, 249681. F. P. 544098. F. P. 29989, Addn. to F. P. 596749. D. R. P. 375072, 392029, 400862. Swiss P. 108090, 108505. Belg. P. 292613, 292843. Swedish P. 59074, 59605. Norw. P. 41025, 41204.

2. E. P. 201882; abst. C. A. 1924, **18**, 3. E. P. 205461. F. P. 563475. F. P. 27985, Addn. to F. P. 563475. D. R. P. 400662. Aust. P. 96156, 100715. Norw. P. 40249.

3. U. S. P. 1608881; abst. C. A. 1927, **21**, 308. U. S. P. 1679034; abst. C. A. 1928, **22**, 3748; J. S. C. I. 1928, **47**, 706-B. U. S. P. 1780391; abst. C. A. 1931, **25**, 178. E. P. 299520; abst. C. A. 1929, **23**, 3344. E. P. 310126; abst. C. A. 1930, **24**, 699.

4. S. Horii, U. S. P. 1729072; abst. C. A. 1929, **23**, 5285.

5. U. S. P. 1828766; abst. C. A. 1932, **26**, 816. E. P. 298705; abst. J. S. C. I. 1929, **48**, 14-B. E. P. 303631; abst. J. S. C. I. 1929, **48**, 204-B. F. P. 663861; abst. Chem. Zentr. 1929, II, 2292. Can. P. 290808.

by peptizing nitrocellulose with castor oil[1], or by the use of celluloid attached to a sheet of waxed tissue paper[2].

E. Hill[3] and A. B. Dick Co.[4] have described a stencil sheet which includes a nitrocellulose occluding or encasing a lubricant, to which lard, tallow, cottolene, or Chinese vegetable tallow is added as a setting agent and to preserve the proper consistency of the finished coating, and retain the composition in the desired state of softness, fluidity and displaceability[5]. Oil soluble resins or resin ethers may be added where dyestuffs, lakes or pigments are to be incorporated, as in the preparation of carbon papers and color compositions for use as a transfer and duplicating media[6]. The J. Ehrlich stencil sheet[7] involves the placing of a plastic composition upon a sheet of receptive paper, over which is sprinkled a thin layer of Lycopodium (club moss), with the object of preserving the plasticity and protecting it from outside moisture.

In the preparation of decorative designs as applied to vases, plates and pottery[8], a stencil is formed by molding a transparent substance upon a model of the article to be decorated, and removing it from the model when set. The model prepared with the design is coated with a cellulose ester solution, and upon evaporation of solvent, the layer is perforated along the outlines of the design and then cut through vertically to permit removal of the model. A suitable solution is given as celluloid 1, amyl acetate 1, acetone 4. H. Shallcross[9] combines lac with nitrocellulose, camphor and oils, and H. Bittner and C. Villedieu have

1. D. Gestetner, Ltd., Can. P. 247337, 259194, 287892.
2. *Ibid.* E. P. 20605, 1890.
3. U. S. P. 1608742; abst. Pulp & Paper Mag. 1927, **25**, #38, 1197. Can. P. 249584, 249681.
4. Danish P. 34343. Holl. P. 14500. Norw. P. 38893. Can. P. 263785.
5. Belg. P. 292613. Belg. P. 292843, Addn. to Belg. P. 243067. Belg. P. 308071. See U. S. P. 1526982.
6. R. Bain, E. Nixon and Lamson Paragon Supply Co., Ltd., E. P. 295118.
7. E. P. 284907; abst. C. A. 1928, **22**, 4742.
8. H. Van Lerven, E. P. 230587.
9. U. S. P. 1674611; abst. C. A. 1928, **22**, 2819.

recommended nitrocellulose, mononitronaphthalene and rosin or castor oil with the usual volatile solvents[1].

(2) *Stencils Prepared with Cellulose Acetate.* S. Horii has conducted a wide investigation as to the suitability of various softening, tempering and colloiding agents to be used in connection with polysaccharide acetates (cellulose, starch and mannan acetates) and has embodied his findings in a series of patents in which is recommended the use of dolphin oil[2], stearin and castor oil[3], liquid wax[4], naphthenic acid[5], naphthenic acid glycerides[6], alone and with a hydrocarbon oil[7], aluminum, iron, calcium or magnesium naphthenates[8], aluminum hydroxide or aluminum tannate[9], chlorinated naphthalene alone[10] or with tsubaki oil[11], phenol resins and fatty acids from tsubaki or sasanqua oils[12], a composition from Japanese seaweed called Funori[13], oleyl or selachyl alcohol from sperm oil[14], or the addition

1. E. P. 7975, 1897.
2. U. S. P. 1790987; abst. C. A. 1931, **25**, 1646. E. P. 310126, 310181. See U. S. P. 1770697, 1785260.
3. S. Horii, U. S. P. 1698705; abst. C. A. 1929, **23**, 1228. E. P. 289511.
4. *Ibid.* U. S. P. 1770697; abst. C. A. 1930, **24**, 4598.
5. *Ibid.* E. P. 261203; abst. C. A. 1927, **21**, 3459; Pulp & Paper Mag. 1928, 1682. See U. S. P. 1594525. Jap. P. 44216.
6. *Ibid.* U. S. P. 1664777; abst. C. A. 1928, **22**, 1832; J. S. C. I. 1928, **47**, 364-B. E. P. 250798; abst. J. S. C. I. 1926, **45**, 534-B. Can. P. 272792.
7. *Ibid.* U. S. P. 1792095; abst. C. A. 1931, **25**, 1958. E. P. 250798; abst. C. A. 1927, **21**, 1337; J. S. C. I. 1926, **45**, 534-B. See U. S. P. 1587954; abst. C. A. 1926, **20**, 2567. U. S. P. 1790987.
8. *Ibid.* U. S. P. 1829750; abst. C. A. 1932, **26**, 816.
9. *Ibid.* U. S. P. 1753204; abst. C. A. 1930, **24**, 2563. U. S. P. 1753205.
10. *Ibid.* U. S. P. 1645141; abst. C. A. 1927, **21**, 4036; Pulp and Paper Mag. 1929, 323. E. P. 275747; abst. C. A. 1928, **22**, 2446.
11. *Ibid.* U. S. P. 1825798; abst. C. A. 1932, **26**, 569. E. P. 275747; abst. C. A. 1928, **22**, 2446.
12. *Ibid.* U. S. P. 1664033; abst. C. A. 1928, **22**, 1660. U. S. P. 1698705; abst. C. A. 1929, **23**, 1229. E. P. 274241; abst. C. A. 1928, **22**, 2037. E. P. 278956; abst. C. A. 1928, **22**, 2819. E. P. 310181; abst. C. A. 1930, **24**, 699. E. P. 350699; abst. C. A. 1932, **26**, 4145. Can. P. 315803. See E. P. 289511.
13. *Ibid.* E. P. 259808; abst. C. A. 1927, **21**, 3459; Pulp and Paper Mag. 1928, 1682.
14. *Ibid.* U. S. P. 1664777; abst. C. A. 1928, **22**, 1832; J. S. C. I. 1928, **47**, 3643. E. P. 289511; abst. C. A. 1929, **23**, 680; J. S. C. I. 1928, **47**, 521-B. See E. P. 250798.

of pigments such as chrome yellow (lead chromate), toluidine red or Bismark brown which absorb the ultra-violet rays[1].

The Japanese stencil paper preferred by him is made by subjecting the bast tissues to the wet beating process until the degree of wetness reaches 40-60 beating units by the Schoper-Riegler beating tester. The finished paper is then coated in the usual manner[2]. A. Davis and A. B. Dick Co. have described tragacanth esters (?) obtained by treating tragacanth with acetic acid, forming tragacanth acetate (?)[3]. Acetylated acacia or gum karaya (kayada or maura) have also been recommended as hygroscopic tempering agents in stencil sheets, in combination with acetylcellulose. Amyl or butyl tartrates or phthalates[4], mono-, di- or tri-acetin[5], and monobenzoylbutyl tartrate in conjunction with zinc oxide[6] are also advocated as desirable components for inducing mobility and softness to the cellulose acetates[7].

A. De Waele[8] uses as an ink-resisting medium, either cellulose acetate, formate, propionate or butyrate with a tempering agent adapted to render the film sufficiently sensitive to be cut by a style or in a typewriter. The composition of C. Dreyfus[9] requires for each 100 parts cellulose acetate, 33 parts boiled linseed oil, 33 parts each triacetin and turpentine, with methylacetone, methyl acetate or acetone as direct solvents, while the *modus operandi* of the D. Williams and J. Rowe stencil sheet involves the

1. S. Horii, U. S. P. 1785260; abst. C. A. 1931, **25**, 567. E. P. 365542; abst. J. S. C. I. 1932, **51**, 336-B. See U. S. P. 1780391.
2. *Ibid.* E. P. 299520.
3. U. S. P. 1861209. See U. S. P. 1665580; abst. C. A. 1928, **22**, 1832.
4. A. B. Dick Co., U. S. P. 1639080; abst. Plastics, 1927, 540. E. P. 261806; abst. C. A. 1927, **21**, 3718.
5. *Ibid.* U. S. P. 1608743. E. P. 261806; abst. Pulp and Paper Mag. 1929, 323. F. P. 599112. Can. P. 270537.
6. A. Davis, Brit. Plastics, 1929, **1**, #5, 164.
7. A. B. Dick Co., E. P. 195977; abst. C. A. 1923, **17**, 3758. F. P. 564731.
8. E. P. 216648; abst. C. A. 1925, **19**, 178. See U. S. P. 1604884. E. P. 223255, 258628.
9. E. P. 127678; abst. J. S. C. I. 1919, **38**, 531-A.

use of glycerol with a resin as softener[1]. The H. Hartmann[2], A. Galland[3], W. Koreska[4] and Grief-Werke[5] all employ an acetylated cellulose.

(3) *Cellulose Ether Stencil Manufacture.* Whereas the nitrocelluloses and cellulose acetate are both insoluble in and antagonistic to fatty oils and fats as well as petroleum hydrocarbons, the cellulose ethers dissolve therein with avidity. In fact, it is but necessary to liquefy some solid fats and normally solid hydrocarbons and stir the cellulose ether therein when it goes entirely into solution. Considerable litigation has revolved around the point as to whether the cellulose esters actually dissolved the oils and waxes used in stencil manufacture, or whether a sort of reticulated framework of cellulose ester was set up in the finished stencil composition, in which microscopic droplets of the fat are encased or enclosed, something analogous to the fatty globules of cream in milk. This question entirely disappears with the use of the etherified celluloses, some types of which appear to produce true solutions with fats and oils. Therefore the cellulose ethers, especially the water-insoluble modifications, appear to be peculiarly adapted for stencil blank formation. Considerable work appears to be necessary along these lines, but this is a field in which it is apparent that the cellulose ethers have a great opportunity for technical usefulness.

A. Davis has described the formation of a stencil sheet in which characters are produced by pressure as by the impact of type or the use of a stylus[6], taking advantage of the carbohydrate ethers as an impregnating material, modified or tempered to make the material readily type-impressionable without preliminary moistening, and substantially insensible to atmospheric changes, being durable

1. Can. P. 264211; abst. C. A. 1926, **20**, 3787.
2. D. R. P. 426091. 3. F. P. 588746.
4. E. P. 350976; abst. C. A. 1932, **26**, 4145. F. P. 560777.
5. F. P. 588573. For coating composition containing casein see their E. P. 235516; abst. C. A. 1926, **20**, 974. Aust. P. 81220.
6. U. S. P. 1594769; abst. Chem. Zentr. 1926, II, 1707. U. S. P. 1861209.

and capable of producing a large number of copies. In preparing the carbohydrate ether especially adaptable to the process, 100 gms. purified cornstarch are dissolved in 900 cc. 10% aqueous NaOH solution, and 200 cc. 30% NaOH solution added. The mass is then warmed to 40-60° and 200 cc. diethyl sulfate added. The mass is then heated 0.5-2 hrs. on the water-bath to induce preliminary etherification, the mass meanwhile becoming more fluid. 500-600 gms. powdered NaOH are next added in solid form to produce a homogeneous solution.

600 cc. ethyl sulfate are now stirred in under constant agitation while the mass is kept at 85-95° for 1-2 hrs., or until a reaction sets in indicated by sharp foaming, the temperature meanwhile rising to about 120°. During this etherification the starch ether separates as it is insoluble in the supernatant liquor, first as a gummy mass which quickly hardens. It is then removed, disintegrated, washed first with water and then with dilute sulfuric acid until neutral, and dried to a white, amorphous, granular solid. The starch ether is now dissolved in ethyl acetate to a 12.5% solution, filtered, and is then ready for the compounding of stencil sheets.

To 100 cc. of this 12.5% starch ether solution are added 30 cc. ethyl acetate, and into this mixture is poured a mass consisting of 15 gms. chlornaphthalene, 12 gms. Japan wax, 8 cc. benzyl alcohol, these three products having previously been melted together to a homogeneous liquid. The product is poured into a suitable vessel and sheets of porous paper drawn through or floated over the surface so that but one side of the paper is coated, and hung up to solidify and permit excess solvent to evaporate. The resulting sheet is not readily stencillizable.

He claims[1] that benzylcellulose stencil sheets in quality are such as to make this cellulose ether highly desirable for their manufacture, the resulting sheets being easily type-

1. A. Davis, U. S. P. 1771165; abst. C. A. 1930, **24**, 4598; J. S. C. I. 1931, **50**, 344-B.

and stylus-impressible and yielding large numbers of copies when used with the usual types of duplicating machines. The benzylcellulose recommended for this purpose is preferably obtained by digesting 5 gms. refined cellulose with 10 gms. NaOH, 30 cc. water for 2 days at room temperature, after which 30 gms. benzyl chloride are added, and the mixture heated to 100° for 7 hrs. Excess of benzyl chloride is now removed by steam distillation, and the resulting, pulpy, fibrous mass washed with water, then with alcohol and finally with ether, and is then dried. The material is again treated with NaOH, and this followed by benzyl chloride, also as before. The ultimate dried product shows a yield of 7 gms., most of which is readily soluble in ethyl acetate, and this solution can be directly compounded with other modifying agents to produce masses from which stencils may be made by drawing over the surface of a sheet of Yoshino paper as previously described.

In detail, the stencil mass may be compounded as follows: The ethyl acetate solution of benzylcellulose is adjusted to a 5% concentration, and to 200 gms. of this solution are added 40 gms. each castor oil and benzoylbutyl tartrate, and 15 gms. tetra- or hexa-chlornaphthalene. The first two named readily mix with the solution, and the latter, although a solid, easily passes into solution, especially if warmed. Pigments or soluble dyestuffs may now be added in order to form a colored sheet and afford visibility to the type or stylus impressions upon the sheet. *p*-Chlorbenzylcellulose or phenylethylcellulose (ethylphenylcellulose) may also be used.

Tragacanth acetate (?) with monobenzoyl tartrate, monoacetylbutyl tartrate, benzoylamyl salicylate and benzoylethyl citrate[1] have been advocated as especially useful for stencil manufacture, being superior in this instance to butyl tartrate or amyl phthalate.

P. Smith[2] combines in the same coating composition,

1. A. Davis, U. S. P. 1834686.
2. U. S. P. 1655249; abst. Pulp and Paper Mag. 1929, 323.

organic cellulose esters and cellulose ethers with the usual tempering and softening agents, the composition being applied to a sheet of Japanese paper either as a unitary or plurality of coatings. Most satisfactory results are obtained by the use of methylcellulose or benzylcellulose mixed with a cellulose acetate hydrated to the point of acetone solubility. If ethylcellulose be used, that degree of ethylation expressed by pentaethylcellulose based on a C_{12} cellulose molecule is preferred, such an ethylcellulose being substantially insoluble in water, and but swelled inappreciably thereby. The cellulose acetate is first dried, then dissolved in acetone, and the cellulose ether manipulated in somewhat the same manner, the two solutions being then mixed. The ratio used is between 25-50% of the ester to the ether, that is, within a latitude of 1 to 4.

The process is carried out by dissolving 700 gms. acetone-soluble acetylcellulose in 6 liters acetone, which is then mixed with 300 gms. ethylcellulose in 4 liters acetone, 30 gms. castor oil and 2 liters benzene being then added. 10-50 gms. acetated glycerol may also be added to impart additional plasticity and a faint tackiness due to its hygroscopicity. Application of the solution to the rice paper is as in the normal manner.

H. Simon[1] employs either cellulose ethers or a cellulose ether-ester as nitrated cellulose ether in the manufacture of duplicating stencils, together with such softening agents as oleic acid, mineral oil or fat. A protein or resinous material may also be associated with the cellulose ether, casein being satisfactory, and protective composition of alkaline casein compounds (sodium caseinate or potassium caseinate) may be used with glycerol or sugar, or an alcoholic solution of palmitic acid and sodium oleate.

A. De Waele[2] prefers those cellulose and starch ethers which are soluble in water, that is, which have not been

1. E. P. 286466; abst. C. A. 1929, **23**, 249; Chem. Zentr. 1928, I, 2767.
2. E. P. 216648; abst. C. A. 1925, **19**, 173.

etherified to the maximum. Our experience with these ethers is that they mix less readily and in lower proportions with oily and fatty matters such as are normally used in duplicating stencil compositions, than do those cellulose and starch ethers of substantially maximum etherification. In his complete specification the use of a water-insoluble ethylcellulose is put forward, as is indicated by the following example taken from the patent description:

Ethylcellulose insoluble in water but dissolving in alcohol and in the form of a solution, is mixed with a suitable proportion of castor oil or a semi-drying oil or other oleaginous material to yield, when applied to a support as Yoshino paper and the solvent evaporated, a coherent coating sufficiently sensitive to be cut cleanly by means of a stylus or typewriter type faces. As a dispersion agent, zinc ricinoleate has been patented by him[1].

The stencil sheet of D. Smith[2] particularly intended to receive the imprint of characters by the impact of type, employs the carbohydrate ethers, especially the starch ethers. In practicing his invention a high-grade commercial corn starch 100 gms. are dissolved in 90 cc. of 10% NaOH solution and then 200 cc. 30% NaOH solution added. The mass is then warmed on the waterbath to 40-60°, when there are added 200 cc. ethyl sulfate and heating continued 0.5-2 hrs., during which time the mass thins. There are now added 500-600 gms. powdered NaOH which rapidly dissolve in the mass to form a homogeneous solution. 600 cc. ethyl sulfate are now stirred in and the mass heated to 85-95° for 1-2 hrs. or until reaction sets in, shown by a rapid foaming, and the temperature spontaneously rises to 120°. During the reaction, the starch is converted into an ether, which being insoluble in the supernatant ether separates to a gummy or gelatinous mass which quickly hardens. It is then removed from the liquid, disintegrated and

1. A. De Waele, U. S. P. 1819078; abst. Plastics, 1931, **7**, #11, 634.

2. E. P. 244543; abst. Pulp and Paper Mag. 1927, **25**, 1197. F. P. 587063, 587064. Dan. P. 36522.

washed free from reactants and to a neutral reaction and dried at a low temperature.

The starch ether thus produced is dissolved in ethyl acetate to a 12.5% solution, dissolving readily, even in the cold. After a small residue is removed by filtration, it is ready for compounding into stencil sheets. To 100 cc. of this starch ether solution, there are added 30 cc. ethyl acetate, and into which is then poured a mass consisting preferably of 15 gms. chlornaphthalene, 12 gms. Japan wax and 8 cc. benzyl alcohol, these three products having been previously melted together. The mass is placed in a vessel and sheets of Yoshino paper drawn over the surface, the sheets being hung up for the excess liquid to drip off and the solvent to evaporate.

(4) *Other Stencil Sheet Processes.* A large number of other basic materials other than the cellulose ethers and esters and their solvents and colloiding bodies already mentioned have been proposed or patented. The basic material in the A. De Waele[1] and the D. Smith[2] processes is viscose for the cellulosic body, being coagulated by means of formaldehyde. J. Bilsky combines a "cellulose compound" with latex rubber and oleic acid[3] E. Schnabel[4] tempers by the addition of hydrogenated fats or oils mixed with wax; while Ditto, Inc.[5], have divulged a method employing a phenol-aldehyde condensate. Chlorinated caoutchouc[6], vinyl acetate resin alone or in conjunction with aluminum stearate and peanut oil[7], diethyl phthalate[8], ethylene- and trimethylene-glycol ricinoleates[9] with sulfonated sperm oil, and bentonite[10] are examples of ink-resisting and tempering agents which have been advocated.

1. E. P. 216307; abst. C. A. 1925, **19**, 177.
2. E. P. 226167; abst. C. A. 1925, **19**, 1619.
3. Can. P. 267699.
4. D. R. P. 405841; abst. J. S. C. I. 1925, **44**, 166-B.
5. E. P. 352460; abst. C. A. 1932, **26**, 4145.
6. M. Deseniss, U. S. P. 1823260; abst. C. A. 1932, **26**, 268.
7. K. Carr, U. S. P. 1830980; abst. C. A. 1932, **26**, 816.
8. C. Cunningham, Can. P. 265988.
9. A. De Waele, E. P. 278445; abst. C. A. 1928, **22**, 2645.
10. *Ibid.* E. P. 228247; abst. C. A. 1925, **19**, 2867.

The earlier A. B. Dick Co. stencil depended primarily upon the use of a mixture of glycerol and water[1], but this was unsatisfactory in ways other than the water-absorptive power of the glycerol, producing sticky masses and usually unsightly copies, but the process was apparently based in part, upon the earlier formulas of E. de Zuccato[2] who produced facsimile copies of writings in 1876 by the use of a mixture of gamboge, methylated spirit and Venice turpentine applied to paper, to which stearin and paraffin wax were afterwards added[3], and also glycerol[4]. C. Dreher[5] added resin soap.

In a series of processes patented by D. Gestetner, Ltd.[6], the art has been considerably advanced, especially by their protein mixture with formaldehyde to toughen and indurate the ink-repellent[7]. Titanium oxide is added to induce opacity[8] so that the cuttings of the stencil will be more apparent. Two or more colors may be added to the stencil coating composition as in the formula of F. May[9], to facilitate reading of the cut stencil. If the coated sheet is wiped on the obverse side for breaking the surface tension of the applied liquid[10], the liquid will penetrate and coat the other side. A. Breuer[11] added talc to increase the opacity; A. Klaber[12] wax to fill the pores; while another process depended upon the addition first of gelatin[13], and then alum-

1. F. P. 442336, 444797. Can. P. 264475.
2. E. P. 1115, 1876. See E. P. 171780.
3. *Ibid.* E. P. 13851, 1893. 4. *Ibid.* E. P. 11946, 1895.
5. E. P. 12668, 1900.
6. U. S. P. 332890. E. P. 1594, 1888. E. P. 237090; abst. C. A. 1926, **20**, 1500. E. P. 249319, 255361. F. P. 567694, 572562, 575403, 575404, 588171, 495850, 599335, 603384, 613055, 613056, 615365. D. R. P. 214720, 424835, 430693. Aust. P. 99018, 101965, 101971. Swiss P. 106566, 106567, 107227, 107879. Dan. P. 34584. Can. P. 245859, 267316, 268275.
7. D. Gestetner, E. P. 246890; abst. C. A. 1927, **21**, 480. Can. P. 247141, 247142.
8. *Ibid.* U. S. P. 1664675; abst. C. A. 1928, **22**, 1832. E. P. 255361; abst. C. A. 1927, **21**, 2764.
9. U. S. P. 1846003; abst. C. A. 1932, **26**, 2289.
10. F. May, E. P. 347652; abst. C. A. 1932, **26**, 4145.
11. D. R. P. 388337, 413188.
12. Aust. P. 26976.
13. Le Materiel Telephonique, F. P. 573639.

inum sulfate to indurate or tan it. Bichromate solution has been used for the same purpose[1].

Bassorin, gelose or tragacanth[2]; ceresin and Japan wax[3]; cassava to increase opacity[4]; a mixture of stearic acid, oleic acid and paraffin (5:2:3)[5]; and isinglass followed by a coating of Zapon lacquer to reduce liability to smudging[6], are some of the compounds added to induce specific effects. Other processes granted patent protection, involved combinations of ideas and the application of products as indicated above[7].

Cellulose Ethers in the Film Industry. Broadly speaking, a film is merely a solidified lacquer, a cellulose derivative solution in which the volatile solvent portion has been removed by an evaporative process, and fundamentally differs only from artificial filaments in the fact that instead of being substantially circular in the evaporated state, the dimensions are that of a rectangle in cross section, in which the diameter is but a small percentage of the width. The rapid growth of the moving picture field and the rapidly increasing use of the same on a reduced scale in the home and for pictorial purposes, has greatly augmented production of film in the past few years, and especially has attention been directed to the production of a film, both for public and private use, in which the inflammability has been reduced to the minimum. The cellulose ethers appear

1. Polygraphische Ges., E. P. 278647; abst. C. A. 1928, **22**, 2645. F. P. 435296.
2. C. Wegl and M. Wegl, F. P. 534494, 543063, and Addn. 29024 too F. P. 543063.
3. E. Marks, E. P. 113338.
4. C. Mills, E. P. 9653, 1903.
5. W. Hutchinson, E. P. 24532, 1902.
6. N. V. Handelmaatschappij, F. P. 590572.
7. P. Gollnick, U. S. P. 1846003. E. Brasseur, U. S. P. 1861260. R. Bain, E. Nixon and Lamson Paragon Supply Co., Ltd., E. P. 295119; abst. C. A. 1929, **23**, 2001. A. Schlesinger, F. P. 193601. Underwood Typewriter Co., F. P. 430403. A. Feurich, D. R. P. 535439; abst. C. A. 1932, **26**, 1406. K. Hazura, A. Nadherny and F. Maly, Aust. P. 100733. J. Buyten & Sohne, Norw. P. 7361. R. John, Norw. P. 40452. H. Kruger, Danish P. 18473.

to lend themselves admirably for the production of photographic films by virtue of their high stability, solvency in a wide range of relatively inexpensive dissolving bodies, and ability to combine with the usual plasticizers and fire-retardants, both liquid and solid.

It appears from present information that the property of brittleness, which has been so troublesome with attempts to use the cellulose acetates in this industry, may be substantially overcome by the blending of plasticizing bodies, and by associating cellulose ethers of different swelling capacity in respect to water and some of the fixed oils.

This topic is taken up under five headings: (1) Films of Nitrocellulose Base; (2) Acetylcellulose Films; (3) Nitro- and Acetyl-cellulose Films; (4) Cellulose Ether Films; (5) Miscellaneous Film Processes and Photographic Operations.

(1). *Nitrocellulose Films.* This work is not concerned with the application of the inorganic cellulose esters as of the nitrocellulose type. Those desiring detailed information upon this subject may consult E. Worden, "Nitrocellulose Industry," vol. 2, pages 828-897, for a statement of the art from the early development to 1911; or E. Worden, "Technology of Cellulose Esters," vol. 4, pages 2795-2915, carrying advancements to 1921, or E. Worden, Chemical Patents Index, United States, 1915-1924, vol. 2, pages 402-418, for progress in the United States as shown by patents granted.

(2). *Films of Cellulose Acetate.* On account of the inflammability of photographic films and films intended for non-photographic purposes when prepared from nitrocellulose, and the focussing of this fact upon the people as the result of an occasional destructive and fatal fire from this source, has resulted in much experimentation and some compulsory legislation looking to supplanting nitrocellulose film entirely by relatively incombustible film where public pictures are shown or in the home.

In was in 1901 that E. Valenta[1] recorded the first experiments in this direction, the cellulose acetate film used by him being insoluble in alcohol and acetone, from which it appears the ester used had been but little hydrated. The next year the Farbenfabriken vorm. F. Bayer & Co.[2] published their formula for preparing print-out emulsion[3], and I. Hoffsümmer[4] followed with an acetylcellulose sensitized plate, film and printing paper. L. Lederer[5] found those types of cellulose acetate soluble in glacial acetic acid as useful for the casting of films and formation of emulsion, and composite films were made in this manner[6].

The W. Beatty moving picture film combines cellulose acetate with dioxydiphenyldimethylmethane[7]; while isoprene with cellulose acetate or benzoate forms the basis of another method of noninflammable film formation[8]. The 4-color film of J. Thornton[9] was disclosed in 1917 with cel-

1. Photo. Corr. 1901, 305; abst. Eder's Jahr. 1902, 582-538; Chem. Zentr. 1901, II, 40; Jahr. Chem. 1901, 891. C. Brown, Safety Eng. Aug. 1929, 65. J. Olsen, A. Brunjes and V. Sabetta, Ind. Eng. Chem. 1930, **22**, 860. G. Schick, Nitrocellulose, 1931, **2**, 199. Clement, Bull. Soc. Franc. Phot. 1921, **8**, 343; abst. J. S. C. I. 1922, **41**, 233-A. R. Blochmann, Kunstoffe, 1925, **15**, 149. Krüger, Phot. Ind. 1928, **26**, 690. G. Kita and G. Kanno, J. S. C. I. (Japan), 1928, **31**, 730, 733, 739. K. Bratring, Kinotechnik, 1931, **13**, 237. L. Clement and C. Riviere, Chimie et Industrie, 1922, **8**, 322. K. Tanemura, J. S. C. I. (Japan), 1930, **33**, 497-B. H. Levinstein, Chem. Trade J. **86**, 127; abst. J. Soc. Chem. Ind. 1930, **49**, 55, 78. L. Eveleigh, Bioscope Supp. 1928, **77**, iii, vi. J. McNally and S. Sheppard, J. Phys. Chem. 1931, **35**, 100. M. Deschiens, Rev. Prod. Chim. 1926, **29**, 767.

2. E. P. 25821, 1902. F. P. 326463; abst. J. S. C. I. 1903, **22**, 820. D. R. P. 169364; abst. Chem. Zentr. 1906, II, 187. Wag. Jahr. 1906, II, 485. U. S. P. 752388, 1904.

3. D. R. P. 153350; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Zentr. 1904, II, 625; Jahr. Chem. 1904, 1168; J. C. S. 1904, **86**, 853. D. R. P. 159524. E. P. 21268, 1901. F. P. 317007. U. S. P. 734123, 790565. Ital. P. 31391. Can. P. 62042.

4. E. P. 3855, 1904; abst. J. S. C. I. 1904, **23**, 622. F. P. 357473, 1905; abst. Mon. Sci. 1907, **67**, 43.

5. E. P. 26503, 1906. F. P. 371358. D. R. P. 191326. Belg. P. 195837.

6. J. Smith and W. Merckens, E. P. 2461, 1907; abst. J. S. C. I. 1907, **26**, 1109. Belg. P. 198836.

7. U. S. P. 1158963; abst. C. A. 1916, **10**, 158.

8. Cie. Generale Des Etablissements Pathe Freres Phonographie et Cinematographe, E. P. 2067, 1915.

9. U. S. P. 1183698, 1245822, 1250713.

lulose acetate as a base. The Celluloid Corp.[1] diminished inflammability to a minimum by employing cellulose acetate, and a difficultly-burnable plasticizer which is a solvent for the organic cellulose ester as triphenyl phosphate is added. The photographic film, roll film and film pack of A. McCurdy[2] is provided with a light-excluding envelope having a face coated with cellulose acetate to render it waterproof. Another photosensitive material has been described[3] in which paper is coated or fabric impregnated with cellulose acetate to render it impervious, or paper may be used which is superficially esterified, and is then impregnated with a light-sensitive salt of silver, chromium, iron or a diazo compound.

K. Tanemura[4] has shown that acetylcellulose film containing triacetin shows elastic and plastic elongation, the load-elongation curves resembling those of cellophane steeped in acetone-water mixtures. The relation between the critical load, *viz.* that corresponding to the transition point, and the percentage of triacetin is linear, the tensile strength of a film containing the plasticizer being unaltered by immersion in water. The Tackles Freres film[5] comprises a coating of white wax or of ox gall applied to a strip of paper or of thin flexible metal, followed by a pasty coating of cellulose acetate in admixture with wood fiber. The sensitized emulsion is then applied, and the film obtained removed from the supporting base[6]. The J. Walsh[7] transparent cellulosic film comprises cellulose acetate, 12-17 parts of an aromatic phosphate and the same amount of a tartaric acid ester, while J. Wells[8] coats an acetylcellulose film base on the back with a cellulose acetate of lower "precipitation value," before the anti-halation backing is

1. F. P. 482239; abst. C. A. 1917, **11**, 3182. Can. P. 300132.
2. U. S. P. 1261747.
3. H. Murray, D. Spencer and Colour Photographs, Ltd., E. P. 337868; abst. C. A. 1931, **25**, 2065.
4. J. Soc. Chem. Ind., Japan, 1930, **33**, 499; abst. J. S. C. I. 1931, **50**, 479-B.
5. Belg. P. 366501; abst. C. A. 1930, **24**, 4474.
6. H. Dreyfus, F. P. 716449. 7. Can. P. 315656.
8. E. P. 366380; abst. J. S. C. I. 1932, **51**, 869-B.

applied. The "precipitation value" is derived from a prescribed determination of the percentage of acetate precipitated from 5% acetone solution when a water-acetone mixture is added to produce a total of 40% of water. The presence of this intermediate layer facilitates the bleaching or washing out of the color backing during the subsequent processing.

The H. Clarke[1] cellulose acetate composition suitable for use as a varnish or for the manufacture of films or sheets is formed of acetylcellulose 10, acetone or methyl alcohol 40-100 and butyl oxalate 1-10 with softeners as dibutylsulfone or monochlornaphthalene. Films cast from the above are said to be practically proof against the action of ordinary photographic chemicals. The V. Sease[2] film comprises cellulose acetate 18, triacetin and triphenyl phosphate 1.8 each and solvent mixture 78, and is intended primarily for the casting of continuous films, whereas the H. Gardner[3] film-forming composition combines acetylcellulose with a resin obtained from *p*-toluenesulfonamide and an aldehyde dissolved in a lacquer solvent with cellulose acetate and butyl acetate or equivalent solvent. Cellulose acetate films may be sensitized by 1% iodoform[4], the image formed by exposure to light being developed in a silver reducing solution containing silver nitrate and ammonia.

The I. G. Farbenindustrie[5] apply light-sensitive material to both sides of a support composed of two or more adherent but separate layers, the material being used in color photography when it is required to expose together two superimposed sensitive layers and thereafter separate them, each with its own support, for development. The support layers may consist of cellulose acetate and one of nitrocellulose, or two layers of nitrocellulose with a layer of acetylcellulose between. Where a four built-up cinema-

1. U. S. P. 1309980; abst. C. A. 1919, **13**, 2443.
2. U. S. P. 1488294.
3. U. S. P. 1564664; abst. J. S. C. I. 1926, **45**, 202-B.
4. M. Beebe, A. Murray and H. Herlinger, U. S. P. 1658510; abst. J. S. C. I. 1928, **47**, 317-B. See U. S. P. 1587269, 1587274.
5. E. P. 357817.

tographic positive film is desired[1], the two partial color images on each of the two thin component film strips are produced by photomechanical printing and are preferably of cellulose acetate. In another process[2], films of cellulose acetate or cellulose citrate are impregnated *en masse* with sensitive material as silver halides or ferric salts so that the film is sensitive on both sides.

If it is desired to impart a matt surface on films[3], cellulose acetate solutions are cast on a sheet or band having a matt or roughened surface prepared by coating with a layer of gelatin impregnated with starch, barium sulfate, kieselguhr or other suitable matting material, the surface so prepared being non-hygroscopic and may be worked upon readily, especially with washes of color. Thus, the polished metal band upon which the cellulose acetate solution is to be cast is coated with a solution comprising gelatin, water, alcohol and barium sulfate.

The Celluloid Corp.[4] prepare films by extrusion of solutions of cellulose acetate at a temperature somewhat below the boiling point of the solvent employed, into an atmosphere maintained at a raised pressure, the quantity of solvent or mixture of solvents being such that the solution does not readily flow at the ordinary temperature. To maintain flexibility after prolonged heating, as at 65°, the addition of sufficient tributyrin to cellulose acetate will insure a permanent flexibility[5]. 10-35% tributyrin based on the cellulose acetate is required. To prepare a practical support

1. J. Thornton, E. P. 230965, 230966, 230967, 230968, 230969, Addns. to E. P. 224569. See also E. P. 214934, 224571, 224572.
2. U. Diem-Bernet, E. P. 271507; abst. C. A. 1928, **22**, 1552; Chem. Zentr. 1927, II, 1924. F. P. 617929; abst. J. S. C. I. 1928, **47**, 69-B; Chem. Zentr. 1927, II, 204.
3. Non-Inflammable Film Co., Ltd., and H. Mallabar, E. P. 295797; abst. C. A. 1929, **23**, 2293; J. S. C. I. 1928, **47**, 744-B. E. Lomberg, E. P. 308358.
4. E. P. 310540; abst. J. S. C. I. 1930, **49**, 943-B; Brit. Plastics, 1930, **2**, #18, 278.
5. S. Carroll, U. S. P. 1572232; abst. C. A. 1926, **20**, 1324; J. S. C. I. 1926, **45**, 315-B.

for making cellulose acetate films[1], it is recommended to flow the solutions upon a sheet of acetylcellulose which has been superficially saponified to the degree that it neither swells nor is soluble in the solvent used, or the support may be made of a cellulose derivative containing free hydroxyl groups which without further treatment, neither swells nor dissolves in the solvent. For identification of the film[2], one or each margin is treated with a mixture of ultramarine dissolved in 2% cellulose acetate in glycol acetate, which prevents penetration of the developing and fixing solution, and thus provides a thin edge of unchanged silver salt.

In order to preserve softness and pliability in an acetylcellulose film[3], it is recommended to add water to the mass during or after manufacture, which water may be extracted from the air by the addition to the film of such hygroscopic substances as glycerol or glycol, or by treating the mass in an atmosphere of steam. The W. Pease[4] method of manufacture of acetylcellulose films consists in making a 5-9% solution in methylethyl ketone together with a plasticizer, casting into film form and allowing to evaporate in a closed chamber at 30-75° with a 50-95% humidity, the outer room temperature being 20-40°. To readily strip the film from the casting surface, the method of A. Chiverton and F. M. Ltd.[5] may be used, which consists of applying by means of rollers to the casting surface (drum or wheel) before deposition of the film thereon, of a mixture of fusel oil with gallipoli oil in a very thin layer.

The J. Walsh and K. Flynn composition for non-inflammable cellulosic films[6] comprises cellulose acetate, triphenyl phosphate and ethyl phthalate, while in a modifica-

1. I. G. Farbenindustrie, A.-G., F. P. 637012; abst. C. A. 1929, **23**, 703. E. P. 279047.
2. *Ibid.* E. P. 300991; abst. J. S. C. I. 1930, **49**, 168-B.
3. J. Michael A.-G. für Chemische und Metallurgische Industrie, F. P. 668369; abst. C. A. 1930, **24**, 1509.
4. E. P. 357079; abst. J. S. C. I. 1931, **50**, 1089-B.
5. E. P. 353136; abst. J. S. C. I. 1931, **50**, 877-B.
6. Can. P. 314577; abst. C. A. 1931, **25**, 5556.

tion of the process[1], it is recommended to replace the ethyl phthalate by a tartaric ester. The base on which the film is made is composed of or coated with a synthetic resin rendered insoluble and infusible by heat[2]. A. Sulzer[3] has described a photographic flexible cut sheet film having satisfactory flexibility and transparency, and having to an unusual degree the properties of flatness and low water permeability, composed of hydrolyzed cellulose acetate having a precipitation value of at least 90% in a solution of water-acetone (40:60) at 20°, with a suitable plasticizer. A photographic film of cellulose formate, acetate or oxalate is rendered permanently flexible by incorporating therein 1-5% of bone oil, clarified neatsfoot oil, whale oil, mutton fat or beeswax, to which plasticizers may be added, it being claimed that gelatin structures adhere readily to such a film[4].

The C. Dreyfus film[5] involves the use of cellulose acetate to which a liquid having a softening or limited solvent action is applied, heating under pressure if desired to impart a flattened cross-section. Di- or tri-acetin, butyl tartrate or tritolyl phosphate is used as plastifiant. The C. Staud and C. Webber film comprises a partially acetylated cellulose afterwards esterified with lactic, tartaric, racemic, malic, glycollic, glyceric, or mandelic acids, to form the corresponding cellulose aceto-lactate, -tartrate, -racemate, -malate, -glycollate, -glycerate or -mandelate[6]. A flowable solution for the manufacture of photographic films is obtained by dissolving one part by weight of the mixed cellulose ester in 4-8 parts by weight of compound solvent.

1. J. Walsh, Can. P. 315656; abst. C. A. 1932, **26**, 1783.
2. British Celanese, Ltd., E. P. 359390; abst. J. S. C. I. 1932, **51**, 225-B. W. Moss, Can. P. 304295.
3. U. S. P. 1833136; abst. C. A. 1932, **26**, 1120. See U. S. P. 1826335.
4. P. King, E. P. 324911; abst. C. A. 1930, **24**, 3720; J. S. C. I. 1930, **49**, 321-B.
5. F. P. 695371; abst. C. A. 1931, **25**, 2862. Can. P. 300448.
6. E. P. 336353. E. P. 338201; abst. C. A. 1931, **25**, 2288; J. S. C. I. 1931, **50**, 242-B. E. P. 344151; abst. C. A. 1932, **26**, 303; J. S. C. I. 1931, **50**, 480-B. Can. P. 312805; abst. C. A. 1931, **25**, 4401. New Zeal. P. 63303.

(3). *Nitro- and Acetyl-cellulose Films.* Combinations of cellulose acetate with nitrocellulose in various proportions for the formation of films and film base have been disclosed in several processes, either to partially reduce the inflammability of the cellulose nitrate, or to take advantage of desirable properties present in both, especially with the idea in view of combining the plasticity of nitrocellulose in conjunction with camphor or camphor substitutes, with the diminished speed of burning of the acetylcellulose component. A film not sensitive to electrical action has been described[1], and prepared by coating a nitrocellulose film on one side with a photographic emulsion, and the other side with either a cellulose acetonitrate or benzoate coating, in conjunction with a plasticizing agent. The J. Haste[2] photo film comprises a light-sensitive gelatino-silver-halide layer attached by a gelatinous substratum to a nitrocellulose coating on a main layer of acetone-soluble cellulose acetate composition, proper adhesion between the different layers being obtained by the use of a cellulose ester lacquer. Flexibility may be augmented by the addition of a small proportion of moisture to the acetylcellulose portion[3], the latter being covered on both sides by a thin coating of nitrocellulose to minimize evaporation. A similar idea is embodied in the A. McDaniel invention[4], but in this the cellulose acetate containing hygroscopic material (as calcium chloride to prevent static markings) forms the base layer, on which is superposed a nitrocellulose coating, and on top of this the photographically sensitive layer.

The I. G. Farbenindustrie[5] first coat the surface of the casting drum with a solution of nitrocellulose of 8% N content by evaporating the ester from a mixture of acetone,

1. Soc. Pathé-Cinema, F. P. 611136, 611137; abst. J. S. C. I. 1927, **46**, 362.
2. U. S. P. 1532819; abst. C. A. 1925, **19**, 1668.
3. J. Haste, U. S. P. 1532818; abst. C. A. 1925, **19**, 1776; J. S. C. I. 1925, **44**, 479-B.
4. U. S. P. 1431894; abst. C. A. 1922, **16**, 4152; J. S. C. I. 1922, **41**, 917-A; Phot. Abst. 1923, **3**, 15.
5. E. P. 288223; abst. C. A. 1929, **23**, 703.

ethylenechlorhydrin and water, and superpose on this an acetylcellulose solution to produce a mixed ester layer film, whereas H. Bradshaw[1] coats the rear side of an acetylcellulose film with a layer of cellulose carbamate, cellulose phenylurethane or cellulose methylurethane. The urethane derivative is dissolved either in alcohol or in a mixture of acetone and alcohol.

(4). *Cellulose Ether Films.* The production of films, especially for photographic work, in which the cellulose ethers have been specified or claimed or both, is a comparatively recent art, so new in fact, that the major portion of information available is encompassed within the processes which have been granted patent protection in the various countries. At the moment, price considerations are the main cause in delaying expansion in this field. The inflammability of the finished film is certainly no greater than that of cellulose acetate. The solvents available (denatured ethyl alcohol, methyl alcohol, benzene, toluene) are much less expensive than those required to make satisfactory acetylcellulose solutions for casting purposes, and the stability, flexibility and lasting qualities of the film under the normal strenuous usage in the moving projection apparatus seem to be satisfactory. An immense amount of experimentation has been carried on and is still in progress in this field of cellulose derivative technology, especially along the lines of increasing the swelling power of the films by the judicious admixture of relatively smaller amounts of the water-soluble cellulose ethers, or by the use of cellulose ethers intentionally not of maximum etherification.

The results which have been achieved in this line up to the present time may perhaps be best understood by detailing the various processes and modifications under the disclosures of the various firms which have apparently specialized in this field of investigation.

1. U. S. P. 1703470; abst. J. S. C. I. 1929, **48**, 378-B.

1. *Cellulose Ether Film Production by Eastman Kodak and Affiliates.* According to J. Capstaff[1], halation is avoided in plates or films for lenticular-screen or multicolor-screen photography or cinematography by including in the support a light-absorbing dye, preferably one which is bleached out by powerful light action, and which is of such density that it allows at least 70% of the incident light to reach the emulsion. Suitable dyes are the cyanins, isocyanins, and carbocyanins, especially kryptocyanin[2]. The dye may be mixed with the film base dope, which may include in its composition a cellulose ether.

The S. Carroll photographic film and compound support[3], is designed to provide a film with a support having the usual qualities demanded by commercial conditions, possesses a diminished rate of burning, and will be so constituted that the markings due to electrical discharges (static) are either prevented or greatly minimized. These desirable effects are said to be accomplished by coating or varnishing both faces of a nitrocellulose support with a layer of cellulose ether, the compound cellulosic support thus produced being finally coated with the gelatino-silver haloid emulsion in the usual manner. That is, the film is built up from the bottom by a cellulose ether, a nitrocellulose, a cellulose ether and a photographically sensitive layer.

The cellulose ether composition to be applied[4] is formed by dissolving 100 parts water-insoluble ethylcellulose in 5-50 parts mono-, di- or tri-acetin (say 10 parts) in 300-500 parts of a volatile solvent, as a mixture of methyl alcohol and methyl acetate (1:9). This composition is of consistency suitable for spreading upon a film-forming surface in a coating, from which the volatile solvent evaporates sufficiently to leave a transparent, flexible sheet, which

1. E. P. 312992; abst. J. S. C. I. 1930, **49**, 841-B.
2. E. Adams and H. Haller, U. S. P. 1374871.
3. U. S. P. 1441142; abst. C. A. 1923, **17**, 938; J. S. C. I. 1923, **42**, 203-A.
4. S. Carroll, U. S. P. 1658369.

is then stripped off in the usual manner. The hygroscopicity of the mixture may be controlled by the use of one or more of the three acetins in varying amounts. The ethylcellulose film which has unusual resistance to long periods of heating without becoming brittle, may be prepared by the addition thereto of mono- or poly-brom phenols, as phenol, catechol, resorcinol, hydroquinone, pyrogallol, phloroglucinol, cresol and thymol, tribromphenol, *p*-bromphenol and bromhydroquinone being especially applicable[1]. It is claimed that when these brom-substituted phenols are purified from free bromine and free hydrobromic acid, tendency to development of acidity and discoloration of the film upon standing, is entirely avoided, or substantially so. The film is prepared by dissolving 100 parts ethylcellulose containing a small amount of alkali and 20 parts tribromphenol in 300-500 parts methyl alcohol-methyl acetate mixture (1:9), the solvents being of sufficient purity to obviate acidifying the solution. This composition is then ready for spreading to produce a film.

Likewise the use of bromcamphor free from bromine and hydrobromic acid has been advocated for incorporation with ethylcellulose in the formation of films, the addition of the halogen in combination materially reducing the inflammability of the mass. If sufficient decomposition develops to overcome the alkalinity in the film, discoloration and deterioration rapidly ensues[2]. In an elaboration of the use of haloid-substituted organic compounds in connection with cellulose ethers for the dual purpose of increasing stability and lessening the burning capacity[3], mono-, di- and tri-brombenzenes, -toluenes, -xylenes, -mesitylenes, -ethylbenzenes, -cumenes and -cymenes have also been recommended for this purpose, specifically monobrombenzene, *p*-bromtoluene and *o*-bromtoluene. One method

1. S. Carroll, U. S. P. 1716418; abst. C. A. 1929, **23**, 3807; J. S. C. I. 1930, **49**, 413-B.
2. *Ibid.* U. S. P. 1716419; abst. C. A. 1929, **23**, 3807; J. S. C. I. 1930, **49**, 413-B.
3. *Ibid.* U. S. P. 1716420; abst. C. A. 1929, **23**, 3807; J. S. C. I. 1930, **49**, 413-B.

of application is to dissolve 100 parts water-insoluble ethylcellulose containing free alkali therein and 10 parts monobrombenzene in 300-500 parts methyl alcohol 10% and methyl acetate 90%, the solvents being free from acidity.

The J. Donohue cellulose ether film is the antithesis of that of S. Carroll in that Donohue sandwiches a relatively thick cellulose ether film or layer between two relatively thin nitrocellulose coatings[1], claiming they withstand such severe tests as several weeks continuous heating to 65°. The laminated structure of the cellulose ether-film is produced either by the application of heat and pressure, or by casting a solution of nitrocellulose on a drum or wheel, superposing over this a thicker cellulose ether solution, and topping with a thin cellulose nitrate coating. The nitrocellulose solution recommended is but a 2% solution in acetone. A greater stability is obtained by substituting cellulose acetate for nitrocellulose in the above. In order to augment the flexibility[2], there is first deposited a cellulose ether which constitutes the support, and as an interunion material of high hygroscopicity, there is then brushed or flowed on a solution of glycol 2.5, acetone and methyl alcohol 20 each, methyl acetate 40, butyl acetate 19, and a trace of cellulose ether or ester in solution. Upon this is placed another layer of cellulose ether and the whole laminated to an indistinguishable whole by means of heat and pressure. The photographically sensitive layer is then flowed on top.

Where it is desired to prepare a photographic film with a base of neutral tint[3], as in those kinds of film that are customarily viewed by transmitted light after images are formed thereon, the base or support may be a cellulose ether which has an objectionable color as yellow or brown. Between the support and the sensitive layer is an inter-

1. U. S. P. 1518396; abst. C. A. 1925, **19**, 576; Kunst. 1925, **15**, 164.
2. J. Haste, U. S. P. 1494479; abst. C. A. 1924, **18**, 2293.
3. J. Haste and E. Ward, U. S. P. 1507174; abst. C. A. 1924, **18**, 3557.

mediate uniting layer or substratum as a color neutralizant, in which is incorporated sufficient dye of a color complementary to the color of the support to neutralize it. For neutralizing the yellow tint of certain supports there is employed a solution of one part of the condensation product between tetramethyldiaminobenzylphenone and phenyl-*a*-naphthylamine (Victoria Blue B) and 0.6 parts of the condensation product of aniline or *o*-toluidine with an indamine prepared by the oxidation of a mixture of equal molecular proportions of *o*-toluidine and 2.5-toluylenediamine (Safranine) in methyl alcohol.

In order to attain increased flexibility without the addition of water, or hygroscopic components whose chief function is to draw and retain moisture, J. Haste[1] carries a sensitized layer by a supporting film composed mainly of a cellulose ether with an intervening layer containing a higher percentage of flexibility-inducing substances than the support layer, using monochlornaphthalene or tricresyl phosphate for this purpose. This interunion zone is relatively thinner than the zones each side which imprison it. A pre-tinted photographic film has been evolved[2] consisting of a sensitive coating on a flexible, transparent, laminated support which includes two relatively thick transparent layers of cellulose ether joined throughout their adjacent faces by a thin intermediate layer, which is colored and protected mechanically and chemically by the cellulose ether layer. Or[3], the film may be built up of a color-neutralizing, light-diffusing and anti-curling base layer, upon which is a cellulose ether support having color to be neutralized, and the upper photographically sensitive layer.

N. Kocher[4] has described the advantages of treating films containing cellulose ethers with water near the freez-

1. U. S. P. 1521881; abst. C. A. 1925, **19**, 616; J. S. C. I. 1925, **44**, 191.
2. J. Haste and E. Ward, U. S. P. 1486245; abst. C. A. 1924, **18**, 1619; Chem. Zentr. 1924, II, 791.
3. *Ibid.* U. S. P. 1507174.
4. U. S. P. 1437810; abst. C. A. 1923, **17**, 879.

ing point to produce a shrinking tendency and thereby reduce shrinkage subsequently. Films containing cellulose addition compounds when successively immersed in the usual developing, fixing and washing baths and finally dried, noticeably shrink, which is objectionable where the film is used in certain processes of color photography which require accurate registration of images, and likewise objectionable in ordinary motion picture work. This preshrinkage is best accomplished by immersion of the film in water at 1° with particles of ice mixed therein. After the shrinkage tendency is thus created, the shrinkage takes place on drying. Whereas shrinkage of water-insoluble ethylcellulose requires cold water, a similar treatment with nitrocellulose or acetylcellulose should be with warm water, or warm, dilute alkaline solutions.

The F. Lovejoy disclosures for making motion picture film strips[1] prepare the margins of nitrocellulose and the central portion of cellulose ether. The film is flowed over a drum from hoppers having the different dopes, to produce strips of alternating composition. Or[2], the film base is made entirely of cellulose ether, and afterwards reinforced on the edges by a coating of nitrocellulose to strengthen it. The film of L. Malone[3] provides a composition containing a cellulose ether and an organic cellulose ester by means of a common solvent of low volatility as pyridine, either alone or mixed with volatile solvents or diluents. However, the point must not be lost sight of in attempting to use large amounts of pyridine, as to its tendency to reduce the viscosity of the cellulose derivative in solution. The formula specified by Malone comprises equal parts by weight of cellulose nitrate, acetone-soluble cellulose acetate and water-insoluble ethylcellulose, dissolved in 4-6 parts of pyridine, based on the combined weight of

1. U. S. P. 1469815; abst. C. A. 1923, **17**, 3919.
2. F. Lovejoy, U. S. P. 1518409; abst. C. A. 1925, **19**, 446; J. S. C. I. 1925, **44**, 152.
3. U. S. P. 1429153; abst. C. A. 1922, **16**, 3758; Chem. Zentr. 1922, IV, 1183; J. S. C. I. 1922, **41**, 807-A; Kunst. 1925, **15**, 12.

cellulose compounds. Or[1], the solvent of the cellulose ether intended to be cast into films may be a mixture of *b*-chlorethyl acetate and benzene; a mixture of butyl acetate 1 and methyl alcohol 3[2]; or a mixture of mesityl oxide and methyl alcohol[3].

An improved film material is said to result by laminating two or more layers of grained film so that the grain of the successive layers is transverse to each other substantially approaching a right angle, thereby producing a film having no "grain" or anistropy. The two-ply film may be of cellulose ether, or cellulose organic ester, or a ply of each[4]. In the preparation of an anti-static photographic film[5], a relatively less expensive nitrocellulose base is first provided which possesses the property of co-acting with the sensitized photographic layer so as to prevent or greatly minimize static (markings due to electrical discharges) by the incorporation therewith of small amounts of a cellulose ether. About 5 parts of water-insoluble ethylcellulose are incorporated with each 100 parts nitrocellulose by means of the common solvent combination methyl alcohol 45%, ethyl acetate 20%, chloroform 35%. The amount of chloroform specified seems to introduce a too expensive element, the formula for casting being nitrocellulose 100, cellulose ether 5 and mixed volatile solvent 500.

In the A. Sulzer method[6], there is first formed a relatively thin base layer of a water-insoluble ethylcellulose dissolved in a mixture of chloroform and ethyl alcohol, on which is deposited the support containing a small amount of solvent so that it will penetrate the interstices of the base and anchor thereto, a mixture of ethyl alcohol and

1. I. Matthews, U. S. P. 1469816. See U. S. P. 1188376.
2. P. Seel, U. S. P. 1469825; abst. C. A. 1923, **17**, 3919.
3. *Ibid.* U. S. P. 1469826.
4. S. Sheppard and J. McNally, U. S. P. 1808998; abst. J. S. C. I. 1932, **51**, 141-B.
5. A. Sulzer, U. S. P. 1418405; abst. C. A. 1922, **16**, 2645; J. S. C. I. 1922, **41**, 567-A.
6. U. S. P. 1432366; abst. C. A. 1923, **17**, 498; J. S. C. I. 1922, **41**, 997-A.

acetone having been found suitable for this purpose. The acetone does not precipitate the cellulose ether under these conditions. The photographically sensitive layer is then placed on top, thus producing the finished film. In a further modification of this principle of using a cellulose ether in association with cellulose acetate or nitrocellulose[1], electrical trouble is prevented by incorporating in its support a layer containing a cellulose ether and cellulose acetate. In preparing the coating composition it has been found advisable to dissolve the cellulose ether and cellulose acetate separately and then mix the two solutions. 45 parts water-insoluble ethylcellulose are dissolved in 50 parts ethyl alcohol and 900 parts chloroform, the acetone-soluble cellulose acetate being dissolved in acetone to a clear solution.

A photographic film substantially free from static is also said to result by applying a non-sweating cellulose ether base layer on which is flowed a nitrocellulose solution containing sodium hypophosphite and glycerol, and over this the usual gelatino-silver-haloid emulsion layer[2]. The cellulose ether layer is deposited from a lacquer composed of ethylcellulose 9, ethyl alcohol 60, chloroform 90, and acetone 300. This coating is substantially non-sweating, that is, their outer surfaces remain satisfactorily free from moisture even in a hot and humid atmosphere. Another variant has been disclosed in an attempt to prepare a film substantially free from static[3], and this consists of a backing of cellulose ether made by flowing on a solution of ethylcellulose 9, alcohol 5 and chloroform 90.

In order to reduce the shrinkage in cellulose ether films[4], which shrinkage is very largely due to the base which supports the sensitive emulsion, the film is first swol-

1. A. Sulzer, U. S. P. 1432367; abst. J. S. C. I. 1922, **41**, 997-A. U. S. P. 1437829; abst. C. A. 1923, **17**, 695; J. S. C. I. 1923, **42**, 119-A.
2. A. Sulzer, U. S. P. 1432368; abst. C. A. 1923, **17**, 498; J. S. C. I. 1922, **41**, 998-A.
3. *Ibid.* U. S. P. 1437828; abst. C. A. 1923, **17**, 695; Chem. Zentr. 1923, II, 1123; J. S. C. I. 1923, **42**, 119-A.
4. *Ibid.* U. S. P. 1482717; abst. C. A. 1924, **18**, 946; J. S. C. I. 1924, **43**, 451-B.

len in a bath of 70% aqueous methyl alcohol at about 70° F. The film to be treated is first immersed in this bath until it has swollen to the degree or extent desired, it having been found that cellulose ether films roughly increase 10% in width and length after 2 minutes immersion. It is then quickly immersed in water wherein it shrinks to less than its original size. It is then dried and may be used in the usual manner. Because of this preshrinking, subsequent changes in dimensions are much less than would be the case without pretreatment.

The A. Trivelli motion picture film is claimed as more durable and less prone to become scratched and marred[1], the surface of the emulsion being protected by a covering of ethylcellulose. This coating may be applied before exposure, being removed prior to development, the emulsion being thus kept drier and much more sensitive. The preferred cellulose ether solution comprises ethylcellulose 4, butyl alcohol 20 and benzene 76; or ethylcellulose 3, amyl alcohol 15 and toluene 80; or ethylcellulose and amyl alcohol 5 each, butyl alcohol 15 and xylene 75. The use of this method for coating motion picture film is also claimed for ordinary photographic films or emulsion surfaces.

In the W. Webb process for treating cellulose ether films shown in Fig. 12, with especial reference to reducing the tendency to curl[2] where water-insoluble ethylcellulose is used, a solvent is applied to the face of the film, but the action is stopped before the body of the film is attacked, and the solvent selected according to the avidity with which it dissolves the etherized cellulose. By referring to the Figure it will be evident that the dope-applying station is a V-shaped trough *61* with adjustable gate *62*, for regulating the thickness of the layer deposited on the casting wheel facing *5*. The film is drawn under tension away from the wheel as indicated by the arrow, passing over the roller

1. U. S. P. 1411677; abst. C. A. 1922, **16**, 1915.
2. U. S. P. 1429179; abst. J. S. C. I. 1922, **41**, 854-A; Phot. Abst. 1923, **3**, 15.

72. As the film becomes set on the wheel, the condition which causes curling is created in the film, and is obviated by depositing a small amount of solvent *9* by means of the

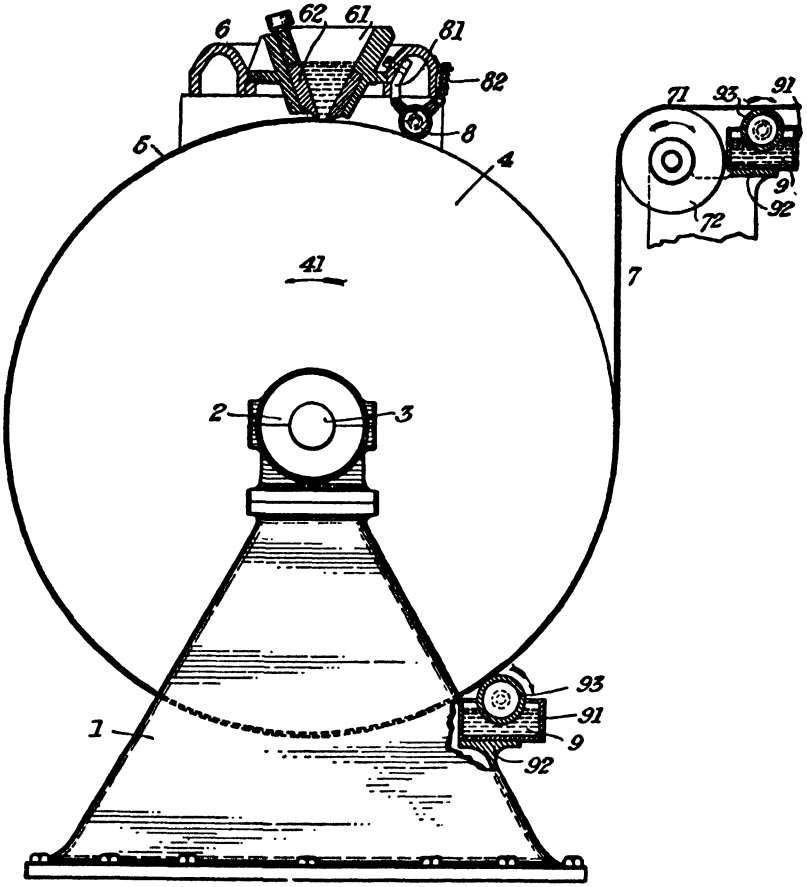


Fig. 12. Webb Process for Treating Cellulose Ether Films.

roller *93*, the film after treatment, being dried in the usual manner.

The film process of L. Lilienfeld[1] employs methyl-,

1. U. S. P. 1217027.

ethyl- or propyl-cellulose as the base and is carried out in manufacture as indicated by the following examples:

a. Ethylcellulose is dissolved in alcohol or a mixture of alcohol and benzene or toluene, and after having been filtered, is cast into film either by means of a drum or by the use of a spreading machine and then dried and detached.

b. Substances which impart suppleness are added to the cellulose ether solution, as triphenyl or tricresyl phosphates or camphor, and the solution either cast as before on an endless wheel, or if non-continuous films are desired, a plurality of normally thicker films than usual are made, compacted into a block by combined heat and pressure, and films prepared from this block by planing or shaving.

2. *Dreyfus and Celanese Cellulose Ether Film-Forming Methods.* In an application filed Sept. 9, 1920, H. Dreyfus[1] described a method for the manufacture of reinforced sheets, webs and plates from methyl-, ethyl- or benzyl-cellulose or other cellulose ethers, addressed more particularly to the coating of meshed fabric, and in 1926 disclosed his method of cellulose ether film formation[2], but first preparing a cellulose acetate film and then floating over this a cellulose ether solution as a unitary or plurality of coatings, the cellulose ether being selected as having different solubility characteristics from that of the acetylcellulose, in order to avoid injuriously cutting into the acetate film by means of the cellulose ether composition. The primary object of the invention was the protection of the original surface from dampness or friction. Iridescent silvery metallic effects on the film were obtained by thoroughly rubbing the film surface with fine crystals of bismuth or antimony oxychlorides, the film having previously been colored

1. E. P. 173021; abst. Chim. et Ind. 1922, **8**, 1298.

2. British Celanese, Ltd., E. P. 274841; abst. C. A. 1928, **22**, 2273; Chem. Zentr. 1927, II, 2788; J. S. C. I. 1928, **47**, 782-B. C. Dreyfus, F. P. 637113; abst. C. A. 1929, **23**, 704; Plastics, 1929, 638. Ital. P. 259388.

black by the incorporation of a sufficient amount of nigrosine.

In the formation of colored films[1], either unitary or multicolored, a mixed solution of water-insoluble methyl- or ethyl-cellulose in organic solvents is prepared, and various azo colors are dissolved therein by means of volatile solvents or solubilizing agents, and used to color the cellulose ethers during their formation into films or sheets for photographic or other purposes. For instance, hexamethyl violet base gives a violet; 4-toluene-1-azo-1-naphthalene-4-azophenol, a gold; 4-methoxy-3-nitrobenzene-1-azodimethylaniline, an orange; 1.4-diaminoanthraquinone, a heliotrope; 1.4-di-(monomethylamino)-anthraquinone, a blue; 2.4-dinitro-4-dimethylaminodiphenylamine, a yellow; and 4-chlor-2-nitrophenyl-4′-tolylamine, a bright yellow.

In the manufacture of artificial and compound films and sheets[2], a solution of methyl-, ethyl- or benzyl-cellulose in association with a synthetic resin of the diphenylolpropane-formaldehyde type, is spread on a stationary or movable smooth surface, and if thick sheets are desired, evaporation after spreading is retarded in order to obtain a more uniform film, the usual plasticizers as triacetin, ethyl phthalate and diacetone alcohol being incorporated in the cellulose ether solution. Films of but 0.005-0.03 inches in thickness may thus be prepared[3]. If the film surface is not of the requisite smoothness, it may be polished by means of tripoli or other abrasive made into a thin magma with a solvent or latent solvent for the cellulose derivative[4], a polishing fluid of low solvency being selected.

Contrary to the established conception, H. Dreyfus[5] has found it economically feasible to prepare sheets and films of or containing the cellulose ethers without the use

1. British Celanese, Ltd., E. P. 285431; abst. C. A. 1928, **22**, 4834; Chem. Zentr. 1928, I, 3132. C. Dreyfus, F. P. 648137; abst. C. A. 1929, **23**, 2822.
2. *Ibid.* E. P. 347647.
3. *Ibid.* E. P. 348099; abst. C. A. 1932, **26**, 2838. See E. P. 347648.
4. *Ibid.* E. P. 352547; abst. C. A. 1932, **26**, 3346.
5. E. P. 355732; abst. J. S. C. I. 1931, **50**, 1045-B.

of substantial amounts of volatile solvents. A homogeneous mixture of cellulose derivative and plasticizer is made and rendered fluid by heat in the substantial absence of volatile solvents, and is then drawn off through an adjustable aperture in the heating tank between two similar water-cooled rolls rotating synchronously in opposite directions. The resulting sheets are conditioned by means of moist air or solvent vapors, and then cut, planed or shaved to the desired thickness.

If it is desired to place the finished cellulose ether film on a textile backing[1], the cellulose ether or ester solution is first deposited upon a polished surface and the volatile solvent evaporated therefrom, and then transferred to cloth wetted with a solvent, being permanently attached thereto by combined heat and pressure. Or the film after formation but still tacky from residual solvent not yet dissipated, may be directly attached to a textile backing by heat and pressure[2]. C. Dreyfus and G. Miles[3] impart flexibility to cellulose ether films by incorporating therewith and therein certain hygroscopic substances as zinc chloride, which is soluble in alcohol and other dissolvants for the cellulose derivatives. They have found that a film made from a solution containing 6% zinc chloride on the weight of the cellulose ether has much greater flexibility than one of similar thickness made from a cellulose ether solution of similar consistency but having no zinc chloride incorporated therein.

3. *I. G. Farbenindustrie Cellulose Ether Films.* In the preparation of protective layers for photographic films[4] a mixed cellulose ester or a cellulose ether-ester is said to be especially useful in preventing the film from rolling up development, fixing and drying, and making it softer

1. C. Dreyfus, F. P. 634345; abst. C. A. 1928, **22**, 3788; Chem. Zentr. 1928, I, 3132.
2. H. Dreyfus, F. P. 39028, Addn. to F. P. 702174.
3. U. S. P. 1611169; abst. C. A. 1927, **21**, 496; J. S. C. I. 1927, **46**, 228-B.
4. E. P. 270347; abst. C. A. 1928, **22**, 1552; J. S. C. I. 1927, **46**, 893-B. F. P. 635281. D. R. P. 501643.

and better adapted to slide, of particular importance in a cinematograph film. In order to impart the desired properties to this protective layer, mixed cellulose compounds more or less foreign to the emulsion carrier have been found most suitable, such as cellulose aceto-stearate (stearo-acetate), cellulose aceto-phosphate (phospho-acetate), ethylcellulose stearate or ethylcellulose phosphate. The application of the principle is shown in the following examples:

a. 6 gms. cellulose aceto-phosphate are dissolved in 375 cc. acetone and 160 cc. water, with 30 cc. methylglycol acetate. The layer produced by applying this solution in the usual manner to the back surface of the film imparts good protection against electrical discharges.

b. For producing a protective layer on the back surface of the film there is used a 1% solution of ethylcellulose stearate or cellulose aceto-stearate in a mixture of 1 part alcohol, 3 parts benzene and 2 parts acetone. This layer greatly diminishes the resistance of the film to sliding in the projection camera.

In the casting of the film on a movable or rigid support, in order to obviate adherence of the film to the support[1], it is modified in structure as by superficial saponification, denitration or other treatment so that it neither swells nor dissolves in the solvent used in the preparation of the film dope. The treatment is claimed to be such that the cellulose ester or cellulose ether (?) is peripherally converted into regenerated cellulose. In the manufacture of artificial films or fibers from cellulose ethers or esters or mixtures, or from inter- and intra-molecular mixed cellulose ethers and esters[2], there is said to occur a disruption of the original cellulose complexes during the transformation of the cellulose to the etherized compound, and that defective or unstable union sometimes results. To compensate this defective union of individual particles, espec-

1. I. G. Farbenindustrie, A.-G., E. P. 279047; abst. J. S. C. I. 1928, **47**, 811-B.

2. *Ibid.* E. P. 293350; abst. C. A. 1929, **23**, 1750; Chem. Zentr. 1928, II, 2206.

ially in artificial fibers made from cellulose ether solutions, they are cemented or agglutinated together by a cement which need not necessarily be of the same material as the particles cemented. The scope of the invention is indicated by the following examples:

a. A solution of 100 gms. ethylcellulose in 900 cc. of a mixture of equal volumes of benzene and methyl alcohol are thoroughly mixed with a solution of 8 gms. linseed oil varnish in 10 cc. benzene. Films made by pouring this solution and dried in the usual way, exhibit, after the linseed oil has solidified, a strength 25% higher than that of films which have been made by pouring the same solution, but without the addition of linseed oil varnish. It has not been settled how far the substances of aldehydic and acidic character produced by the drying of the linseed oil may play a favorable part by union with the cellulose complex.

b. The ethylcellulose solution in Ex. a. is thoroughly mixed with a solution of 2 gms. urea and 2 gms. hexamethylenetetramine in 20 cc. of methyl alcohol-benzene (1:1). Film strips cast from this mixture and dried at 70° for 23 hrs. have a strength about 42% higher and an extensibility of about 50% greater than a film strip made by casting the same solution without the addition of the urea and hexamethylenetetramine, but with the same duration of drying.

c. 50 gms. acetaldehyde are added while cooling, to 50 cc. 50% aqueous NaOH, and the whole thoroughly mixed while cooling. There is obtained spontaneously the known aldehyde resin of copper-red color. This is washed with water, then with dilute acetic acid, pressed in the cool state, and 6 gms. of it dissolved in a few cc. of benzene-methyl alcohol, are added to a solution of 100 gms. ethylcellulose in a mixture of 450 cc. each methyl alcohol and benzene. After thorough mixing, the solution free from bubbles is cast into film form. The film while transparent, is a bright yellow color, and has a strength about 48% higher than

that of the same ethylcellulose film without the above stated addition.

An inexpensive film composition from the viewpoint of solvent has been disclosed[1], utilizing carbon bisulfide as the cellulose ether solvent. Thus:

a. A solution of cellulose ether having about 2.5 ethyl groups per C_6 cellulose is a mixture of 84% carbon bisulfide and 16% ethyl ether and of 8% ethylcellulose concentration, when worked up at 24°, yields a film containing numerous small bubbles, but if the same solution is worked up at 5°, a clear, lustrous and correspondingly strong film results.

b. A mixture of 92% ether and 8% CS_2 containing 9% ethylcellulose (2.5 ethoxyl groups), when worked up at 20° produced a non-transparent film of poor tenacity and flexibility, but the same solution manipulated at 3°, and only raised to a higher temperature (30-40°) after the first drying, yielded a stronger, transparent film, practically free from bubbles.

A novel method has been described for the formation of films, fibers, foils and capsules, employing solutions of ethylcellulose, ethylcellulose acetate or propionate, or cellulose acetonitrate[2], comprising preparing a solution of the cellulose derivative as 19 parts ethylcellulose (47% ethoxyl) in 81 parts dioxane. The solution is extruded through a slit of circular orifices into a precipitating bath containing ammonium sulfate and sulfuric acid in water, and the coagulated film is washed and dried, in much the same manner as regenerated films are prepared from viscose solutions at the present time.

4. *Disclosures of Cellon-Werke, A. Eichengrün.* Thin films of cellulose ethers and esters are prepared by applying a solution of the derivative in a thin layer to a base formed of a material to which the cellulose ether does not adhere[3], and which preferably has a repellent action towards such

1. I. G. Farbenind., A.-G., E. P. 302667. Swiss P. 140429.
2. K. Weisbrod, D. R. P. 542814; abst. C. A. 1932, **26**, 3111.
3. E. P. 202306; abst. Kunst. 1925, **15**, 101.

derivative. The base material is preferably a cellulose compound that possesses a different solubility to the cellulose ether from which the film is to be produced, and it is preferable should have but a slight solvent action on the base. The base material may be rendered repellent by additions of oils, fats, and alcohol-soluble metal salts.

In producing thin foils and film-like bands of alcohol-soluble ethylcellulose on a manufacturing scale and at great speed[1], highly viscous or concentrated or easily solidifying solutions are used, being applied upon extremely long and endless bands of flexible material, from which the solidified film may be withdrawn without difficulty. The bands upon which the film is cast constitute a series of loops or as a series of loops without pulling or tensioning, which includes a drying device, so that the foil may be continuously wound as a roll at the completion of the process. By use of a drum or wheel of 12-16 meters periphery, the drying period is adjusted to less than one revolution.

5. *Methods of Spicers, Ltd.* A photographic film has been described[2] formed of cellulose ethers mixed with pure, finely divided cellulose, and a white opaque pigment, to which hexachlorethane and zinc, tin and aluminum chlorides may be added to reduce inflammability. Incorporated with a cellulose ether are 10 parts finely divided cellulose, 10 parts zinc oxide or titanium white, 100 parts acetone oil, 4 parts cedar wood oil and 4 parts plasticizing agent are given as a representative formula for the material to be used as supports for photographic emulsions. A machine has been devised for spreading the materials[3].

In order to obviate possibility of cockling or distortion during evaporation of the residual solvent[4], the film after

1. A. Eichengruen, U. S. P. 1688457; abst. C. A. 1929, **23**, 277. E. P. 224848, 241590. D. R. P. 469317.
2. H. Hands and Spicers, Ltd., E. P. 282980; abst. C. A. 1928, **22**, 3848.
3. *Ibid.* U. S. P. 1666377. E. P. 281803. Can. P. 275953, 291437. New Zeal. P. 58031.
4. *Ibid.* E. P. 287635; abst. J. S. C. I. 1928, **47**, 444-B. F. P. 659387. Can. P. 281686.

leaving the casting surface is passed through a space charged with water vapor at a temperature considerably above normal room heat, the object being to extract the residual solvent, remove objectionable odor, and the mist of water vapor effectually removes any electric charge from the surface of the film, thus eliminating risk of sparking and possible ignition of the solvent vapor in the vicinity. The film is maintained in a stretched or distended condition during this treatment. Or[1], the sheets or films may be passed through a bath containing 0.5-1% caustic soda solution or of sodium acid sulfate, the whole being electrically earthed. A softening agent as alcohol, and an oxidizing agent as hydrogen dioxide may also be added to the bath, or the oxidation may be subsequently carried out in a separate bath. A mechanical device for coating has also been patented[2].

6. *Usines Chimique Rhone-Poulenc Procedures.* Cinematographic or other films are formed by coagulating a solution of cellulose ether while in the form of a film produced by surface tension between supports such as tapes, wires or threads (which may serve as marginal supports)[3], the precipitation being induced by extrusion into a liquid or gaseous medium, and consists in forming with these solutions by surface tension, liquid films between two or more solid threads or plates serving as supports. Decorative effects may be obtained on films or sheets of methyl-, ethyl- or benzyl-cellulose by uniting one or more colored or decorative cloths made of threads of the cellulose derivative[4], which must be plastic when heated, so that the structure of the cloth completely disappears into the complex sheet obtained.

1. H. Hands and Spicers, Ltd., U. S. P. 1811689; abst. C. A. 1931, **25**, 5030. E. P. 301439. F. P. 645912. D. R. P. 487646.
2. Spicers, Ltd., and A. Wickham, U. S. P. 1881108. E. P. 369608; abst. J. S. C. I. 1932, **51**, 463-B.
3. Societe des Usines Chimiques Rhone-Poulenc, E. P. 318250; abst. C. A. 1930, **24**, 2290. F. P. 688200; abst. C. A. 1931, **25**, 815.
4. *Ibid.* E. P. 305189; abst. C. A. 1929, **23**, 4819. F. P. 648152.

7. *Pathe Cinema Cellulose Ether Films.* Filaments, films or threads are made from cellulose ether solution by first coagulating in an aqueous bath[1], and then with or without preliminary drying, subjecting the product to controlled treatment with a solvent in liquid or vapor form to convert it from opaque to a polished, transparent condition. In order to obtain the maximum of transparency in the cast films or the precipitated foils[2], it is necessary that the solvents for the cellulose derivatives be in the substantially anhydrous condition.

8. *Other Cellulose Ether Film-Forming Processes.* The Non-Inflammable Film Co. and D. Phillips[3] prepare opaque cellulose ether films by adding a pigment as zinc oxide or lithopone, but with increased addition of pigment the film becomes more brittle and of lower tensile strength. According to their invention a double film is made by pouring two films one on top of the other, only one of the films containing opaque-inducing material. For instance, one part of cellulose ether is dissolved in a suitable low-boiling solvent, and 1-1.5 parts gold or aluminum bronze powder is added and thoroughly incorporated by stirring. This is then spread with a suitable apparatus and when the film is dry, a clear film is cast thereon, or a film containing but a small proportion of pigment as zinc oxide.

The Celluloid Corporation[4] flow films or sheets of methyl- or ethyl-cellulose or cellulose acetate or propionate by extruding them or causing them to flow at elevated temperatures, thus enabling the use of smaller amounts of solvent to be employed and results in greater rapidity of drying and consequently in an increased rate of production. Volatile and low-boiling solvents are partially replaced by plasticizers as monomethylxylenesulfonamide, butyl tar-

1. Pathe Cinema, Anciens Etablissements Pathe Freres, E. P. 247974; abst. C. A. 1927, **21**, 649. F. P. 606543. Swiss P. 119678.
2. *Ibid.* E. P. 267112; abst. C. A. 1928, **22**, 1237. F. P. 624278.
3. E. P. 331214; abst. C. A. 1931, **25**, 178.
4. E. P. 310540; abst. C. A. 1930, **24**, 723.

trate or ethyl phthalate, the solvent mixture comprising acetone and dioxane.

A film for episcopic projection has been described[1] comprising cellulose ethers with particles of finely divided metals embedded therein as image carriers. Bronze powder is said to be especially suitable for the purpose. A supporting layer of cellulose hydrate is attached to the gelatin side of a film after it has passed through all the baths, and may be attached while the film is still moist[2], or after it has dried. While water soluble adhesives may be used, organic solutions are preferable. As a temporary base, the use of cellulose ethers has been described. The inflammability of the combined films may be reduced by addition thereto of relatively small amounts of sodium silicate, ammonium fluoride, chloride, bromide or phosphate, or triphenyl or tricresyl phosphates. According to E. Pfiffner[3], dielectric films of cellulose ethers and esters may be formed by superposing separate films of cellulose ethers before they have completely hardened, so that they may be united by pressure and heat without passage of any impurities from one film to the other. They are used as dielectrics in the preparation of electric condensers.

The film-like wrapping tissue of C. Olson[4], which is non-porous, non-hygroscopic and non-inflammable, is made by dissolving ethyl- or benzyl-cellulose in suitable solvents, is prepared by flowing a solution of the desired concentration, the speed of production depending upon the thickness of film if it is desired to produce a transparent product, or the coating may be applied to various kinds and thicknesses of paper, for the purpose of producing a wrapping material for packages. The J. Chamberlain and H. Periam photographic film[5] comprises a base layer treated with a sub-

1. K. Bratring, D. R. P. 357010; abst. Chem. Zentr. 1922, II, 816.
2. *Ibid.* E. P. 307431; abst. J. S. C. I. 1930, **49**, 840-B. D. R. P. 519137.
3. E. P. 267917; abst. Chem. Zentr. 1927, II, 521.
4. U. S. P. 1458592; abst. C. A. 1923, **17**, 2645.
5. E. P. 304632; abst. C. A. 1929, **23**, 4630.

stance for providing a homogeneous surface layer which, while not necessarily soluble in water, yet is receptive to an aqueous solution. The base layer may be cellulose ether mixed with a composition containing gelatin or glycerol or both. An ethylcellulose dissolved in benzene and a gelatin composition added thereto which has a small amount of sulfonated castor oil has been found to be miscible and suitable for the purpose.

Films and fibers are producible by dissolving a cellulose ether or cellulose formate in a common solvent with casein[1], aqueous solutions of sodium, potassium, calcium or zinc thiocyanate or isothiocyanate being suitable. The G. Frenkel composite film comprises a first layer made so thin (suitably about 0.01 mm.) as to require a very short time for drying and after being stripped from its support, is used as a carrier band for additional layers, which may comprise various cellulose ethers[2]. In improving the water-resistance properties of those cellulose ethers not of maximum etherification[3], the films are treated with a water-miscible liquid which is capable of swelling the cellulose gel, and at the same time with a water-immiscible plasticizing agent so that the material is simultaneously rendered water-resistant and softened. Methylcyclohexyl adipate and/or amyl phthalate are stated as suitable.

In the production of films of unusual length of cellulose derivatives[4], a layer of the cellulose derivative as ethylcellulose is first formed, then a metallic surface is formed on the layer, and this covered by another layer of the cellulose ether whereby the static electricity engendered or received is drawn from the surfaces. First there is formed a film of but 0.01 mm. in thickness[5], which is allowed to

1. Societe pour la Fabrication de la Soie Rhodiaseta, D. R. P. 512160; abst. C. A. 1931, **25**, 1083. Belg. P. 330795.
2. E. P. 332255; abst. C. A. 1931, **25**, 204.
3. Wolff & Co. and R. Weingand, E. P. 324677; abst. C. A. 1930, **24**, 3900. F. P. 642176. D. R. P. 487618. E. P. 298631, 300496. See Ital. P. 271076, 274753.
4. G. Frenkel, F. P. 698800; abst. C. A. 1931, **25**, 3482.
5. *Ibid.* F. P. 698801; abst. C. A. 1931, **25**, 3482.

dry and used as a support for further layers. C. Field[1] softens the cellulose ether field by the use of ethyl lactate in amount equivalent to about 1% by weight of the film[2].

The Farbenfabriken vorm. F. Bayer & Co.[3] have drawn attention to the fact that most colloidal layers as gelatin, acacia, glue, and casein adhere so strongly to a base as to be removable only through destructive means, and have suggested a method by which it is possible to remove such colloidal layers by the application of a cellulose ether coating as an intermediate layer, as indicated in the following example: Glued paper is coated with a solution of 5 parts ethylcellulose, 0.5 parts triphenyl phosphate and 94.5 parts of benzene to which 5% alcohol has been added, and allowed to dry. After drying, a light-sensitive silver bromide gelatin layer is applied in the usual way. On the resulting negative paper an exposure now is made, which may be developed, fixed and washed in the usual manner, preferably by use of a suitable hardening bath. After drying, the gelatin layer carries the exposure, can be removed, and yields a transparent gelatin film that is copiable in the usual manner. By the application of a corresponding barium paper, clear, removable films are obtainable. The Mimosa A. G. process for preparing direct photographic positives[4] consists in exposing an emulsion-coated cellulose ether film and reversing the image from the exposure in the customary manner[5].

1. E. P. 348723; abst. Chim. et Ind. 1932, **27**, #3, 656.
2. M. Schmidt and W. Krieger, D. R. P. 470731; abst. C. A. 1931, **25**, 1173.
3. D. R. P. 362030; abst. J. S. C. I. 1923, **42**, 203-A.
4. F. P. 685795.
5. Those interested in the mechanics of film production may consult K. Flynn, Can. P. 316713. I. G. Farbenindustrie, F. P. 678459. E. P. 279047, 288223, 316301, for a cellulose ether photographic film spool. K. Hickman, U. S. P. 1638577. E. P. 280162. Wolff & Co. and R. Weingand, E. P. 300496. E. Bleibler, E. P. 343814, 359278. H. Dreyfus, F. P. 716449. W. Pease, E. P. 329691. A. Maurer, D. R. P. 537488. H. Elling, D. R. P. 533619. J. Zdanowich, Swiss P. 131023. A. Eichengrün, U. S. P. 1824337. Zellstofffabrik Waldhof and A. Bernstein, E. P. 344982. H. Hands, U. S. P. 1811689. Celluloid Corp., E. P. 315840. B. Gaisenband and C. Piestrak, F. P. 485068. J. Haste, U. S. P. 1494479, 1514283. F. P. 588258. H. Van Doerhoef, U. S. P.

Cellulose Ethers in Color Photography. Due to the wide range of solvents available for the cellulose ethers, and solvents which have a high dissolving capacity for dyestuffs and lakes, together with the number of plastifying, softening and ancillary bodies which may be associated with the cellulose ethers harmoniously to obtain specifically desired results, indicate that the etherified celluloses should find wide application in connection with color photography.

The colored element of S. Sheppard[1] relates more particularly to a translucis, colored, finely divided substance in a supporting medium capable of use with photographically sensitive material in the art of photography, and provides a colored medium for various photographic uses, primarily to the incorporation of a dye capable of being used in a photographically coated medium. Whereas gelatin is ordinarily used for photographic coating purposes, there is a tendency for desirable types of dyes to bleed and run, or to wander from the gelatin into aqueous solutions, so that the color is either discharged or is not permanently located, with the result that the colored mass is not well adapted for photographic or photomechanical purposes, since intensity and definition are affected by the wandering of the dye. He utilizes as a dye-carrying medium, cellulose ethers or esters, with or without latent solvents such as camphor, coloring the film by means of basic dyes which are readily dissolvable in the usual range of cellulose ether solvents.

In a process patented in England[2], a film of cellulose ether to which a multicolor screen is to be applied by dyeing, a resist pattern is applied thereto, the parts unprotected by the resist being bleached and redyed, which is

1746751. G. Tocco, F. P. 719146. J. Wells and C. Wynd, U. S. P. 1878559. La Cellophane, F. P. 714274. E. Bleibler, Can. P. 324660. Spicers, Ltd., and A. Wickham, E. P. 369608. C. Dreyfus, Can. P. 322361. O. Demaret, F. P. 702624. W. Stuber, U. S. P. 1846230.

1. U. S. P. 1290794; abst. C. A. 1919, **13**, 818; J. S. C. I. 1919, **38**, 200-A.

2. J. Goldsmith, T. Baker and Spicers, Ltd., E. P. 337073. U. S. P. 1818927. See E. P. 224571, 257501, 321222, 322432, 339238.

then coated with an isolating layer of substantially waterproof nature and a surface layer of material receptive to dyes is applied over this coating. In an analogous process of forming a multicolor screen on a film of cellulose ether[1], the surface is made receptive to dyes by applying a layer of cellulose acetate without dye-inhibiting additions. A solution of cellulose acetate in tetrachlorethane is specified for this purpose.

The I. G. Farbenindustrie[2] have described the preparation of a layer for use in the bleach-out process which comprises a nitrogen-free basic oxonium dyestuff other than a xanthocyanin. Such dyestuffs are, for example, 3.6-dihydroxy-3-phenylxanthoxonium chloride and its ethers and 3.6-dimethoxy-9-*o*-carbmethoxyphenylxanthoxonium chloride. A layer for the production of multicolor pictures comprises a mixture of resorcinbenzeindimethylether bromide, anilinodimethylaminoazonium phenyl chloride and 2.7 - dimethyl - 3 - dimethylamino - 6 - methylaminoazonium phenyl chloride in a mixture of ethylcellulose butyrate and nitrocellulose.

In the production of a multicolor screen upon a support of a cellulose derivative as cellulose acetate[3], a greasy resist containing a dye is applied as by printing, to the surface of a film in a series of lines or a geometrical pattern. The dye migrates from the resist into the surface of the film so that, after removal of the resist as by a solvent, a colored series of lines or pattern remains on the film. The resist may be a greasy ink, or thickened linseed or other vegetable oil used with oil-soluble dyes such as oil orange or oil red, or may include a dye solvent as acetic acid to enable the dye to penetrate into the surface of the film. Before the resist is removed from the film, the interspaces between the lines, which are not protected by the resist, may be

1. Spicers, Ltd., J. Goldsmith, T. Baker and C. Bonamico, E. P. 334265. See E. P. 217557, 321222, 322432.
2. E. P. 343212.
3. E. P. 334243; abst. Chem. Zentr. 1930, II, 3891.

dyed with a color different from that in the resist, so that when this is removed a two-color screen remains.

In the preparation of regular pattern multicolor screens by means of dye-repellent resists[1], the dyes in a non-penetrative condition or medium are applied to intermediate surface layers only of a film support formed of cellulose ether, a powdered dye being rubbed or spread onto the film, or a dye such as cochineal in suspension may be applied[2]. Or[3], there may be applied on the surface of the film a constituent of coloring material and afterwards printing successively on the surface of the film, lines or other geometric designs, by one or more agents each containing a compound capable of reacting with the constituent to form a differently colored dye. For instance, a solution of diazotized 4-amino-4′-ethoxydiphenylamine for the red lines, and a solution of diazotized 2.5-dichloraniline for the blue lines.

The T. Baker[4] process for obtaining prints in natural colors in which a light-sensitive layer coated over a multicolor screen on a transparent support is printed through the support from a negative associated with a multicolor screen of cellulose acetate, is attached by an adhesive as dammar to a translucent stripping support as celluloid or parchmentized paper. To avoid the moire effect in copying by projection from a master cinematograph film[5], a sheet of plane glass scored or indented with lines is placed in front of, or behind the projection lens. The lines may be formed as concentric circles about 0.125 inch apart. J. Smith[6] coats with color-screen a film of acetylcellulose, by ruling thereon with fish glue solutions containing suitable dyestuffs, the glue being afterwards insolubilized with

1. J. Goldsmith, T. Baker, C. Bonamico and Spicers, Ltd., E. P. 339238; abst. C. A. 1931, **25**, 2378.
2. *Ibid.* E. P. 352949.
3. *Ibid.* E. P. 333865; abst. C. A. 1931, **25**, 652; J. S. C. I. 1930, **49**, 1093-B. F. P. 698258; abst. C. A. 1931, **25**, 2930; Chem. Zentr. 1931, I, 2572.
4. E. P. 337040. See E. P. 282980, 328336.
5. T. Baker, E. P. 337041. 6. U. S. P. 1390252.

formaldehyde vapor. The intermediate space of the cellulose ester film is then stained by means of a solution of a dye in aniline oil or nitrobenzene. In making multicolor screens having a regular straight-line pattern[1], a film of cellulose derivative as the acetate is coated with a solution of cellulose nitrate alone or with softening and plasticizing agents, before applying the dyes, or the nitrocellulose coating may contain the dye.

The dye layer forming the backing of anti-halation films may be protected from abrasion or contact with an emulsion surface which might be affected by such contact[2], by an outer coating of an isolating colloid as cellulose acetolactate (lactoacetate), and resins or gums. The G. Ellis and C. Dreyfus method of producing colored films comprises preparing a cellulose ether or ester solution[3], incorporating therein a difficultly soluble dyestuff by means of a solubilizing agent which has an affinity for the cellulosic compound, mixing to uniform consistency and then casting a film from the solution.

M. Schmidt and W. Krieger[4] have discovered that light-sensitive stable diazo compounds may be incorporated into cellulose ether solutions or emulsions to produce light-sensitive films. It has been found that an aqueous solution of methylcellulose, which in general has a well defined tendency to coagulate when mixed with a slightly acidified solution as diazotized *p*-aminodiphenylamine and 1.8-aminonaphthol-3.6-disulfonic acid, remains quite clear. By pouring such an alkylcellulose solution admixed with a light-sensitive substance upon a smooth surface, clear films are obtained which may readily be detached. This process can be applied in the preparation of positive as well as negative

1. Versicolor Dufay (Compagnie d'Exploitation des Procedes de Photographie en Couleurs L. Dufay), E. P. 322432; abst. C. A. 1930, **24**, 2681. See E. P. 20111, 1908; 217557, 254032, 281803, 287635, 301439, 321222.

2. Kodak, Ltd., and R. Crowther, E. P. 364852; abst. J. S. C. I. 1932, **51**, 322-B.

3. Can. P. 297375.

4. U. S. P. 1756400; abst. C. A. 1930, **24**, 2959; J. S. C. I. 1930, **49**, 588-B. E. P. 311196; abst. C. A. 1930, **24**, 796. D. R. P. 470731.

diazotypes. In order to obtain positive negatives, it is advisable to use the diazo compound in combination with an azo component. There may be obtained, for instance, materials suitable for the preparation of negative diazotypes, by adding diazotized aminosalicylic acid to a solution of a cellulose ester or ether. In this case, the development of the negative picture may be accelerated by subjecting the film before exposure, to the action of an alkali as gaseous ammonia.

The invention is illustrated by the following:

a. 50 parts of purified aqueous solution of methylcellulose of 8-10% strength are mixed with 10 parts of a weakly mineral acid, light-sensitive solution containing 1.5 parts *p*-phenyliminoquinonediazide sulfate and 1 part resorcylic acid in 100 parts water. By pouring the mixture on a suitable base as paper, layers are obtained which can be dried at ordinary or elevated temperatures. It is advantageous to add a mineral salt to the light-sensitive solution[1].

In the production of polychromatic screens for color photography according to the details as laid down by Spicers, Ltd.[2], a means has been devised whereby a polychromatic screen may be brought immediately onto a commercial cellulose acetate or cellulose ether film without the necessity of a pre-treatment. The screen is prepared on a cellulose ether film by first placing on the surface of the film an azo dye constituent and then printing lines or other geometrical designs on the film surface with an agent that contains a compound capable of reacting with the component with the formation of a dye. In one form of carrying out the invention, the reaction, taking place as the result of the printing-on of the first series of patterns, is allowed to go to completion before the second series is introduced which will produce a second color. The total amount of the first applied dyestuff is exhausted on the surface on

1. H. Wade, F. P. 667253. T. Baker, Nature, 1931, **127**, 821.
2. D. R. P. 525611.

which the reaction with the first agent occurs, so that nothing remains that can react with the second agent, and consequently no overlapping colors are formed[1].

Societe Kodak[2] have described a folding screen composed of ethylcellulose with suitable plastifying agents. The color-backed motion picture film of J. Wells[3] is built up of successive layers of cellulose acetate of low precipitation value on which is superposed a layer of cellulose acetate of high precipitation value.

It is sometimes desirable or necessary that photographic roll films be exposed behind a suitably light filter, especially in the case of films having a panchromatic sensitive layer[4], but this is said to be unnecessary when the film is provided with a transparent foil which lies over the light-sensitive layer and containing a dye suitable for use with the particular emulsion, so that it acts as a light filter. The foil must be of a material which does not chemically act upon the light sensitive layer, cellulose ether or cellulose ether-ester having been found especially suitable for this purpose[5]. Prints may be obtained by exposing a light-sensitive cellulose ether preparation and developing[6], a suitable combination being ethylcellulose, acetone, benzene, methyl violet, chloroform, and a wood oil-linseed oil varnish[7]. For printing on photographic film strips[8], a dye such as cerasin red is used with glycol acetate.

Artificial Sponge. In operating under the patented process of V. Ottorepetz[9] a concentrated solution is prepared of a cellulose derivative, and this is mixed with a fibrous

1. U. S. P. 1446049. 2. F. P. 636906.
3. U. S. P. 1870662.
4. I. G. Farbenindustrie, A.-G., E. P. 338741; abst. C. A. 1931, **25**, 2379.
5. R. Weingand, U. S. P. 1846575; abst. C. A. 1932, **26**, 2387.
6. K. Dörken, E. Hochuli and H. Herminghaus, D. R. P. 542598; abst. C. A. 1932, **26**, 3197.
7. L. Clement, U. S. P. 1866965. W. Moss, Can. P. 322362.
8. H. Lummerzheim and E. Schnitzler, U. S. P. 1828974; abst. C. A. 1932, **26**, 662. See also I. G. Farbenindustrie, A.-G., E. P. 356981.
9. E. P. 23196, 1913; abst. J. S. C. I. 1914, **33**, 858. See E. P. 21524, 1914.

material as cotton and a water-soluble substance as sugar or salt. The paste thus obtained is immersed in water or dilute acid to dissolve out the chemical introduced, the voids due to such solution forming the pores in the "sponge," while the cellulose derivative in association with the cotton filaments remains as the sponge body or substance.

In another process[1] a mixture of a concentrated organic cellulose derivative with a water-soluble component as above, or a constituent which is soluble in some solvent not dissolving the cellulose derivative, is used with an animal or mineral fiber as a fortifying superstructure, then the mass is immersed in water or other solvent to dissolve out the extraneously added material and leaves the cellulose derivative superstructure in a highly porous condition.

A more recent method has been described[2], the cellulose ester or ether being combined with a proportion of viscose solution, or viscose solution is used without admixture of other cellulose compound, cotton, flax or hemp fiber being added as framework and sodium sulfate as the pore-forming material. Heat is applied to decompose the viscose, and then the water-soluble constituents are lixiviated out with cold or warm water.

Cellulose Ethers in Prosthetic Dentistry. Shortly after the discovery of the nitrocelluloses and their thermoplastic possibilities came to be appreciated, the dental profession occupied themselves extensively in attempts to replace rubber in dental work by pyroxylin compounds. For some time there had been bitter antagonism between the dental profession and the manufacturers of indurated rubber on account of the alleged exorbitant prices charged for ebonite and similar indurated rubber articles. P. Ber-

1. G. Pum, U. S. P. 1142619; abst. C. A. 1915, **9**, 1978. P. Roeder and B. Raabe Akt. Ges., F. P. 463498; abst. C. A. 1914, **8**, 3225. P. Roeder and B. Raabe, Aust. P. Addn. 8607 to Aust. P. 63556. Swiss P. 67258. Belg. P. 261288. D. R. P. 280111.

2. L. Mostny, U. S. P. 1611056. E. P. 245049; abst. J. S. C. I. 1926, **45**, 122-B; Oil, Paint and Drug Rep. 1926, **109**, #12, 68. Can. P. 270288; abst. Chem. Zentr. 1926, II, 846.

ard[1] had devised a lacquer of pyroxylin, alcohol, ether and a small amount of castor oil, colored pink with carmine to simulate the color of the gums, and intended to be applied as a varnish for artificial gums and as an enamel for the bases of artificial teeth, but it had a short life, being devoid of thermoplastic properties. Then two dentists working independently, J. McClelland[2] and L. Streeter[3] attacked the subject. The former prepared the first dental plate of collodion, but there was so much ether and alcohol in the formula that it warped and buckled in use and produced irritation in the mouth from not fitting. Streeter endeavored to remedy the distortion by veneering the dental plate with other material, but it was soon found that the thin film of pyroxylin became detached during mastication, and that particles of food were prone to lodge under it, so both these ideas were abandoned[4].

Then along came J. Hyatt with the idea that the bulk of volatile solvent must be reduced, and he applied a combination of pressure with camphor as colloidant and prepared the first really usable dental plates in 1870[5]. But there were people who objected to the flavor of camphor with each of their meals, so that the Hyatt dental plate did not find a very wide acceptance. D. Lichtenberg-Madsen[6] used a special kind of celluloid comparatively low in camphor, and L. Eilbertson[7] compounded a perfumed dental composition of a nitrocellulose base with sodium bicarbonate (ant-acid), salol and iodoform (as antiseptics) and "essence of rose," intended primarily for temporary tooth fillings. Anyone familiar with the taste and smell of iodo-

1. E. P. 639, 1858. See E. P. 1884, 1857.
2. U. S. P. 77304. 3. U. S. P. 88228.
4. For the application of celluloid in the manufacture of cliches, see Jannin, Technol. 1880, **40**, 264; Impr. 1880, **17**, 107; Archiv. 1880, **17**, 211, 243, 245; Gew. Bl. Würt. 1880, **32**, 310; J. f. Buchdr. 1880, **47**, 690; Printer, 1880, **1**, 78; Lorsch., J. Buchdr. 1901, **68**, 76; Z. Reprod. 1901, **3**, 77.
5. U. S. P. 105338.
6. E. P. 25519, 1899. See J. Schmidting, U. S. P. 725879.
7. U. S. P. 825268. E. P. 14475, 1900.

form will probably agree that it would require considerable essence of rose to effectually mask it.

Then the voice of cellulose acetate began to be heard in the land, — a product noninflammable, inodorous and tasteless and not requiring camphor as a plasticizing agent —and attention was directed to this as an ideal material for prosthetic dental work, for cliches, dentures and obturators for cleft palates. A patent in France was granted[1] for a dental plate composition composed of cellulose acetate dissolved in a solvent and combined with innocuous ores, mineral oxides and earths to impart rigidity; and in Germany to P. Harter[2] for the use of Cellon (a plastic cellulose acetate) dissolved in acetone and having pigments incorporated therein. The first to propose the use of the cellulose ethers for the manufacture of dentures and in other branches of dental technique was A. Burlin, S. Leicester and L. Holman[3] on an application filed in England Feb. 11, 1925, in which they specified the use of "water insoluble ethers of cellulose." Their method of procedure is to combine with the cellulose derivative suitable plasticizing agents to induce moldability, using the minimum of volatile solvent to guard against subsequent distortion, using a press temperature of about 160°. After the article has been formed, it is plunged into cold water and left until perfectly cold. As colloiding agents, benzyl alcohol, benzoin, benzil and triacetin are recommended.

Benzylcellulose forms the basis of another dental plastic composition evolved in France[4]. Unlike the acetylcelluloses, the cellulose ethers are unaffected by the ptyalin and alkaline secretions of the mouth, and their melting point is so high as not to soften by the ingestion of foods or liquids of maximum temperature, as hot soups, tea, cof-

1. V. Lapierre, F. P. 692400; abst. C. A. 1931, **25**, 1348; Chem. Zentr. 1931, I, 650.
2. D. R. P. 296272; abst. Kunst. 1919, **9**, 187.
3. U. S. P. 1615212; abst. C. A. 1927, **21**, 822. E. P. 251373; abst. C. A. 1927, **21**, 1355.
4. Soc. Anon. Des Laboratories "Odont-Email," F. P. 683418; abst. C. A. 1930, **24**, 4597.

fee or cocoa. The dental plastic may be made either of ethylcellulose or benzylcellulose in conjunction with phenyl or cresyl phosphates, a representative formula being: Benzylcellulose 100, triphenyl phosphate and tricresyl phosphate each 5, crystallizable benzene 360 and 98% alcohol 40. Benzylcellulose is preferred on the grounds of its high resistance to the action of chemical agents, its low impermeability and good thermoplasticity. The above composition is inserted into a mold, a heat of 170° maximum applied, and the fabricated article then cooled, as by replacing the steam in the press by cold water.

Celluloid has been proposed as a dental filling[1], in the preparation of a dental polishing device[2], and for the formation of a dental polishing disc[3].

Pencils, Crayons, Sealing Wax. The ready miscibility of the cellulose ethers in fatty and waxy materials on the one hand, and the wide range of dyes available which color both fats, waxes, oils and the cellulose ethers, has caused attention to be focussed on the possibility of the use of ethyl- and benzyl-cellulose for this purpose, and some interesting information has been disclosed. For instance, in the H. Mayer process for producing colored pencils[4], a water-insoluble cellulose ether is gelatinized with a high-boiling solvent as *b*-naphthol-methyl ether, a phenol-resin may be added with a softening agent or not as desired and depending upon the rigidity desired in the completed product, and appropriate coloring matter is added by means of a solvent harmonious to the cellulose ether if a dyestuff is to be used, or if a pigment is employed, this is mechanically incorporated into the composition.

The I. G. Farbenindustrie[5] report that cellulose ethers combined with acids of high molecular weight, as lauric, stearic or palmitic, forming the corresponding cellulose

1. H. Black, U. S. P. 1294355.
2. W. Hough, U. S. P. 1138479. 3. G. Parks, U. S. P. 1506078.
4. H. Meyer, D. R. P. 535981; abst. C. A. 1932, **26**, 1134; Chem. Zentr. 1931, II, 3402.
5. E. P. 325014; abst. C. A. 1930, **24**, 3868; J. S. C. I. 1930, **49**, 470-B. Can. P. 298013.

laurate, stearate or palmitate, in conjunction with fats (mutton suet) and waxes (carnauba or beeswax) together with an organic pigment of low specific gravity, may be used for the manufacture both of crayons or sealing wax. As an example, they suggest dissolving 50 parts of ethylcellulose at 130° in a mixture of 50 parts of stearic acid and 30 parts of ceresin. In the solution so obtained is then stirred in 10 parts carnauba wax and 3 parts of an azo-dyestuff soluble in fat. The mass while still fluid is stirred to a homogeneous mass and poured into molds to solidify by cooling for the preparation of crayons.

By combining the cellulose ethers with the higher fatty acids or their glycerides (fats) products result which may serve as the basis for paint masses, artificial materials and for writing and drawing pencils, especially marking crayons. In connection with the production of paints, it is pointed out that the cellulose ether compositions do not sink into the wood as do linseed oil base paints and varnishes which require a preliminary filling coat.

The Anglo Pencil Co., Ltd., and M. Smith[1] ornament pencils by applying to the article a transfer having a backing of aluminum or other metal foil, adherence of the transfer being secured by the use of a fixing medium which acts as a solvent of the varnish coating of the pencils, as a lacquer of cellulose ether or cellulose acetate.

X-Ray Screen. In Roentgen ray work and the preparation of calcium tungstate and other luminous screens, collodion has been extensively employed, as evidenced by the contributions of F. Amseder[2], A. Edwards[3], M. Levy[4], W. Martin[5], W. Price[6] and E. Saleil[7]. P. Hewitt[8] prefers to use cellulose acetate for the same purpose.

1. E. P. 326882; abst. C. A. 1930, **24**, 4945.
2. D. R. P. 237015; abst. Wag. Jahr. 1911, **57**, II, 508.
3. E. P. 111913; abst. J. S. C. I. 1918, **37**, 75-A.
4. E. P. 10098, 1897. D. R. P. 106576; abst. Chem. Zentr 1900, I, 698.
5. E. P. 24618, 1904.
6. U. S. P. 753310; abst. J. A. C. S. 1904, 26R, 429.
7. F. P. 468806; abst. J. S. C. I. 1914, **33**, 986.
8. E. P. 16271, 1911.

The F. Balch fluorescent screen used to intensify the image produced on a sensitive plate or film by X-rays[1] comprises cellulose acetate dissolved in a mixture of tetrachlorethane, methyl alcohol, Canada balsam, cold pressed castor oil and urea, to which is added calcium tungstate dissolved in the same solvent combination. N. Cahn[2] has described a surgical stitching material of silk, catgut or other product impregnated with thorium or other chemical yielding the necessary shadow in the Roentgen ray photograph, and is at the same time radio active, and hence an aid to healing.

The Kopp & Joseph light filter for absorbing ultraviolet rays[3] contains a non-glucosidic coumarin derivative which is mono- or poly-substituted by hydroxyl, amino ,carboxyl or phenyl groups. J. Eder (see p. 63, n. 4)[4] has shown that the skin may be protected against the action of light of short wave length by the use of aesculin and quinine sulfate, and has discovered that compounds containing at least two condensed aromatic systems, especially such derivatives of naphthalene as display a blue fluorescence, as the naphtholsulfonic acids or their salts or the naphthylaminesulfonic acids or their salts, and homologous anthracene derivatives have an excellent protective action. Sodium 2-naphthol-3.6-disulfonate is especially valuable for protection against sunburn.

R. Jahoda and L. Lilienfeld[5] have described the preparation of a fluorescent screen for X-ray use, containing calcined zinc sulfide in association with the cellulose ethers, an appropriate binder for the zinc sulfide, which should be associated with at least one metal or with silver sulfide, being prepared by dissolving water-insoluble ethylcellulose in a mixture of methyl alcohol and methyl acetate. The

1. U. S. P. 1532795; abst. C. A. 1925, **19**, 1664.
2. E. P. 354284; abst. Silk J. 1932, **8**, #94, 53.
3. D. R. P. 253334; abst. C. A. 1913, **7**, 433; J. S. C. I. 1913, **32**, 47.
4. U. S. P. 1511874; abst. C. A. 1925, **19**, 153; J. S. C. I. 1924, **43**, 967. See D. R. P. 119687.
5. U. S. P. 1817005; abst. C. A. 1931, **25**, 5351.

zinc sulfide is prepared, sorted and sludged and then added. This mixture can be made into films or brushed or flowed on to a base, and dried at not to exceed 100°. The screen prepared has no considerable afterglow.

Tracing Cloth. In the M. Renker process for manufacturing tracing cloth[1], the cloth base is treated with a solution of a cellulose ether or with a mixture of cellulose ether and ester solutions, the solvents used being of such a nature as not to dissolve the fat or oil used in finishing the tracing cloth, i.e., cocoanut fat, as contained in the emulsion applied in the usual manner. Suitable solvents for this purpose are methylglycol, methylglycol acetate, ethylglycol and ethylglycol acetate. In carrying out the invention, ordinary tracing cloth is smeared with a solution of the cellulose derivative in methylglycol and dried at 60-70°. An extremely thin film is deposited on the tracing cloth, thus rendering it waterproof, while preserving its transparency.

Tracing cloth is usually produced from linen, or more recently from cotton fabrics, but long staple cotton produces a fabric which when coated, is non-homogeneous in degree of transparency. It has been proposed to correct this defect by making the tracing cloth of fabrics of squirted or drawn threads[2], as real or artificial silk threads, the weave of which is almost mathematically uniform, and therefore, when artificial silk is used for tracing cloth, it is claimed an almost absolutely homogenous transparent article is produced without any cloudy unevenness.

Rubber with Cellulose Ethers. Many attempts have been made to combine in a homogeneously appearing solution, mixtures of nitrocellulose or cellulose acetate with latex or vulcanized rubber products. The inherent barrier to so doing is the fact that there are relatively few solvents

1. E. P. 297993; abst. J. S. C. I. 1928, **47**, 889-B; Chem. Zentr. 1929, I, 1299.
2. R. Schwickert, A.-G., and O. Huber, E. P. 357068; abst. J. S. C. I. 1931, **50**, 1045-B. Can. P. 319991.

harmonious to both. R. Ditmar[1] has sought to combine acetylcellulose with caoutchouc by virtue of the use of cyclohexanol, it being claimed the solution so formed may be dyed and used for a lacquer having unusually high plastic properties. Another process has been divulged in which cyclohexanone is the mutual solvent[2], the addition of *ar*-tetrahydrohydronaphthol being advocated as a desirable softening agent. Cyclohexanol is the mutual solvent in the method of C. Macintosh & Co., Ltd., S. Brazier and G. Thompson, for the bonding of articles or parts formed of india-rubber and cellulose derivatives. Such a solvent combination is applicable to the cellulose ethers, the water-insoluble modifications of which readily dissolve in this solvent[3].

In the textile industry, it is claimed those prepared from or containing cellulose ethers or esters may be improved by treating them with a dispersion of rubber latex[4], and preferably in conjunction with an inorganic pigment or other substance practically insoluble in water, zinc oxide or graphite being suitable for this purpose. The British Celanese, Ltd.[5], have described a method for the treatment of textiles of organic substitution products of cellulose as the cellulose ethers with dispersions of rubber latex, with or without the addition of vulcanizing agents to increase their tensile strength and resiliency, claiming such treated fabrics are less likely to slip, ladder or run. The rubberized fabric may be embossed by prior treatment with wetting or solubilizing agents[6], using solvents of methyl-, ethyl- or benzyl-cellulose for this purpose.

1. Chem. Ztg. 1921, **45**, 819; abst. J. S. C. I. 1921, **40**, 709-A; Chem. Tech. Uebers, 1923, **47**, 6.
2. P. Allman, H. Morris and L. Marlor, E. P. 274968; abst. C. A. 1928, **22**, 2292; Plastics, 1928, **4**, #9, 508.
3. E. P. 305745; abst. J. S. C. I. 1929, **48**, 295-B.
4. C. Dreyfus, F. P. 690406; abst. C. A. 1931, **25**, 1103; Chem. Zentr. 1931, I, 712.
5. E. P. 346511; abst. C. A. 1932, **26**, 2067; J. S. C. I. 1931, **50**, 801-B; Textile Mfr. 1931, **57**, #680, 306; Silk J. 1931, **8**, #88, 54. C. Dreyfus, Can. P. 292670.
6. British Celanese, Ltd., E. P. 296450; abst. Silk J. 1928, **5**, #55, 78. C. Dreyfus and W. Blume, Can. P. 292858.

A rubber tubing has been described[1] with an external reinforcing of fabric which is then coated with a cellulose derivative composition or with a phenolic condensation product to increase its water-resistivity. To protect rubber surfaces[2], they may be first covered with an albuminoid layer which can be tanned if necessary, upon which is placed the cellulose derivative solution, the hose being intended primarily for carrying coal gas and such purposes where a minimum of porosity is necessary. In the P. le Play method of increasing the durability of lacquers[3], rubber or rubber latex is incorporated in solutions of organic cellulose derivatives by means of a mutual solvent, while in the A. Huegel process[4], lacquers are produced from these two classes of compounds by the use of methyl oleate or butyl cinnamate as the solvent for both. A. Hutin[5] has discussed the subject of mixed lacquers of rubber and cellulose derivatives, and pointed out the paucity of solvents which are good dissolvants for both.

As a paint suitable for use on sheet materials containing rubber[6], it is advocated to first dissolve a resin as wax-free shellac or dammar in a low-viscosity cellulose acetate or cellulose ether solution with a high-boiling solvent as ethyl lactate or benzoate, then mix with a colloidal pigment in castor oil or a liquid plasticizer as tricresyl phosphate and a thinner as toluene or xylene.

With the cellulose ethers, in contradistinction to the cellulose esters as acetylcellulose, by virtue of the ready solubility of the former in some aliphatic hydrocarbons (petroleum ether, ligroin, benzine) and in most liquid carbocyclic hydrocarbons (benzene, toluene, xylene) and cer-

1. A. Gregg, E. P. 300357; abst. C. A. 1929, **23**, 4103.
2. Ketschendorfer Kunstlederfabrik, A.-G., D. R. P. 390094; abst. J. S. C. I. 1924, **43**, 528-B.
3. F. P. 595208; abst. J. S. C. I. 1926, **45**, 401-B; Chem. Zentr. 1926, I, 1744.
4. D. R. P. 483002; abst. C. A. 1932, **26**, 1078.
5. Rev. Gen. mat. Plastiques, 1926, **2**, 208; abst. C. A. 1926, **20**, 3089.
6. P. Schidrowitz and D. Burke, E. P. 304334; abst. C. A. 1929, **23**, 4925.

tain nitrogen products of the same (pyridine, quinoline, piperidine), all of which are ready solvents of rubber, and also due to the fact that the cellulose ethers are dissolvable in carbon bisulfide which readily dissolves both vulcanized and unvulcanized rubber, it is much easier to combine the cellulose ethers with rubber by virtue of the much greater range of applicable solvents.

The waterproofing process applicable to cellulose ether fabrics as disclosed by British Celanese, Ltd., and especially to open-mesh fabrics[1], comprises the application of a rubberizing solution to the under face of the fabric in such a manner that it does not penetrate through to the face. The rubber paste of the I. G. Farbenindustrie[2] combines methylcellulose with natural rubber latex, as indicated in the two following examples:

1. 100 gms. natural rubber latex which are preserved by the addition of a small amount of ammonia, and containing 20% rubber, are stirred with 2 gms. of a water-soluble methylcellulose at 15° until a smooth solution is formed. The solution is then heated to 55° whereupon methylcellulose separates together with the rubber. The stiff paste is then contrifuged on a heated centrifuge in a bag, a short extraction concentrating the mass to a 50% rubber content or more. On diluting this paste with cold water a rubber milk is again obtained.

2. 50 gms. artificial latex obtained by the polymerization of isoprene with an aqueous solution of Turkey-red oil and sodium phosphate, are mixed at 15° with 15 gms. of a 10% aqueous solution of trimethylcellulose. The mixture is then left to stand for several hours at the ordinary temperature, when two layers are formed, the upper, aqueous layer containing in solution the majority of the emulsifying agent, which rubber-free liquid may be drawn off.

1. E. P. 347422; abst. J. S. C. I. 1931, **50**, 801-B; Chem. Zentr. 1931, II, 1365.
2. E. P. 305490; abst. C. A. 1929, **23**, 4848; J. S. C. I. 1930, **49**, 730-B; Chem. Zentr. 1929, I, 2929. F. P. 668907; abst. C. A. 1930, **24**, 1764.

The latex is then heated to 40-60° and the precipitate freed from water as in Ex. 1.

The coating composition of the Canadian Industries, Ltd.[1], comprises mixing with 100 parts disaggregated rubber, from 1-100 parts ethylcellulose, together with perilla oil, a softener and cobalt linoleate in amount from 0.001-10% of the weight of the oil. The W. Hengstmann[2] plastic material is composed of a mixture of a cellulose ether, natural or artificial resin and an ester of a dibasic acid of the aliphatic series. Ethylcellulose or benzylcellulose with methyl or ethyl adipate is preferred. As a specific example, ethylcellulose is dissolved in a mixture of benzene, ethyl acetate, ethyl adipate and acetone, to which a benzene solution of resin and a small amount of adipic acid may be added. The mixture is pressed into blocks or plates under high pressure at about 60° and allowed to dry. Sulfur or compounds liberating sulfur may then be added to the mixture, which is vulcanized during molding by heating to 160°.

By the utilization of a mixture of saturated and unsaturated hydrocarbons obtained by polymerization of olefines or gases containing olefines at high temperatures[3], solvents are obtained which dissolve both the cellulose ethers, caoutchouc and many of the resins, the products being excellent for paints, lacquers and enamels. For example, 5 parts ethylcellulose are dissolved in 95 parts of high-boiling polymerization fraction (b. pt. 120-220°) and to this is added rubber dissolved in a polymerization fraction of the same nature, but boiling at 78-150°. The two are then mixed in equal or other proportions. Or, 5 parts ethylcellulose and 1 part caoutchouc are dissolved in a fraction of b. pt. 120-220°, this solution constituting a lacquer of unusually high elasticity, tenacity and adhesion. Asphalt may be dissolved also in the enamel if a colored paint is

1. Can. P. 306541.
2. F. P. 691728; abst. C. A. 1931, **25**, 1345. D. R. P. 499676; abst. C. A. 1931, **25**, 568.
3. I. G. Farbenindustrie, F. P. 681677; abst. C. A. 1930, **24**, 4343. F. P. 626117 and Addn. 35190.

desired. In another patent[1], a suitable lacquer is said to result when 4 parts ethylcellulose and 1 part caoutchouc are dissolved in 95 parts of a fraction boiling between 70-110° and obtained by compression from the gas obtained in the cracking of lignite.

A linoleum cement has been described containing synthetic rubber from dimethylbutadiene in conjunction with linoxyn and cellulose derivatives[2]. The plastic mass of the I. G. Farbenindustrie[3] comprises a cellulose ether with natural rubber or rubber obtained by the polymerization of erythrene, isoprene or dimethylbutadiene with harmonious solvents. The H. Morris ink suitable for intaglio printing contains rubber, gutta percha or balata and a cellulose ether or ester, mixed with soluble dyes and pigments, and thinners as butyl alcohol, toluene, methylethylene glycol and tetrahydronaphthalene[4].

Cellulose Ether Transfers.[5] By virtue of their high plasticity and ability to amalgamate with various resins, both natural and synthetic, the cellulose ethers offer many opportunities formerly difficult if not impossible of attainment, and this superiority of the cellulose ethers over all other derivatives of cellulose is peculiarly exemplified in the preparation of transfers and other compositions where a slow rate of fusibility coupled with a high degree of thermoplasticity are necessary requisites. While the cellulose ethers are not fusible without decomposition, strictly speaking, they enter into permanent combination with other materials such as resins and waxes under the application of heat, it being merely necessary to agitate the etherized cellulose in a melted wax or resin solution to produce a

1. I. G. Farbenind., A.-G., F. P. 682540; abst. Kunst. 1931, **21**, 45. Cf. F. P. 643413 and Addn. dated 7th Jan. 1929; 2nd Addn. dated Mar. 12th, 1929. F. P. 645335 and Addn. dated Feb. 23, 1929.
2. *Ibid.* E. P. 348077; abst. Brit. Plastics, 1931, **3**, #30, 270.
3. Swiss P. 142751. Ital. P. 270550, 271648, 271899. Norw. P. 47842.
4. E. P. 320410; abst. C. A. 1930, **24**, 2622.
5. For information contained in this topic, the Author is indebted to Dr. Winthrop S. Lawrence.

homogeneous and transparent mixture, imparting to the combination, the desirable properties of the cellulose ether.

The high viscosity, water-insoluble ethylcellulose and benzylcellulose may be brought into combination with such products as ethyl abietate, methyl abietate and cumar to form a very plastic and slowly fusible composition, of permanent value in producing heat transfers that will not sink into the fabric to which the mark is applied. In this respect, the results obtained resemble in appearance that produced by a decalcomania. Being readily dissolvable in solvents of high hydrocarbon content, solutions of ethylcellulose and other cellulose ethers may be used in the preparation of sizes where the comparatively low cost of solvents offsets to a degree, the comparatively higher cost of the cellulose ether.

In the use of these ethers in resinous and waxy combinations, the resin or wax is first melted with heat until thoroughly liquid, and the ether then stirred in. The temperature is raised with stirring until the ether is entirely dissolved, additions of oils and other products being preferably made to the resin or wax before incorporation of the cellulose ether therein. Compositions containing properly plasticized ethylcellulose readily form flexible films characterized by great toughness and flexibility. In these respects it resembles to a high degree the organic cellulose esters, and differs from the nitrocelluloses in an almost entire absence of flammability. It is markedly superior to cellulose acetate in its much wider compatibility with fusible materials, and in its greater solubility in inexpensive solvents and solvent combinations. Films of highly ethylated ethylcellulose are so pliable that it is possible to distribute such a derivative properly plasticized and in solution, onto the surface of an impervious paper and later completely strip it without breaking the film. It is probably safe to say that there is no other material now known that so readily lends itself to the making of plastic combinations of this nature, which have a slow rate of fusi-

bility over a range of temperature as does ethyl- or benzylcellulose. It may be combined with resin to impart toughness and flexibility usually with a liquid plasticizer, or may be combined with waxes to produce soft, flexible compositions that begin to liquefy at relatively low temperatures, and yet on continued heating never really become limpid. Such combinations with wax have a soft feel and do not stiffen paper or fabrics when applied thereon.

In printing compositions ethylcellulose finds many applications, especially in the intaglio process, where the slow fusibility imparted to the composition, coupled with the fact that it does not sink into the fabric or other material to which it is applied, are the main desirable features.

W. Lawrence[1] has described a method of decorating leather in one or more colors by a direct lithographic process so as to produce a maximum number of color combinations at a minimum expense, which comprises connecting the leather to a mount by means of an adhesive embodying a drying oil, then causing the adhesive to solidify or set without permitting it to enter the pores of the leather to an extent sufficient to substantially stiffen the leather, the exposed surface of the leather being then printed upon before detachment from the mount.

In the preparation of transfers[2], especially multicolor transfers, the "primary element" of the transfer is preferably made from ethylcellulose or benzylcellulose which begin to soften at about 150°. In order to produce a slow-melting composition with the use of cellulose ethers they are plasticized by means of highboilers as tricresyl phosphate. In order to obtain an impression of relatively low penetrating power, it is recommended to incorporate 100 parts ethylcellulose with 90 parts paracoumarone resin, 45 parts diethyleneglycol monoethyl ether, 75 parts ethyl abietate and 35 parts No. 6 lithographic varnish. A quick-

1. U. S. P. 1703675, 1718966.
2. Kaumagraph Co., E. P. 333768; abst. C. A. 1931, **25**, 605.

fusing composition for the background may comprise 100 parts rosin, 25 parts beeswax and 30 parts ultramarine blue.

In order to make a two-color transfer, an ordinary paper base is first printed with the "primary element" or design by means of the ordinary intaglio method, as by the use of the ordinary intaglio roller. The background is then printed with the cellulose ether fusible composition by means of the same intaglio printing method, and may be limited solely to the design, or may be of greater extent. In order to apply the transfer to a piece of fabric, the ink side of the transfer base is applied to the fabric, and the other side of the transfer base has a hot iron applied thereto. The soft, waxy background first melts and thoroughly permeates the fabric. The less fusible element then melts but does not penetrate the fabric, because the latter has already become saturated with the background composition. Hence the background is printed last and is transferred first. The printed matter or design has a light color and the background is dark, thus acting as a mask to hide the weave of the fabric. The use of a dark background is particularly desirable when the fabric has a complicated weave or pattern.

In a supplementary process[1] a representative formula for the production of a gold transfer which will duplicate the effect of a decalcomania is given as 15 parts ethylcellulose, 10 parts ethyl abietate, 10 parts cumar (m. pt. 120°), 10 parts blown castor oil, 15 parts gold bronze, and 15 parts diethyleneglycol monoethyl ether. Diethyleneglycol monobutyl ether is also applicable. After ageing on paper for a day or two, this composition gives a solid transfer for hosiery and similar products, the transfer being full and sharp. A superior result is secured over ordinary resinous compositions, which are relatively harsh and rigid. On account of its fineness and softness, ethylcellulose is

1. W. Lawrence and Kaumagraph Co., E. P. 338611; abst. C. A. 1931, **25**, 2532.

said to be preferable to benzylcellulose in the above composition.

The usual designs transferred by means of cellulose ether compositions are flexible and adherent and give a superior solid and brilliant appearance. When ethylcellulose and benzylcellulose are suspended in a liquid as that above given, the mixtures may be heated up to 300° without observable decomposition. The cellulose ethers suspended in the liquid begin to soften at 100° and become thick viscous liquids at 300°, in fact, it is so viscous that it more resembles a plastic substance than it does a liquid.

The I. G. Farbenindustrie[1] produce transfer pictures for the application of decorative designs, trade marks and monograms in the varnishing arts by the use of cellulose ethers, as indicated by the following specific example:

Paper pretreated in the usual manner for the manufacture of transfers is first printed with a lacquer containing a cellulose ether prepared by dissolving 160 parts ethylcellulose in a mixture of 25 parts tricresyl phosphate, 30 parts castor oil, 20 parts glycol abietate (colophony esterified with glycol), 400 parts xylene, 200 parts butanol and 150 parts ethyleneglycol monoethyl ether (ethyl glycol). Upon this layer the desired picture is applied by intaglio printing with a lacquer consisting for example, of nitrocellulose 150, tricresyl phosphate 70, Milori blue 65, glyceryl abietate 35, xylene and butanol each 150, and 350 parts ethylglycol acetate. The layer containing the picture is then covered by means of a lacquering machine with a clear lacquer consisting of nitrocellulose 200 in ethyl alcohol, dibutyl phthalate 100, colophony 50, ethyl alcohol and ethylglycol each 200, and 250 parts ethylglycol acetate. The finished transfer is then applied to the article to be ornamented by moistening it with ethyl alcohol and pressing it onto the surface of the article.

1. E. P. 317871; abst. C. A. 1930, **24**, 2258; J. S. C. I. 1929, **48**, 863-B.

In the J. Guerard process of engraving[1], suitable indiscriminately for the production of all sorts of plates as lithographic and intaglio plates and for typographical plates in relief, use is made of a varnish composed of gum resins in alcohol-ether and a solution of a cellulose ether in acetone. Such a varnish forms on the support receiving it, a dry, white, opaque, dull layer or stratum, forming a surface resembling that of bristol board, and hence particularly suitable for drafting, the layer being non-fragile and resistant to friction. It can, however, be worked with a point as easily as softer coatings while being superior in that it may be completely removed on contact with the tool without any particular skill.

The use of cellulose acetate is the cellulose derivative described in the patented method of R. Müller and W. Stelkens[2], E. Seyfferth[3], and the transfer ink type of protective composition of W. Lawrence[4]. The decalcomania paper of R. Tull[5] with a design thereon, is provided with a coating including nitrocellulose, an ester gum, dibutyl phthalate, ethyl oxybutyrate and pigments, a second coating being provided containing oil paint ground in varnish.

Stains of copying inks or pencils, or from typewriter ribbons[6], are removed by the use of a composition of pasty consistency, containing a cellulose ether swollen by water, such as methyl- or ethyl-cellulose or cellulose glycollate or glycolcellulose. Soap and glycerol may be added.

Artificial Wire Glass. Glass Substitutes. In the production of window glass substitutes according to the process of Kalle & Co.[7], call attention to the fact that wire

1. U. S. P. 1850929.
2. F. P. 701353; abst. C. A. 1931, **25**, 4097.
3. U. S. P. 1499844; abst. C. A. 1924, **18**, 2810. E. P. 196008, 196324. Can. P. 227269.
4. U. S. P. 1596545; abst. C. A. 1926, **20**, 3349; Plastics, 1927, **3**, #5, 218.
5. U. S. P. 1826228; abst. C. A. 1932, **26**, 569.
6. I. G. Farbenindustrie, A.-G., E. P. 340232; abst. C. A. 1931, **25**, 4097.
7. Kalle & Co., A.-G., and A. Dulitz, D. R. P. 515531; abst. C. A. 1931, **25**, 2581. Kalle & Co., A.-G., E. P. 371222, Addn. to E. P. 367288; abst. J. S. C. I. 1932, **51**, 600-B.

fabrics which have been coated with solutions of cellulose derivatives possess good permeability to light when of sufficiently large width of mesh, yet have the drawback of being weather-proof to but a limited extent due to the action of the elements upon the wire. They propose to obviate this inherent defect by using as a base for such wire fabrics, a zinc coated wire or aluminum wire, or a fabric, the warps of which consist of wire, and the wefts of textile threads. The result is that the warp wires are not bent on weaving, remain evenly imbedded in the mass forming the film when the fabrics shrink later on, and are thus protected from external damage. When preparing window glass substitute according to the invention, care must be taken that the textile threads used as wefts are freed from air before weaving, as by heating in a lacquer solvent, after which the fibers are impregnated with a cellulose ether or ester lacquer. In a specifice example given, 15 parts ethylcellulose are dissolved in a mixture of acetone 47, alcohol and benzene 5 each, benzyl alcohol 3, and ethyl lactate 25. Or, 10 parts ethylcellulose may be dissolved in a mixture of benzene 60, alcohol 10 and ethylglycol 20, the coated wire and textile being preferably dried while still under tension in order to guard against unequal shrinkage.

The transparent material of the Celluloid Corp.[1] comprises sheets made from polymerized vinyl compounds as vinyl acetate, reinforced with an open mesh or reticulated material and containing plasticizers. Or[2], the composite sheet material may be formed by embedding a flexible open work in a filled composition having ethylcellulose as a basis. The sheets so formed are said to be adopted for wall coverings, being sheets which are highly flexible and shock-resistant.

In the E. Haver[3] composition for coating wire gauze or netting, the latter is filled with a solution of cellulose

1. E. P. 366077; abst. J. S. C. I. 1932, **51**, 357-B.
2. M. Ximenez, E. P. 310541; abst. C. A. 1930, **24**, 723.
3. U. S. P. 1842093. E. P. 335775; abst. C. A. 1931, **25**, 1692. Can. P. 319788.

derivative as cellulose acetate, and containing in addition 1-2% of rubber, paraffin or paraffin oil admixed therewith. As solvents triphenyl phosphate and methylglycol acetate are advocated. The glass substitute of J. and A. Colle[1] is intended primarily for greenhouses and comprises a reinforced film in rolls obtained by impregnating with a cellulose derivative lacquer, a metallic reticular glass base so designed that the relation of the width of the meshes and size of the wire comprising the strands is such that a maximum of transparency and tensile strength is obtained in the finished product after coating.

Reinforced transparent sheets are obtained by working according to the I. G. Farbenindustrie process[2] which consists in coating with a polymerization product of a butadiene or its homologues to an open-mesh fabric of tinned iron wire or vegetable fiber, and hardening the coating. The hardening process is carried out at 70-300°, no heating being required where oxygen is present. The repair of broken sheets prepared as above may be effected by painting over with concentrated solutions of the polymerization products, or by pieces of film pasted thereon. The mesh of the fabric is preferably 40 mm. or less.

Cold frames, roofing of manure beds or of greenhouses may be made by combining netting or open-mesh fabrics with a sheet of cellulose ethers[3], the sheet being first coated, then pressed with the simultaneous application of heat, to form a compact and smooth surface. The glass substitute of the British Celanese, Ltd.[4], and of which they produced many miles in length during the war period 1914-1918, consists of an iron or steel wire screen or netting coated wholly or partially with a cellulose acetate lacquer, to which may be added a polymerized vinyl compound resin. When

1. U. S. P. 1580287; abst. Plastics, 1927, **3**, #2, 80.
2. E. P. 336075.
3. I. G. Farbenindustrie, A.-G., E. P. 306242; abst. C. A. 1929, **23**, 5019; J. S. C. I. 1929, **48**, 298-B; Chem. Zentr. 1929, II, 512.
4. E. P. 308587; abst. C. A. 1930, **24**, 239; J. S. C. I. 1930, **49**, 99-B; Brit. Plastics, 1930, **1**, #10, 446. C. Dreyfus, Can. P. 295668, 307035. See E. P. 307462.

such wire is used as a fence to shield a road from the enemy and camouflaged by painting, it forms an excellent screen of practical visual impenetrability.

In the coating of wire, which may or may not afterwards be used for the manufacture of screens, W. Dickie[1] recommends in order to insure uniform coating, that the wire carrying the liquid coating material pass up axially and centrally, the surplus removing orifice of the rotary tubular doctor surrounding and being coaxial with the wire traveling through it. In another method[2], the filament under tension, and straightened, is conducted through the coating substance and thence led through a tube the internal diameter of which exceeds the gauge of the filament. The length and bore of the tube is selected according to the thickness of the coating applied and the nature and viscosity of the coating composition. The W. Moss method of coating foraminous material comprises applying to the reticulated material a cellulose ether coating as a solution of methyl-, ethyl- or benzyl-cellulose in association with a diphenylolpropane-formaldehyde synthetic resin, acetone being a solvent harmonious to both[3]. Baykogarn A. G.[4] and A. Zimmerli[5] have illustrated types of apparatus for the coating of wire with cellulose derivatives.

The "sunculator" is a "Cel-O-Glass" carriage hood[6] of cellulose ether or cellulose ester film, forming the back and sides of a baby carriage, so the baby can "get the beneficial ultra-violet light while protected from the burning infra-red rays." T. Wilder and C. Vack[7] have contributed a paper on the antirachitic effect of winter sunshine through acetylcellulose reinforced sheets (Celoglass), and H. Schmidt[8] has discussed the difficulties encountered in using wire net-

1. U. S. P. 1485254.
2. J. Lahousse, U. S. P. 1498738. 3. U. S. P. 1860687.
4. D. R. P. 535241; abst. C. A. 1932, **26**, 884.
5. U. S. P. 1677576; abst. C. A. 1928, **22**, 3300. Can. P. 264990; abst. C. A. 1927, **21**, 1011.
6. S. Atkins, Plastics, 1932, **8**, 237.
7. Am. J. Diseases Children, 1930, **39**, 930; abst. C. A. 1930, **24**, 4328.
8. Kunststoffe, 1931, **21**, 217; abst. C. A. 1932, **26**, 818.

ting as a support for cellulose acetate films. Artificial wire glass production methods have been outlined by F. Ohl[1].

Cellulose Ethers in Plastics. The nitrocelluloses have no definite melting point, inflaming at temperatures before sintering, whereas the cellulose ethers have well-defined softening and melting points without decomposition. This point is of great advantage in the preparation of thermoplastic compounds of ready moldability, and coupled with the fact that the cellulose ethers, in contradistinction to all other known cellulose derivatives are soluble in fats, waxes, high molecular solid aliphatic acids and their glycerides, places the etherified celluloses in a unique position in the plastic art for the reason that in many instances they may be plasticized without the use of any volatile solvent or solvent composition. The best known example of a cellulose derivative plastic—nitrocellulose-camphor in the finished article celluloid—requires considerable amounts of methyl and ethyl alcohols in their formulation, which necessitates the installation of systems of solvent recovery, and considerably augments the cost of production from this necessity. Furthermore, in comparison with the cellulose acetates wherein the range of softening point is within narrow limits, the methyl-, ethyl- and benzyl-celluloses as a class, and as individual groups depending upon the degree of etherification or hydrogen hydroxyl displacement in the cellulose, offer a wide range of sintering, softening and melting temperatures, thus admitting of a selection of materials depending upon the properties desired in the finished product.

In addition to these valuable properties of the cellulose ethers *per se* for incorporation in plastics, are the two entirely new classes of compounds which result therefrom, that is, the cellulose ether-esters, wherein an incompletely etherified cellulose is further treated with an esterifying agent, an example being the formation of ethylcellulose acetate. Furthermore there arises a whole series of mixed

1. Kunstoffe, 1932, **22**, 28; abst. C. A. 1932, **26**, 2291.

cellulose ethers as ethylbenzylcellulose, partaking of the properties of the individual alkyl and aralkyl substituents, having their special characteristics as to melting points, solubility and degree of miscibility with various solvents, diluents, extensifiers, softeners, plasticizing bodies and fatty, oily and waxy products, which greatly extends the range of possible usefulness of the etherified celluloses as a group. So that, in taking a retrospective view of the cellulose ethers, ether-esters and mixed esters, we have at our disposal a large and continual growing number of desirable bodies with a large variety of thermoplastic possibilities. And to still further add to the apparent commercial attractiveness of this group in its entirety, is the fact that nearly all of them are freely soluble in such inexpensive liquids as the petroleum hydrocarbons, either alone or in association with methyl alcohol or benzene-denatured ethyl alcohol.

This work is not concerned with the nitrocellulose thermoplastic combinations only in those instances wherein the plastifying bodies proposed appear to be especially applicable with the cellulose ethers. The fact of the much wider range of solubility, tolerance and compatibility of the cellulose ethers for liquids and solids having a softening, plastic or solvent-plastic influence as compared with the cellulose nitrates and cellulose acetates, has caused and is causing a most meticulous search through these older arts for plastifiants which have been temporarily discarded as unsuitable bodies for this purpose in the nitro- and acetyl-cellulose arts, as possible valuable adjuncts in etherified cellulose thermoplastics, and in this connection only, will they be briefly touched upon.

Furthermore, inasmuch as it has repeatedly been demonstrated that certain liquids and solids which have been found useful in cellulose organic ester (cellulose acetate) moldable products are also useful when incorporated with the cellulose ethers, this topic will be reviewed under the two headings of "Acetylcellulose Plastic Combinations,"

and those extensifying and flexilizing direct and ancillary bodies which have been advocated and patented as direct cellulose ether plastifying bodies, either alone or in conjunction with other products.

1. *Cellulose Acetate Plastics.* The carbohydrate carboxylates in a plastifiable condition first sprung into prominence in a search for the production of moving picture films of diminished inflammability hazard, and as the result of several unfortunate conflagrations in moving-picture theatres directly traceable to film ignition in the projecting apparatus.

A process for the production of colored plastics has been described by the Badische Anilin & Soda Fabrik[1] in which the cellulose ester is milled with a swelling or softening agent, as camphor, and with an inorganic or organic coloring matter which is insoluble in the other components of the mixture. Milling is continued until, when a sample is dissolved in a liquid which is a solvent for the cellulose ester but not for the color, substantially no separation of the color takes place, after keeping for several days. The mass then contains the dyestuff in a colloidally dispersed condition, and is more or less transparent in a thin layer. By dissolving such plastics in solvents, solutions are obtained which are suitable for colored coatings on wood, glass, metals or fabrics. In one example, colloidal silver is formed in the plastic itself. Glyceryl acetate (acetin) or glyceryl butyrate without the addition of volatile solvents[2], is said to efficiently and permanently plasticize acetylcellulose.

A printing surface has been described, in which cellulose acetate is used for forming matrices for making stereotype plates, which are made of material softening at

1. U. S. P. 1589700; abst. C. A. 1926, **20**, 3084. E. P. 247288; abst. C. A. 1927, **21**, 649; J. S. C. I. 1926, **45**, 315-B. F. P. 493893; abst. Chim. et Ind. 1920, **3**, 353. Can. P. 250537. Swiss P. 113741; abst. Nitrocellulose, 1931, **2**, #4, 87. India P. 11022. See F. P. 588903.

2. Actualite Illustree Soc. Anon., E. P. 234140; abst. C. A. 1926, **20**, 804; Chem. Zentr. 1925, II, 2190.

a lower temperature than the matrix. A typographic plate is pressed onto a softened heated mass of plastic organic composition material as acetylcellulose, to form a matrix from which stereotype plates of a similar composition are prepared. A metallic trellis or other skeleton may be imbedded in the stereotype plate during manufacture.

The molding mixture of A. Weith and O. Holzmann[1] combines fibrous cellulose acetate ground in a ball mill to an impalpable powder (at least 100 mesh fineness) with a similarly ground potentially-active phenol resin, and the two materials mixed in substantially equal proportions to a thoroughly commingled mass by further grinding. This mixture, without the interposition of solvents, is then hot-pressed or otherwise treated in the usual manner. Urea-aldehyde type of synthetic resin may also be used[2], in which case a plasticizer as ethyl lactate, amyl tartrate or butyl citrate is added. W. Beatty advocates the use of dioxydiphenyldimethylmethane as addition to cellulose acetate for plasticization[3]. Cellulose formate, acetate, butyrate, benzoate or stearate with camphor and phenol- formaldehyde have also been recommended[4].

Acetylcellulose with a relatively small amount of powdered glass, bone meal, magnesite and glue constitutes the molding material of H. Buchholz[5], while C. Cachon[6] prepares a plastic material suitable for the manufacture of fancy goods by uniting one or several thicknesses of cloth, preferably artificial silk, between two sheets of plasticized acetylcellulose by means of a solvent of low dissolving power which will soften the sheets sufficiently so they may be

1. U. S. P. 1720192; abst. Plastics, 1930, **6**, #2, 89.
2. Bakelite Corp., E. P. 327969; abst. J. S. C. I. 1930, **49**, 677-B; Chem. Zentr. 1930, II, 1454. F. P. 670841; abst. C. A. 1930, **24**, 1946. See L. Redman, U. S. P. 1732533. E. P. 281993, 301133.
3. U. S. P. 1158960; abst. J. S. C. I. 1915, **34**, 1205. F. P. 447645; abst. J. S. C. I. 1913, **32**, 283.
4. W. Bonner, U. S. P. 1173337; abst. C. A. 1916, **10**, 1084; Chem. Ind. 1916, 465.
5. U. S. P. 1568955; abst. C. A. 1926, **20**, 822.
6. F. P. 633626; abst. C. A. 1928, **22**, 3499; Chem. Zentr. 1928, II, 407.

united by presspre. Decorative "characters," e.g., of cellulose acetate, are applied to thermoplastic articles of the same material[1], the characters having lower plasticity (according to the proportion of plasticizer used) than the articles, and then welding in place under heat and pressure. Liability of exudation of plastifier may be obviated by incorporating also a small proportion of synthetic resin[2], which appears to act as a permanent absorbent. To prepare a cellulose acetate plastic which at the same time is of diminished inflammability, the formula acetylcellulose 10, triphenyl phosphate 1-2 and ethyl phthalate 1-1.5 forms the basis of a Canadian patent[3].

The F. Clouth plastic embodies the use of anthracene oil with cellulose acetate[4], preferably with the admixture of a substance which mixes harmoniously with the anthracene oil such as triphenyl phosphate, sulfanilid, triacetin or ethyl lactate, the latter two where softness is required. Anthracene oil augments the elasticity and imparts increased waterproof properties. Creosote oil may also be added, where the odor is not objectionable. H. Dreyfus prepares plastic material having a basis of cellulose acetate, the softening components are kneaded with the cellulose ester at elevated temperatures (90-150°) in combination with mono-, di- or tri-methyl (or ethyl) urea, which also acts as a stabilizer by virtue of its ant-acid properties, should the acetylcellulose decompose with the liberation of traces of acetic acid[5]. The C. Dreyfus and G. Schneider molding powder is prepared by introducing 100 parts finely powdered cellulose acetate and about an equal weight of water into a jacketed mixing machine[6], and thoroughly mixed for about a half hour and until an indistinguishable magma

1. Celluloid Corp., E. P. 357457; abst. J. S. C. I. 1931, **50**, 1107-B.
2. J. Walsh and A. Caprio, Can. P. 324327.
3. J. Walsh and K. Flynn, Can. P. 314577.
4. E. P. 319723; abst. J. S. C. I. 1920, **39**, 568-A.
5. U. S. P. 1528291; abst. J. S. C. I. 1925, **44**, 312-B; C. A. 1925, **19**, 1497. C. Dreyfus, Can. P. 297377. See E. P. 179208.
6. U. S. P. 1732330; abst. C. A. 1930, **24**, 239; J. S. C. I. 1930, **49**, 138-B.

results. Then there is added to this damp mixture 30 parts triacetin in solution in 100 parts benzene and the whole mixed 2 hrs., after which heat is gently applied until practically all of the benzene and nearly all of the water has been driven off. The product is then dried and finely pulverized.

In the preparation of composite articles[1], a fabric made of or containing cellulose acetate or cellulose ether is caused to adhere to a suitable core as papier mache, clay and shellac, by application of heat and pressure, ornamental effects on small buttons being obtained. A cellulose acetate of high viscosity, preferably above 600°, forms the basis of another thermoplastic process[2], which may be tinted blue by means of an anthraquinone derivative[3]. For thermoplastic and moldable compounds[4], combination of cellulose acetate with the condensation product of toluenesulfamide and benzyl alcohol has been advanced, a small amount of acetone and ethyl lactate being also incorporated where films are to be prepared therefrom[5].

The K. Monroe method of making compound cellulose acetate plastic is indicated in Fig. 13, the method also being suitable for cellulose ether[6], in which *1* is a face view of one of the plastic sheets, *2* an elevational view of the stacked sheets, *3* an elementary showing of the manner of cutting portions of the stack *2*, to provide units for making the block, *4* indicates the manner of making the cut portions *3*, zig-zag, *5* shows the zig-zaged cut portions *4*, in the press, *6* is a side elevation of the block made in the press, *7* an edge view of a sheet from the block, and *8* a face view of the finished sheet, simulating mother-of-pearl and other variegated shell structures, giving an edge grain ef-

1. British Celanese, Ltd., E. P. 365143; abst. J. S. C. I. 1932, **51**, 357-B.
2. C. Dreyfus, F. P. 673029; abst. C. A. 1930, **24**, 2292. Can. P. 299650.
3. C. Dreyfus, W. Moss and A. Kline, Can. P. 309983.
4. W. Moss and B. White, Can. P. 319729; abst. C. A. 1932, **26**, 2609.
5. G. Schneider, Can. P. 310251.
6. U. S. P. 1657172; abst. C. A. 1928, **22**, 1041.

fect in the composite article. In the same manner, imitation ivory may be produced, the individual sheets having alter-

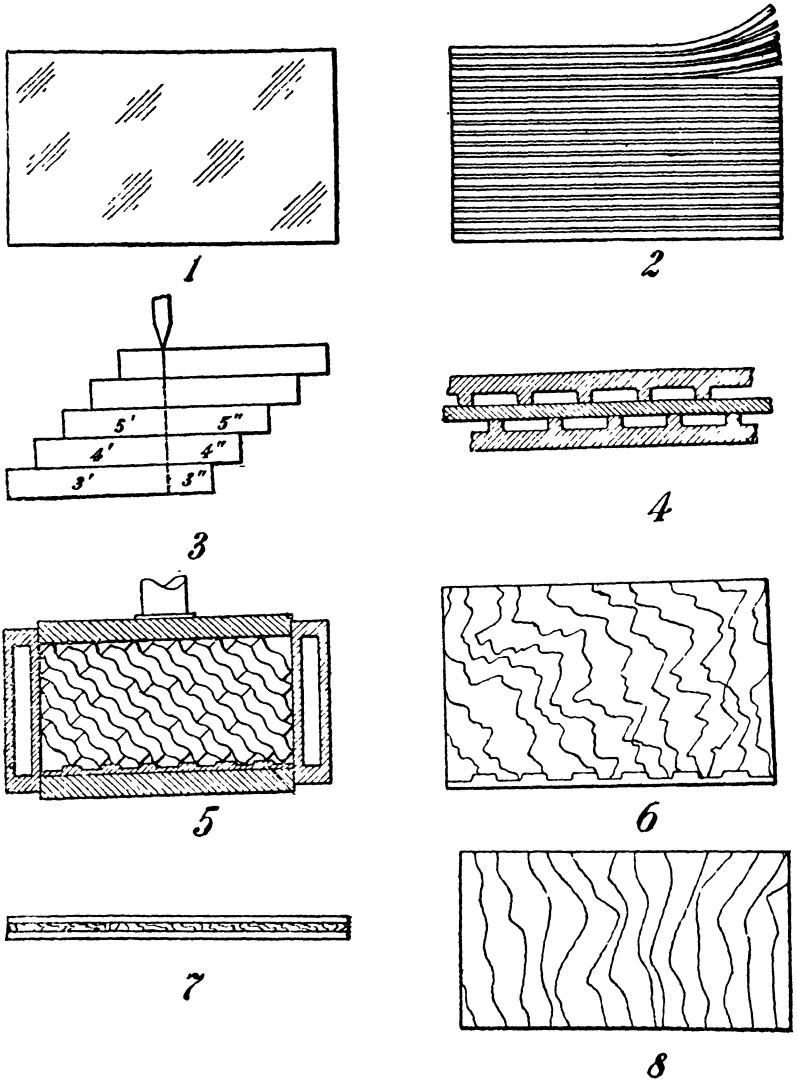


Fig. 13. Monroe Method of Plastic Formation.

nately a larger proportion of zinc oxide pigment incorporated therein to simulate the "grain" of the ivory.

The formula of M. Theumann[1] for the production of celluloid-like masses involves adding to 75 parts acetylcellulose, 33 parts acetone, 52 parts benzene, 14 parts methyl or ethyl alcohol, using a cellulose acetate soluble in acetone but insoluble in ethyl acetate. Cellulose acetate incorporated with condensation products of chloral and amides constitutes the plastic composition of H. Clarke[2], the chloral or chloral hydrate being combined with ureas, formamide, acetamide, or alkylurethanes as methyl, ethyl, propyl or butyl carbamates. Thus, 10 parts acetylcellulose are incorporated with one part of compound containing 2 mols. chloral and 1 mol. urea dissolved in 40 parts acetone, or 40 parts cellulose acetate with 3 parts chloral hydrate and 3 parts *N*-butyl carbamate dissolved in 160 parts acetone.

The plastic composition of A. Eichengruen[3], said to be especially suitable for plastics and moldable bodies where high resistance and unusual tensile strength is required, consists of affiliating 10 gms. acetylcellulose with 3 gms. each acetylmethylanilid (ethylacetanilid) and ethyl lactate, and 10 cc. each alcohol and benzene, the whole heated to 70°. After solution, 20 gms. zinc oxide are admixed and the whole poured on a slab to cool, and used in this condition. Or[4], the acetylcellulose in a very fine state of subdivision is admixed with small amounts of volatile solvents and submitted to high pressure at a temperature approaching the decomposition point and allowed to cool. If the operation is carried out at a lower temperature and pressure, 2.5% of water or alcohol may be added in conjunction with such solid substances as naphthalene or camphor, and then extruded into the shape and size required.

1. U. S. P. 1818108; abst. C. A. 1931, **25**, 5558.
2. U. S. P. 1809234; abst. C. A. 1931, **25**, 4403.
3. U. S. P. 1185074; abst. C. A. 1916, **10**, 2044; Chem. Ztg. 1916, **40**, 794; J. S. C. I. 1916, **35**, 734; Kunst. 1916, **6**, 315. F. P. 418744; abst. J. S. C. I. 1911, **30**, 79; Mon. Sci. 1913, **79**, 551. D. R. P. 287745; abst. C. A. 1916, **10**, 2145; Kunst. 1915, **5**, 274; Chem. Zentr. 1915, **86**, II, 864; Chem. Ztg. Rep. 1915, **39**, 422.
4. Cellon-Werke and A. Eichengrün, E. P. 147904; abst. Chem. Met. Eng. 1920, **23**, 1228; Caout. Gutta Percha. 1921, **18**, 10962.

It is claimed that the tendency to crack and craze of acetylcellulose plastics may be obviated by incorporating in the plastic mass 4-oxy-1-*ter*butylbenzene or a nucleated halogen derivative of the same, such as 3-brom-4-oxy-1-*ter*butylbenzene (m. pt. 50°) or 3.5-dibrom-4-oxy-1-*ter*butylbenzene (m. pt. 78°), the inflammability being also reduced by virtue of the presence of the halogen in the compound. A recommended formula is 100 parts acetone-soluble collulose acetate, 20-40 parts 4-oxy-1-*ter*butylbenzene and 1 part urea in 600 parts acetone. The mass is allowed to macerate at room temperature in a closed vessel until gelatinization takes place, and is then worked up in the usual manner[1].

R. Herrmann[2] prepares "ungelatinized cellulose acetate" plastic masses by first disintegrating the ester to a fine powder and then pressing under 100-150 atms. at a high temperature close to the decomposition point, whereby completely homogeneous masses of great mechanical stability are said to be obtained. The process is said to be carried out more easily and the strength of the pressed mass increased if inert fillers as asbestos, mica, barytes, sawdust or pigments as zinc oxide be added. K. Hickman and D. Hyndman[3] have given directions with 24 illustrations, for the construction of apparatus for preparing cellulose acetate sheeting.

Liquid ethylene oxide or propylene oxide is used as solvent for cellulose acetate, alone or in conjunction with acetone or ethyl alcohol, a primary or unhydrolyzed acetate being used which is insoluble in these two latter solvents. The alkylene oxide is removed from the composition before being worked up. Butylene oxide may also be used[4]. The product obtained by condensing succinic acid with glycerol,

1. W. Gump, U. S. P. 1740854; abst. C. A. 1930, **24**, 1217; J. S. C. I. 1930, **49**, 780-B; Brit. Plastics, 1930, **2**, #16, 183.
2. U. S. P. 1510779.
3. J. Frank. Inst. 1929, **207**, 231; abst. C. A. 1929, **23**, 2607.
4. I. G. Farbenindustrie, A.-G., E. P. 346827; abst. J. S. C. I. 1931, **50**, 643-B; Chem. Zentr. 1931, II, 3178. D. R. P. 527736; abst. C. A. 1931, **25**, 5288.

when dissolved in methyl acetate and combined with acetone-soluble acetylcellulose and methylglycol acetate forms a thermoplastic composition especially adapted for filling, knifing and priming compositions[1]. Much less plasticizer is required where fibrous cellulose acetate (cotton acetylated in the presence of a cellulose ester non-solvent as benzene or carbon tetrachloride) is submitted to the action of friction cylinder and afterwards ground to a macroscopically indistinguishable mass[2]. In 1929 R. Jones[3] published a detailed article on cellulose acetate plastics.

Condensates of Chinese wood oil, aniline or toluidine and zinc or aluminum chlorides[4] have been detailed as suitable adjuncts for incorporation with acetylcellulose for heavy enamels, or solid molding bodies. By varying the proportion of wood oil condensate a wide range of viscosities are possible. The G. Leysieffer method kneads the cellulose ester into a plastic mass first softened with water and then volatile solvents added[5], the product being rolled out while hot into thin sheets so the moisture and solvent will evaporate, acetin having previously been admixed with the ester. Afterwards the sheets are pulverized, and the powder molded under pressure at a temperature above its melting point. If soft and pliable masses are desired, di-, tri-, tetra- or penta-ethylene glycol or their corresponding benzoates may be added, diethyleneglycol dibenzoate being specifically recommended[6]. Glycol, glyceryl or benzyl salicylates form the plastifying component of A. Pouteaux[7], designed for malaxation with acetylcellulose. R. Simmonds[8] has described the utilization of the organic cellulose esters in the plastics industry.

1. I. G. Farbenind., A.-G., E. P. 322540. Can. P. 297081, 297082.
2. *Ibid.* F. P. 685162; abst. C. A. 1930, **24**, 6013.
3. British Plastics, 1929, **1**, #4, 141.
4. L. Lilienfeld, D. R. P. 246443.
5. D. R. P. 470579; abst. C. A. 1929, **23**, 1750. E. P. 156752.
6. O. Loehr, U. S. P. 1783176; abst. C. A. 1931, **25**, 414; Plastics, 1931, **7**, #3, 177.
7. F. P. 541643; abst. Chem. Zentr. 1923, II, 642.
8. Plastics, 1931, **7**, 502; abst. Nitrocellulose, 1931, **2**, #10, 1991.

The H. Stadlinger method of molding plastic masses by extrusion[1], which is analogous to the spraying of metals, requires a raw material which is plastic at 160° and sets immediately at room temperatures such as the cellulose ethers or acetylcellulose. He gives methods for the formulation of "Trolit W" (secondary cellulose hydroacetate with certain softening and gelatinizing mixtures), "Trolitul" (polymerized vinyl compounds), and "Trolitan S" (phenol-resin condensates). The "fireproof" cellulose of R. Roland[2] comprises acetylcellulose and methyl or ethyl alcohols 25 each and chlorbenzene, tetrachlorethane, benzyl benzoate, triacetin and dichlorhydrin, 10 each. The materials are admixed at 75° and are then ready for extrusion or sheeting.

G. Trümpler[3] first admixes cellulose acetate with softeners to a pasty consistency with the addition of alcohol, then heats either in boiling water or salt solution to drive off the alcohol and leave a loose mass which is dried and pulverized, when it is then in condition to be molded while hot. The S. Ushakov invention describes a process wherein organic cellulose esters are mixed with a product obtained by treating alkalicellulose with benzine chloride (?) or xylene, the combination being then worked into a plastic mass in the usual manner without a volatile solvent[4]. It is dissolvable in the usual solvents and may be attenuated to any desired consistency. In the manufacture of variegated rods, artificial horn or onyx[5], irregular-surfaced layers of cellulose ester material of different colors are charged into a mold, the interstitial spaces filled with a liquid or pasty binder, and extruded by simultaneous heat and pressure. W. Werring[6] has surveyed the uses of ace-

1. Chem. Ztg. 1932, **56**, 409, 431; abst. C. A. 1932, **26**, 4419; J. S. C. I. 1932, **51**, 736-B.
2. U. S. P. 1713482; abst. C. A. 1929, **23**, 3343. E. P. 318818; abst. C. A. 1930, **24**, 2600. F. P. 667792; abst. C. A. 1930, **24**, 1217. Can. P. 293385.
3. F. P. 668124; abst. C. A. 1930, **24**, 1476.
4. Russ. P. 23611; abst. C. A. 1932, **26**, 2593.
5. E. Weber, D. R. P. 538065; abst. C. A. 1932, **26**, 1732.
6. Bell Lab. Record, 1931, **9**, 470.

tylcellulose molded materials as applied to the telephone industry[1].

The following commercial plastics are all said to contain cellulose acetate: *Aceloid,* Cie. Petit-Collin-Oyonnithe; *Acelose,* American Cellulose Co.; *Aceta,* Cie. Petit-Collin-Oyonnithe; *Acetaloid,* Acetate Products Corp., Ltd.; *Acetex,* England, Chem. Trade J. 1925, **85**, 396; *Acetoid,* Punfield & Barstow, Ltd.; *Acetol,* Soc. Usines Rhone-Poulenc; *Amzylolithe,* Soc. Lyonnaise de Celluloide; *Bennetate,* B. A. Parker; *Bernit,* Zelluloidwaren Fabrik; *Bexoid* (?), British Xylonite Co., Ltd.; *Celastoid,* British Celanese Ltd.; *Cellemit,* Verein f. Chem. Industrie; *Cellit,* Farbenfabr. vorm. F. Bayer & Co.; *Cellobase,* Raymond Boisde; *Cellon,* Deutsche Celluloid Fabrik; *Cellosite,* Ettore Rossi; *Celluin,* Paul Rie & Sohn; *Cellutite,* G. Convert & Cie.; *Cel-O-Glass,* Acetol Products, Inc.; *Cervinite,* Zelluloidwaren Fabrik; *Cinelin,* Cinelin Co.; *Clubman, Crayonne* (?), A. W. Kanis; *Cristalux,* Acetate Products Corp., Ltd.; *Cristore* (?), Speights Ltd.; *Curvitas* (?), A. W. Kanis; *Firmoid,* Bluemel Bros. Ltd.; *Glider* (?) A. W. Kanis; *Hagolit* (?), Gebr. Eckert; *Hycoloid,* Hygienic Tube & Container Co.; *Insuloid,* Harold Levey; *Isoloid,* Charles Martin; *Ivory Cross* (?), A. W. Kanis; *Lithene,* Plastic Moulding Co., Ltd.; *Lonarit,* Lonarit-Ges.; *Lumarith,* Celluloid Corp.; *Marblene* (?), Waite & Son Ltd.; *Marbloid,* Speights, Ltd.; *Masuron,* John W. Masury & Sons; *M E C,* Minerva Engineering Co.; *Moldite,* American Cellulose & Chem. Mfg. Co.; *Nacrolaque,* Jos. H. Meyer Bros.; *Neophan,* Cellonwerke; *Neutex,* Sicherheitsglas Neutex; *Newtex,* England; *Novolithe,* Soc. Bellignite; *Opalax* (?), A. W. Kanis; *Orthospan,* Medical Supply Assn. Ltd.; *Oyocetil,* Soc. l'Oyonnaxienne; *Pearlite* (?), Speights, Ltd.; *Plastacele,* du Pont Viscoloid Co.; *Plastilume* (?), W. V. Hutchinson; *Plastin,* Soc. des Matieres Plastiques; *Plastine,* Soc. Nobel Francaise; *Plynalith,* Isaac Frankel; *Press Mass,* American British Chemical Supplies Inc.; *Protectoid,* Celluloid Corp.; *Reliance,* Reliance, Ltd.; *Rhodialine, Rho-*

1. C. Dreyfus, Can. P. 318561.

doid, Soc. Usines Chimiques Rhone-Poulenc; *Ronisol,* Soc. La Ronite; *Securite,* Cie. Petit-Collin-Oyonnithe; *Sicoid,* Soc. Industrielle Celluloide; *Similoid, Sinur,* Blücher, 153; *Splintex,* Splinterless Glass Co., Ltd.; *Sterlin,* Germany; *Tortaloid,* Fiberloid Corp.; *Trolit,* Rheinische-Westfaelische Sprengstoff, A. G.; *Vitalite* (?) New York Wire Cloth Co.; *Vitreo-Colloid,* J. M. Newton Vitreo-Colloid, Ltd.; *Xetal,* England; *Zellith* see *Cellit; Zellon* see *Cellon;* and *Zellugol,* Kunst, 1931, **21**, 87.

2. *Cellulose Ether Plastics.* The oily and resinous condensation products obtained by condensation of benzyl chloride, benzal chloride, benzyl alcohol, xylyl chloride and *p*-xylylidene chloride on one hand[1] and naphthalene, methylnaphthalene, anthracene, phenanthrene on the other, may be associated with the cellulose ethers, especially ethyl- and benzyl-cellulose, in the formation of artificial compounds of desirable molding properties. By combining an equal weight of the condensation product from xylyl chloride and naphthalene with ethylcellulose, a pliable mass is obtainable which may be worked up in the cold by cutting, drilling or turning on a lathe, and which has high tensile strength. This process, applied for February 15, 1918, is one of the earliest clear disclosures of the practical production of cellulose ether plastic bodies[2]. In 1932 A. Blackall[3] described the benzylcellulose first exhibited by Imperial Chemical Industries, Ltd., at the British Industries Fair, and intended to be used free from volatile materials, and which does not warp. For straight molding, it is stated a pressure of 0.5 ton per sq. in. is sufficient, while for injection molding the normal pressures and equipments are used, no curing or hardening process being necessary. There is also the important advantage when working with the cellulose ethers, that all scrap may be re-used. "Cups made from it were shown which had a perfect porcelain

1. Farbenfabriken vorm. F. Bayer & Co., D. R. P. 301713, 302521.
2. *Ibid.* D. R. P. 336476.
3. Plastics, 1932, **8**, 207.

glaze, and it would be practically impossible for an expert to tell that they were not china without touching them."

In order to induce plasticization with the minimum of solvent (and thereby reduce the evaporable solvent to the lowest possible point)[1], it is suggested to first treat the cellulose ether with solvent in a vapor form in a closed container, and then cause uniform diffusion throughout the mass by admitting a limited amount of volatile dissolvant. When methyl- or ethyl-cellulose is the etherified cellulose operated upon[2], alkylated[3] or aralkylated[4] sulfonamides, either alone or in conjunction with lower boiling solvents, offer a range of plastic bodies of excellent stability and covering a wide range of desirable physical characteristics. The British Celanese, Ltd.[5], prepare compositions containing cellulose ethers intended as molding powders, by first pulverizing the cellulose ether and mixing with one or more plasticizers or softening bodies, no volatile solvents being used at any stage. Thus, 80 parts ethylcellulose, cellulose acetate or cellulose butyrate, are ground until it passes a 100-mesh sieve, the grinding being then continued with 20 parts butyl phthalate, and 50-100 parts zinc oxide. When a pebble mill is not used, the cellulose compound may be rolled on hot rolls with the plastifiers, causing the whole to pass into an indistinguishable mass, which after cooling, is finely ground and is then ready for use. This powder together with powders of a similar composition but with dyestuffs, pigments or lakes incorporated therein, may be alternately spread or sifted upon a surface until a layer of the desired thickness is built up, which, when compacted by heat and pressure, enables sheets of variegated appearance to be obtained by sawing at right angles or other angle to the compacted block[6]. As plasticizer may be added

1. W. Crooks and C. Walton, U. S. P. 1835997.
2. H. Dreyfus, E. P. 164386; abst. C. A. 1922, **16**, 494.
3. *Ibid.* E. P. 164384; abst. C. A. 1922, **16**, 494.
4. *Ibid.* E. P. 164385; abst. C. A. 1922, **16**, 494.
5. E. P. 282723; abst. C. A. 1928, **22**, 3988. Can. P. 285231. F. P. 644935. Belg. P. 343438.
6. C. Dreyfus, E. P. 303898; abst. C. A. 1929, **23**, 4582. F. P. 606536. Can. P. 270404.

the resinous product obtained by distilling lactic acid alone under a reflux condenser until a light colored product of m. pt. 30-35° is produced[1]. It is preferable for best results[2] to employ an ethyl- or benzyl-cellulose of very high viscosity characteristic. Their benzylcellulose plastic is associated with one or more synthetic resins of the phenol-aldehyde, glyptal, zinc butyl phthalate or coumarone type[3], or a benzenesulfonamide-aldehyde[4] or xylenesulfonamide-aldehyde resin condensate[5]. Another admixture which combines both plasticity and marked fire-retarding qualities is ethyl- or benzyl-cellulose with *p*-toluenesulfonamide-benzaldehyde synthetic resins[6], with bromtricresyl phosphate or mono-, di- or tri-bromacetanilid, specifically diacetyl-2.4.6-tribromanilid.

The celluloid-like molding powder of H. Dreyfus[7] is prepared by treating a cellulose ether in finely comminuted form with a plastifying agent in the absence of volatile solvents, the plastifiant being projected onto the cellulose compound either alone, or in a liquid carrier such as ether which is removed by volatilization before coming in contact with the cellulose ether. In the polishing of these cellulose ether-synthetic resin plastics[8], where an abrasive alone is used, fine scratches appear on the surface of the finished article due to the polishing composition, but if this is admixed with a small proportion of cellulose ether solvent, a softening action is set up which removes all scratch marks and imparts a high gloss to the material.

In the A. Eichengrün method for producing pressed masses from cellulose derivatives[9], concentrated viscous

1. W. Moss and C. Dreyfus, E. P. 311657; abst. C. A. 1930, **24**, 981.
2. British Celanese, Ltd., E. P. 309913.
3. *Ibid.* E. P. 313133; abst. J. S. C. I. 1930, **49**, 726-B.
4. C. Dreyfus, E. P. 315807; abst. C. A. 1930, **24**, 1754.
5. *Ibid.* E. P. 315808; abst. C. A. 1930, **24**, 1754.
6. British Celanese, Ltd., E. P. 340101, 340102. F. P. 675745.
7. F. P. 713702; abst. C. A. 1932, **26**, 1783. Can. P. 302649. E. P. 366070.
8. British Celanese, Ltd., E. P. 352547.
9. E. P. 290989; abst. C. A. 1929, **23**, 1267.

solutions of cellulose ethers with or without the addition of softening agents, synthetic resins or rubber, are extruded in the form of a heated paste through narrow apertures. The extruded material, on reduction of the pressure, swells up and forms a porous mass which is pressed in heated molds or extruded in a hot, fluid condition through suitable apertures to form the finished article. He claïms that in addition to the usual two stages or phases of dissolution of a cellulose ether usually termed either solution or gelatinization[1], a third or intermediate transition takes place termed "swelling" but more aptly a "welling up," wherein the structure of the cellulose derivative has not been visually extinguished. He claims this welling up stage does not absorb solvents, the addition of benzine for instance, intumescing finely divided cellulose ethers while the individual particles show no disposition to agglomerate. A cellulose compound in this state of pseudo-gelatinization (if that is a correct word) is much more susceptible to the action of plastifiants it is alleged, and a smaller proportion may be used to produce a homogeneous, moldable body. His process is exemplified by the following example:

100 gms. benzylcellulose in ground condition are moistened with a mixture of 20 gms. turpentine and 20 gms. alcohol and after standing for several hours at room temperature, are rolled into sheets or other forms after admixture with pigments or coloring matter, and without any preliminary drying or curing, may be immediately transformed into molded objects.

It is claimed the addition of resin oil to solution of cellulose ethers produces a plastic mass which is not only readily moldable at unusually low temperatures, but imparts a softness of feel to the finished article which in general is desirable[2]. Before being added to the etherified cellulose, the resin oil may be treated with alkali to remove

1. E. P. 291386; abst. J. S. C. I. 1930, **49**, 138-B. Swiss P. 143406. Belg. P. 351703.

2. B. Gaisenband and C. Piestrak, F. P. 483316; abst. C. A. 1922, **16**, 4063.

acid products and with sodium acid sulfite to eliminate aldehydes, the light hydrocarbons being removed by fractional distillation.

Where printing blocks are to be prepared by the general method consisting of a coating composition of a cellulose ether alone or in admixture with a synthetic resin[1], it is recommended to first brush on a heavy solution of the cellulose ether-resin on the support which is somewhat permeable by water, and sufficiently friable to permit a design to be cut therein to expose the support, but convertible by moderate heating into a hard and impermeable layer without melting. In treating supports of metals such as zinc, aluminum or copper, the metal may preliminarily be given a dark coating as by dipping in a bath composed of potassium permanganate and HCl.

C. Immerheiser and E. Knebel[2] have found that it is possible to product colored cellulose ether plastics, if the cellulose compound in the presence of a relatively small amount of solvent or gelatinant, is incorporated with the dyestuff, lake or pigment by means of a repeated rolling or mixing operation until the color has approached that state of subdivision represented by the colloid state. Such prepared pastes may be thinned with volatile solvents in the usual manner, and the insoluble portion will stay in suspension for an almost indefinite period of time. In thinning such a paste, a centrifugal with return arrangement or a form of homogenizer should be found advantageous.

Colored copper or chromium compounds are said to be especially suitable for this purpose, as indicated by the following specific examples[3]:

1. Ethylcellulose 15 parts is dissolved in 100 parts benzene and ethyl alcohol with 1 part castor oil. In the lacquer thus obtained there are dissolved 2 parts of the

1. J. Guerard, E. P. 294987; abst. C. A. 1929, **23**, 2050.
2. U. S. P. 1830944. F. P. 634457; abst. C. A. 1928, **22**, 3747. Swiss P. 140728.
3. W. Mueller, K. Holzach and H. Krzikalla, D. R. P. 517491. F. P. 634457.

chromium compound of the azo dye from diazotized 5-nitro-2-amino-1-oxybenzene and 1-phenyl-3-methyl-5-pyrazolon whereby a viscous, transparent, red solution is obtained of favorable fastness to light. By diminishing the benzene-alcohol, solid bodies may be formed. Solutions of methylcellulose or benzylcellulose may be similarly colored.

2. If the chromium compound of the azo dye from diazotized 4-chlor-2-amino-1-phenol-6-sulfonic acid and *b*-naphthol is used, a clear violet color results. If the chromium compound of the dye from diazotized 1-amino-2-naphthol-4-sulfonic acid and *a*-naphthol is used, there is obtained a light-fast blue compound.

The artificial material evolved by H. Persiel[1] when water-insoluble binders such as methyl- or ethyl-cellulose are formed into an aqueous dispersion, is admixed by spraying, kneading or otherwise commingling, and is then dried with substances which are capable of swelling or dissolving the binding agent. This apparently inexpensive method of plastic formation is susceptible to wide application to a variety of useful purposes, as indicated by the following illustrative examples:

1. 100 parts nitrocellulose are intimately kneaded with 100 parts each methylcellulose and water until a cement-like mass results. By further kneading or grinding with 100-500 parts of a filler as sawdust, kieselguhr or chalk previously wetted with water, a primer is obtained suitable for light-colored wood or for the preparation of solid objects. If used as a primer it is applied in the usual manner, after further dilution with water.

2. 100 parts water-insoluble ethylcellulose are made into a paste with 150 parts ultramarine blue by means of a solution consisting of 1 part sodium butylnaphthalenesulfonate in 50 parts water. After dilution with water to spreading consistency, or using for molded articles without further dilution, the dried material is mixed with benzene-alcohol 60:40 and sprayed on as for a paint, or ad-

1. U. S. P. 1848268. E. P. 319371; abst. C. A. 1930, **24**, 2558.

mixed with a smaller proportion of benzene-alcohol and malaxated to the desired consistency, then pressed or extruded to the form desired.

3. 100 parts oil varnish are intimately mixed with a solution of 28 parts methylcellulose in 252 parts water and ground with sufficient cork powder so that a mass is obtained that can just be formed. This mixture is rolled in a thin layer upon a tissue or cardboard base, and after allowing to partially dry, is covered with a short-oil varnish whose diluent penetrates into the layer, dissolving the emulsified oily particles and causing them to coalesce into a coherent film. By drying in the open air, the mass hardens so as to form an elastic layer. The mixture may thus be applied repeatedly, and built-up layers formed of any desired thickness.

4. 100 parts ester resin are fused and 20 parts methylcellulose introduced therein at 90-100°, the methylcellulose passing entirely into solution upon stirring, and without the addition of any volatile solvent. While vigorously stirring, a boiling solution of 10 parts resin soap in 200 parts water is added, stirring being continued until the mass has cooled to room temperature. Then the thickly liquid dispersion is mixed with 150-250 parts of sawdust so that a kneadable mass is formed from which may be prepared shaped bodies such as bars, plates and buttons. After the pressed bodies have been allowed to dry a little, they are placed in a mixture of 50 parts each oil varnish and benzene until their surface has slightly swollen, after which they are completely dried, turned and polished if desired.

Please observe that in these four examples, water is the solvent used in nearly each instance, and where the relatively inexpensive benzene is employed, but small proportions are used.

If 10 parts ethylcellulose are kneaded with 10-12 parts *iso*amyl phthalate (a colorless liquid, b. pt. 185-190° at 8 mm.) and one of the usual solvents so as to obtain a heavy,

homogeneous syrup[1], a leather-like product is obtained of high suppleness. Fillers may be added until a solid which may be extruded is formed. The hardness, elasticity and plasticity may be varied within considerable limits by the proportion of filler incorporated to cellulose ether used. Such cellulose derivatives as ethylcellulose laurate, cellulose laurate, cellulose elaidate or cellulose aceto-laurate (lauro-acetate) may be transformed into moldable masses without solvents by means of mechanical pressure at a relatively high temperature (100-150°). For ethylcellulose laurate a pressure of 3 atms. and 120° is advised, whereas with ethylcellulose and a highly fatty acid ester, 20 atms. at 120° is recommended[2].

For the purpose of preventing the induration of artificial resins upon standing[3], in which event their solubility in organic solvents nearly always diminishes upon ageing, the addition of not to exceed 10% (based on the weight of resin) of a cellulose ether, other than an aralkylcellulose, keeps the resin in a softened and pliable condition almost indefinitely. For a phenol-aldehyde condensation product, the addition of 3% of ethylcellulose is specified. As an example of specific procedure, 35 parts of the artificial resin prepared by causing a halogen-fatty acid to react with a fusible phenol-aldehyde condensation product are dissolved in 65 parts water and 35 parts 10% aqueous methylcellulose. The clear solution is applied upon the material to be coated by spraying or by means of a brush and then hardened by heating to 150°. This method is especially suitable where viscous or solid polymerization products of alkylene oxides are used in conjunction with the cellulose ethers[4].

The plastic composition of G. Balle and K. Sponsel[5] is prepared by mixing aqueous solution of alkylcelluloses

1. I. G. Farbenindustrie, E. P. 252328, Addn. to E. P. 245469.
2. *Ibid.* E. P. 289063. F. P. 648154.
3. *Ibid.* E. P. 315835; abst. Brit. Plastics, 1931, **3**, #25, 37.
4. *Ibid.* E. P. 352042; abst. C. A. 1932, **26**, 3391. E. P. 346550.
5. D. R. P. 542287, Addn. to D. R. P. 527197; abst. C. A. 1932, **26**, 2317. F. P. 615876 and Addn. 35939.

with colloidal substances capable of being converted into an insoluble form by the action of heat or of light of short wave length, such suitable colloids being drying oils and fusible phenol-aldehyde or urea-aldehyde condensation products. The colloid is then converted into the insoluble form before, during or after the manufacture of films or molded objects, and are stable to water. The practical working of the process is as follows:

1. 10 parts commercial phenol-formaldehyde condensate is dissolved in 100 parts alcohol and this solution finely dispersed in 800 parts 10% aqueous methylcellulose solution. From this admixture films may be cast directly, or the solution may be concentrated and then extruded for the formation of solid articles. The solubility is greatly diminished by submitting the finished film or object to a heat treatment of 100-140°.

2. An intimate mixture is made of 1000 parts 10% aqueous methylcellulose solution and 5 parts linseed oil or linseed oil varnish and this mixture after homogenizing, is directly castable into film form, or into solid masses after concentration. The final step in the process is heating at 100-110° and then allowing to stand in the air during at least 4 hrs. In this manner a portion of the linseed oil is converted into linoxyn which produces an insoluble mass with the methylcellulose.

Instead of using an alkylcellulose[1], films of regenerated cellulose from viscose may be used, and thus rendered waterproof without additional waxy or cellulose ester coatings. Urea-formaldehyde condensates may be used with water-soluble alkylcelluloses to insolubilize them in this manner[2]. Plastic masses are also producible from methylcellulose which is soluble in water above 16°, by incorporating a proportion of water-insoluble ethylcellulose, acetylcellulose or a cellulose nitrate[3], or a water-solu-

1. I. G. Farbenindustrie, D. R. P. 547665, Addn. to D. R. P. 516751; abst. C. A. 1932, **26**, 3667.
2. C. Neubauer, D. R. P. 527403; abst. C. A. 1931, **25**, 4725.
3. I. G. Farbenindustrie, D. R. P. 534852; abst. C. A. 1932, **26**, 1440. See D. R. P. 531642; abst. C. A. 1932, **26**, 305.

ble methyl- or ethyl-cellulose may be insolubilized by treatment with an aldehyde in the presence of a reaction-promoting agent, methylcellulose being rendered water-insoluble by heating at 95° with formaldehyde and KOH[1], the alkylcellulose being first cast into the configuration desired, and then submitted to the aldehyde treatment.

Plastic masses insoluble in water and organic solvents are prepared by emulsifying a mixture of cellulose ethers insoluble in water or of cellulose esters, but dissolvable in organic solvents, and also cellulose ethers which are water-soluble[2], drying the emulsion, and adding sufficient softening agent to render the mass stable during drying. Thus, a nitrocellulose solution prepared from pyroxylin, butyl acetate and butyl alcohol, is mixed with a diluent as benzene and aqueous methylcellulose solution. The mass is emulsified and dried. The formation of a plastic has been described[3] obtained by condensing crude solvent naphtha containing coumarone and indene with *m*-xylenylmethyl ether, *m*-xylenylethyl ether or cresylmethyl ether and incorporating the resinous mass thus obtained with the cellulose ethers, the synthetic resin being readily dissolvable in cyclohexanone and aliphatic and hydroaromatic hydrocarbons. Rubber obtained from dimethylerythrene may also be used in this connection[4].

Certain terpene compounds with the cellulose ethers are said to produce plastics favorable to those obtained by camphor with the nitrocelluloses[5], especially borneol and isoborneol being particularly good gelatinizing agents for ethylcellulose, which may be associated with smaller amounts of benzyl alcohol or butyl phthalate. The process is carried out as by the two following examples:

1. K. Sponsel and G. Balle, D. R. P. 538686; abst. C. A. 1932, **26**, 2316. See D. R. P. 538110; abst. C. A. 1932, **26**, 1781.
2. H. Persiel, G. Balle and K. Sponsel, D. R. P. 540872; abst. C. A. 1932, **26**, 2318.
3. I. G. Farbenindustrie, E. P. 314810; abst. C. A. 1930, **24**, 1530.
4. *Ibid.* E. P. 304612; abst. C. A. 1929, **23**, 4848. Swiss P. 142751.
5. *Ibid.* Aust. P. 118635; abst. Kunst. 1931, **21**, 93.

1. 3 kilos shredded ethylcellulose are kneaded with 500 gms. benzene, 260 gms. 98% ethyl alcohol and 500 gms. isoborneol for 16 hrs. at 30° in a closed mixing or kneading apparatus, sheeted in a rolling machine under slow drying and finely pulverized. It may then be pressed into homogeneous plastic masses at 125-127°.

2. 3 kilos shredded ethylcellulose are mixed with 500 gms. spent oil from camphor manufacture, which contain chiefly fenchol and borneol, 200 gms. ethyl alcohol, and 300 gms. benzene, and kneaded for 48 hrs. at ordinary temperature, when the weight will reduce to 3.6 kilos. It is then powdered and plasticized in a block press at 115° and then cut into plates at 100°.

The I. G. Farbenindustrie have described methods for the formation of cellulose ether plastic masses by the use of condensation products of polyvinic alcohols with aldehyde in association with the etherized cellulose[1], claiming a high degree of plasticity for the compounds thus formed, with a considerable range in hardness and flexibility, depending upon the preponderance or otherwise of the synthetic resin over the cellulose ether. Thus:

1. An 18-20% ethylcellulose solution in a mixture of methylene chloride and ethyl alcohol is mixed with a 15% solution of a product of condensation of a polyvinic alcohol with formaldehyde. The solution may immediately be extruded into filaments or films, or malaxated until the proportion of total solids increase to the point that moldable articles may be cast therefrom.

2. A mixture is formed of 100 parts 20% ethylcellulose (48-49% ethoxyl) in a mixture of alcohol 2 to benzene 8, and an alcoholic solution (20%) of polyvinyl alcohol-benzaldehyde added. A perfectly transparent mixture results which may be immediately used for lacquers or for film formation, or the solvent evaporated therefrom, and the hot mass extruded into moldable articles.

1. F. P. 718542; abst. C. A. 1932, **26**, 3377. E. P. 372647, Addn. to E. P. 367274.

Plastic combinations have been described[1] in which hydroxyethylcellulose acetate (soluble in chloroform, acetone and hot benzene) containing three acetic acid residues per C_6 cellulose, are dissolved in either 20% by weight of tricresyl phosphate or 20% *p*-toluenesulfonamide, with ethyl alcohol or benzene-alcohol as the volatile solvent portion, homogenized in a kneader at 100°, forming a transparent, readily moldable mass, which take dyes, lakes and fillers in large amounts without serious impairment of the tensile strength of the mass. In a similar manner plastics may be formed using cellulose acetobutyrate, or cellulose tripropionate.

Cellulose ethers in the wet condition may be kneaded in a medium which includes ethyl lactate, butyl acetate, chloroform, and raw or blown linseed, castor or tung oils, the water being gradually removed during the malaxating process, which may be conducted by means of hollow, steam-heated cylinder rolls[2]. A. Landucci[3] prepares films or plastic masses of cellulose ethers of a transparent and polished appearance by dissolving the cellulose compound in a suitable solvent mixture but of high concentration, and then extruding the mass as a filament, rod or sheet into cold water, preferably 4-10°, the precipitation being complete in 1-2 min., depending upon the diameter of the precipitated mass. The opaque mass is then freed from water by drying in the air, when the opacity gradually is overcome and a transparent product remains.

Waste pieces of ethylcellulose or other cellulose ether scrap, made plastic by gelatinizing media[4], are directly workable into the finished preparation by softening the mass plastic by combined pressure and heat, and then mold-

1. I. G. Farbenindustrie, E. P. 366116; abst. C. A. 1931, **25**, 4673. F. P. 704862.

2. Imperial Chem. Industries, Ltd., E. P. 316322. Imperial Chem. Industries, Ltd., and B. Foster, E. P. 331837; abst. J. S. C. I. 1930, **49**, 872-B. E. P. 358393; abst. Chem. Zentr. 1932, I, 2117.

3. U. S. P. 1658725; abst. C. A. 1928, **22**, 1237. See M. Theumann, U. S. P. 1845821; abst. C. A. 1932, **26**, 2316.

4. P. Balke and G. Leysieffer, E. P. 181697. Belg. P. 291528, 303245, 303246. Swiss P. 115322, Addn. to Swiss P. 91157.

ing small bodies a little larger than the required dimensions. These are then finished in dies under pressure and heat into the finished article. The G. Leysieffer[1] process for the manufacture of highly heat-proof molded articles from cellulose ethers, consists in treating the cellulose derivative with a quantity of a highly volatile solvent as benzene, methyl or ethyl alcohols or acetates, which is just sufficient to induce swelling to the maximum without actual solution, the material being then rolled into thin leaves at a temperature above the boiling point of the solvent, powdering the sheets, and then heating the powder in molds to a temperature above that of the melting point of the etherized cellulose. For example, 300 gms. ethylcellulose are placed in a kneading machine with just sufficient benzene to induce maximum intumescence. To this are added 300 gms. talc and a small quantity of coloring matter. After all the ingredients have been well mixed to a homogeneous mass, the latter is removed from the mixer and transferred to heated rollers and rolled into very thin sheets at 100° until all solvent has dissipated. After the leaves have cooled and reduced to a fine powder, the powder is placed in a steel mold heated to about 160° and pressed to the desired shape and configuration. Note that the solvent cost in this method is very low.

W. Lindsay[2] further reduces the inflammability of cellulose ether plastics by selecting a low-burning solvent plastifiant as liquid tricresyl phosphate as gelatinant, adding to the mixture 50% (of the weight of cellulose ether) of calcium sulfate as white pigment, the process being especially applicable for the formation of artificial ivory and horn products for the toilet industry. The G. Petroff[3] moldable composition comprises a method for the coloring and protection against atmospheric influences of cellulose ether and other plastic products, by subjecting them to the action

1. U. S. P. 1427690. E. P. 156752. D. R. P. 343183. F. P. 528399. Swiss P. 51574.
2. U. S. P. 1493209; abst. C. A. 1924, **18**, 2077.
3. U. S. P. 1865586.

of an alcoholic solution of a dyestuff in which a small proportion of shellac or hydroquinone is dissolved, keeping the article in the hot solution for 1-2 hrs. depending upon the temperature.

Moldable compositions made according to the disclosures of L. Lilienfeld[1] are formed from ethylcellulose, benzylcellulose or other cellulose ether, plasticized by the addition of oily products obtained by the action of acetylene on tar oil constituents boiling above 140° and in the presence of aluminum chloride. The operation of the method is indicated in the following examples:

Celluloid-like Masses. 25-50 gms. of the prepared oil (obtained by reacting on the higher boiling portions of solvent naphtha with acetylene in presence of $AlCl_3$) are mixed with 75-120 gms. water-insoluble ethylcellulose, benzylcellulose or ethyl starch or benzyl starch optionally, together with a solvent for the ether, and then treated in the usual manner for the production of celluloid-like masses.

Artificial Leather. In a mixture of 60 parts benzene and 30 parts alcohol or 90 parts benzene alone, 10-15 parts water-insoluble ethylcellulose are dissolved and mixed with 7.5-15 parts of oil as in Ex. 1. A pigment as lampblack is next incorporated, and the mass is spread on fabric with a doctor blade in the usual manner of manufacturing artificial leather coatings, a plurality of layers being applied, and finally embossed to the design desired.

In the fabrication of plastic sheets according to the E. Potter disclosure[2], a material of decreased cost and high rigidity and resistance to distortion is obtained, by sandwiching a sheet of celluloid between two sheets of casein plastic of substantially the same diameter by means of a cellulose ether cement. The surfaces contiguous to the cellulose ether solution upon pressure aided by heat are

1. U. S. P. 1563204; abst. J. S. C. I. 1926, **45**, 483-B. E. P. 149319; abst. J. S. C. I. 1922, **41**, 95-A.
2. E. P. 235350; abst. Plastics, 1926, **2**, 206. Soc. Anonyme l'Oxyonnaxienne Fabrique de Matieres Plastics, E. P. 235350; abst. C. A. 1926, **20**, 988.

said to amalgamate into an indistinguishable mass transparent, free from bubbles, irrespective of the number of superimposed sheets thus agglutinated.

According to G. Trümpler[1] finely divided cellulose ethers suitable for the formation of plastic bodies may be obtained by making a thick solution of a cellulose ether with either dissolved or finely dispersed pigment or lake incorporated therein and containing little or no plasticizing material, and then precipitating the cellulose ether in a finely divided condition by a coagulant which exerts no dissolving power on the plastifier or coloring matter contained in the mixture. The result is a precipitation of cellulose ether, plastifiant and color in substantially the proportion existing in the original solution. Water is the recommended precipitant. The cellulose ether magma after drying, is granulated and used directly in molding operations[2].

F. Small and W. Dickie[3] have described a device for cutting thin sheets from cellulose derivative plastics by means of an electrically heated cutting edge, whereby the severing is accomplished primarily by a fusing action.

Laminated Glass Sheets.[4] The prime factor in hastening development of non-shatterable or splinterless glass

1. E. P. 294251; abst. J. S. C. I. 1930, **49**, 53-B. Soc. Chim. des Usines du Rhone, E. P. 275558. F. P. 622733 and Addn. 33066. Swiss P. 127543. E. P. 285829.

2. For data on glyceryl phthalate synthetic resins, see: U. S. P. 1082106, 1085112, 1091627, 1091628, 1091732, 1098728, 1098776, 1098777, 1108329, 1108330, 1108331, 1108332, 1119592, 1141944, 1285117, 1413144, 1413145, 1424137, 1489744, 1581902, 1592082, 1634969, 1642078, 1642079, 1645415, 1663183, 1667189, 1667197, 1667198, 1667199, 1667200, 1678105, 1678623, 1690515, 1709490, 1715688, 1722554, 1722566, 1722776, 1739446, 1739447, 1739448, 1739771, 1757104, 1783165, 1783166, 1783167, 1783168, 1785930, 1803174.

3. U. S. P. 1637715.

4. For data elsewhere in this work on laminated glass, see p. 164, n. 7; 260, n. 1, 4, 5; 294, n. 5; 424, n. 7; 438, n. 3, 4; 480, n. 4; 495, n. 3; 517, n. 1; 525, n. 5; 593, n. 3; 655, n. 5; 660, n. 4; 663, n. 2; 665, n. 1; 688, n. 4; 690, n. 6; 735, n. 4; 740, n. 7; 754, n. 5; 766, n. 5; 789, n. 1; 816, n. 4; 820, n. 2; 827, n. 6; 833, n. 2; 836, n. 7, 8, 9; 842, n. 4; 844, n. 4; 846, n. 4; 851, n. 3; 884, n. 2, 3; 895, n. 1; 906, n. 6; 915, n. 1; 924, n. 3; 930, n. 3; 938, n. 1; 953, n. 7; 993, n. 4; 994, n. 3; 996, n. 1, 3; 998, n. 2; 999, n. 2; 1000, n. 2; 1011, n. 5.

has undoubtedly been the rapid expansion of the automobile industry with its attendant accidents, the initiation of legislation for the compulsory equipment of automobiles and public conveyances with safety glass in order to diminish and localize injuries incident to collision. It has been estimated that in the United States in 1931, 53% of the non-fatal injuries sustained in automobile accidents on the public highway were at least partially caused by flying glass. Therefore the extreme importance of any method or invention looking to the protection of the population by providing a glass more resistant to shock, or if broken which will be more nearly splinterless.

The general method of formation of laminated glass[1] is to sandwich between two sheets of glass a thermoplastic, transparent sheet acting as a binder for the individual panes, thus producing "duplex glass," or a sheet of glass with a plastic cellulose compound attached to both sides, on the outside of each sheet there being affixed another sheet of glass, forming "triplex glass." That is, duplex comprises two sheets of glass with an adhesive or thermoplastic sheet in juxtaposition with one side of each, whereas triplex represents three sheets of glass, the center sheet bearing adhesive or a thermoplastic sheet on each side, and two outer sheets of glass with adhesive or plastic sheet attached to the inner side of each. The proposition of producing multiple sheet glass appears simple, for it merely involves pressing two sheets of glass onto an intermediate plastic sheet until the two adhere into a unitary appearing pane, but in reality the problem is far more complex. It is necessary for instance, that:

1. The thermoplastic sheet be free from airbubbles after pressing; that it be free from tiny undissolved particles ("star dust"); that it have a high resistance towards ultraviolet light; that the plasticizing body added to the cellulose compound to form the lacquer or agglutinating sheet shall not crystallize upon long exposure to the light, or decompose with the evolution of acid, alkaline or other

1. G. Watkins, Can. P. 320841.

products which may affect the film; that chromatic or spherical aberration be not produced when glass and plastic are united; and that the cementing membrane shall possess the maximum of strength and tenacity with the minimum of thickness.

2. The glass shall be smooth and regular in texture and of even surface that there may be no distortion of view. That glass and plastic shall be substantially of the same degree of color, i.e., that they shall approach equally to the standard of absolute whiteness and transparency. That the glass, when subjected to impact, shall so shatter that the pieces radiate substantially equally from a common center, rather than to break unequally and hence increase liability of pieces falling away from the main sheet. That a certain plasticity which appears in the compound sheet in warm weather shall show the minimum of brittleness in extremes of winter cold.

The G. Watkins[1] method of producing safety glass comprises reacting a water-soluble adhesive (as gelatin) and a pyroxylin plastic solvent, and depositing the solution on one surface each of two sheets of glass, interposing a non-brittle layer between, and then subjecting the sandwich thus formed to the simultaneous action of heat and pressure to produce a composite structure. T. Holt and J. Stuart[2] use celluloid for the intermediate layer, which H. Kinon[3] claims has a superior stability to light, and that by its use a definite factor of safety can be produced. Where celluloid is used[4] it should be first softened with a solvent diluted with an inert liquid, the point of maturity being determined by touch of the hand, the success of the process depending upon the skill with which this is done. Important is the temperature and the concentration of solvent.

1. U. S. P. 1854496; abst. C. A. 1932, **26**, 3351. U. S. P. 1867787. Libbey-Owens Glass Co., F. P. 681039; abst. Chim. et Ind. 1932, **27**, #3, 653.
2. E. P. 337158.
3. Kunst. 1931, **21**, 225; abst. C. A. 1932, **26**, 818.
4. T. Pesch, Chem. Ztg. 1931, **55**, 935; abst. J. S. C. I. 1932, **51**, 146-B.

H. Ford and R. McCarroll[1] interpose a sheet of cellulose between sheets of rough, translucent glass, which are united with a composition having the same n as the glass, e.g., 50-55% cellulose nitrate, 20-25% of a urea-formaldehyde condensation product, 10-15% camphor and 10-15% tolyl phosphate. The Celluloid Corp.[2] employ dibutyl phthalate, urea and triacetin as the plastifying portion, while R. Wampler[3] uses casein. Flat or curved compound sheets have been described of two panes[4], one of which is approximately 0.01 inch thick, with an interposed celluloid sheet approximately 0.015 inch cemented between. In the F. Hallauer process[5], one side of two sheets of glass is covered on one face with a layer of gelatin, glue or egg albumen, and a coating of the same material is placed on both sides of a sheet of celluloid. The three sheets are then contacted and immersed in a bath dissolving the liquid but not the celluloid, as benzene or a plastifying agent. A glass surface may be conditioned for subsequently cementing it to a surface of celluloid[6], by depositing on the glass surface a thin liquid film of cellulose derivative solution free from camphor, and then converting the liquid film into a solid film free from volatile matter. The J. Walsh and J. Stevens process is similar[7].

The patented processes of L. Bartelstone[8], J. Robertson[9], W. Morgan[10], H. Gardner[11], E. Benedictus[12], and

1. E. P. 365828; abst. J. S. C. I. 1932, **51**, 343-B.
2. E. P. 339762. See E. P. 305694.
3. Can. P. 320836.
4. J. Nye and W. Stainer, E. P. 364277; abst. J. S. C. I. 1932, **51**, 262-B.
5. F. P. 715914; abst. C. A. 1932, **26**, 2029.
6. L. Bartelstone, U. S. P. 1835746; abst. Plastics, 1932, **8**, #3, 134.
7. Can. P. 308522.
8. U. S. P. 1835747. F. P. 666396. Can. P. 305295. See U. S. P. 1611139.
9. E. P. 321157; abst. C. A. 1930, **24**, 2568. D. R. P. 535109; abst. C. A. 1932, **26**, 1087. F. P. 662816; abst. Chem. Zentr. 1929, II, 2813.
10. U. S. P. 1848190.
11. U. S. P. 1836914; abst. C. A. 1932, **26**, 1087.
12. U. S. P. 1182739.

A. Bardin[1], involve the application of the general principles as above outlined, with minor improvements and modifications, all involving the use of some form of nitrocellulose. Benzoin[2], gelatin and resins[3], triacetin and a vinyl compound[4], a synthetic resin[5], vinyl acetate[6], urea-phenol-aldehyde resin[7], triacetin and monoethyl-*p*-toluenesulfonamide[8], lactic acid with ethyl lactate[9], acetone oil or diacetone alcohol[10], benzyl alcohol[11], tetrahydronaphthalene[12], lactic acid resin[13], urea-thiourea-dicyanodiamide resin[14], a polyglycol[15], formic acid[16], toluenesulfonamide-formaldehyde resin[17], dibutyl phthalate[18], alkyl phthalate with ethyleneglycol ether[19], or a condensation product of maleic anhy-

1. D. R. P. 320339; abst. Kunst. 1920, **10**, 109.
2. N. Mattingley and Lancegaye Safety Glass, Ltd., E. P. 344454; abst. J. S. C. I. 1931, **50**, 541-B.
3. D. Polden and British Safety Glass Co., Belg. P. 361956.
4. W. Moss, U. S. P. 1831462. Can. P. 308608.
5. *Ibid.* Can. P. 317919; abst. C. A. 1932, **26**, 1409.
6. *Ibid.* U. S. P. 1831462. Soc. Des Usines Chimiques Rhone-Poulenc, E. P. 339872; abst. C. A. 1931, **25**, 2827; Chem. Zentr. 1931, I, 1809; Brit. Plastics, 1931, **2**, #23, 530. British Celanese, Ltd., E. P. 341890, 341891; abst. J. S. C. I. 1931, **50**, 395-B. Soc. des Usines Chimiques Rhone-Poulenc, F. P. 658563; abst. C. A. 1929, **23**, 5291.
7. W. Moss and K. Crutchfield, U. S. P. 1870018. Can. P. 323574; abst. C. A. 1932, **26**, 4432. British Celanese, Ltd., E. P. 342337, 342458; abst. J. S. C. I. 1931, **50**, 395-B; Chem. Zentr. 1931, II, 2921; C. A. 1931, **25**, 4374; Brit. Plastics, 1931, **3**, #26, 82.
8. Societe des Usines Chimiques Rhone-Poulenc, E. P. 345176. See E. P. 316955.
9. C. Field and D. Haslett, E. P. 348723. See E. P. 321189.
10. C. Cross, C. Fox, L. Hebbs and Triplex Safety Glass Co., Ltd., E. P. 324898; abst. C. A. 1930, **24**, 3872; J. S. C. I. 1930, **49**, 820-B.
11. Soc. des Usines Chimiques Rhone-Poulenc, E. P. 305189; abst. J. S. C. I. 1929, **48**, 679-B. E. P. 316955; abst. C. A. 1930, **24**, 1951; J. S. C. I. 1930, **49**, 1029-B; Brit. Plastics, 1930, **2**, #19, 322; Kunst. 1931, **21**, 141.
12. H. Allen, U. S. P. 1655933; abst. C. A. 1928, **22**, 1023.
13. W. Moss, U. S. P. 1871725. Can. P. 308606.
14. W. Davis, U. S. P. 1864983; abst. C. A. 1932, **26**, 4432.
15. G. Watkins, U. S. P. 1873691. Can. P. 320840.
16. British Safety Glass Co., F. P. 677404; abst. Kunst. 1931, **21**, 163.
17. W. Moss, Can. P. 317726, 318145.
18. *Ibid.* Can. P. 308607. Can. P. 311770; abst. C. A. 1931, **25**, 3795. F. Dehn, E. P. 336732, 338988. British Celanese, Ltd., E. P. 340927; abst. J. S. C. I. 1931, **50**, 350-B; Brit. Plastics, 1931, **3**, #26, 82. See E. P. 306397.
19. Triplex Safety Glass Co., Ltd., W. Lyttleton, J. Wilson and H. Dick, E. P. 328919; abst. C. A. 1930, **24**, 5451; Kunst. 1931, **21**, 93.

dride with castor oil, butyleneglycol or a high molecular unsaturated alcohol[1], show the variety of plasticizing and agglutinating bodies which have been proposed as being especially valuable under conditions defined in the process. J. Talbot[2] reverses the operation, that is, he seals a single sheet of glass between sheets of cellulose acetate. No advantages are seen in the process.

Many are the methods which have been described for the utilization of cellulose acetate in the preparation of non-shatterable and bullet-proof glass, it being pointed out that whereas with nitrocellulose, continued exposure to sunlight as prevails in summer on the windshield of an automobile, is prone to cause incipient decomposition of the cellulose ester with liberation of nitric acid or oxides, which rapidly decompose the adjacent film substance, and eventually render the glass worthless. While cellulose acetate is not free from decomposition and liberation of acid radical, yet the evolution of small amounts of acetic acid does not have the destructive effect upon the film as does nitric acid.

In the J. Rowe method involving the use of acetylcellulose[3], a layer of clear varnish is applied to the inner side of the glass, and the cellulose ester interposed between, while N. Mattingley and A. Rea[4] employ a mixture of caoutchouc with mastic or dammar for primary adhesion to the glass. An acetic acid solution of gelatin forms an excellent primary adhesive[5], because it is likewise a solvent of the acetylcellulose sheets. Acetamide or formamide, likewise solvents both of gelatin and cellulose acetate[6], form the essence of another process. In order to increase ad-

1. I. G. Farbenindustrie, A.-G., E. P. 363933, and Addn. E. P. 363940; abst. J. S. C. I. 1932, **51**, 262-B.
2. E. P. 313273; abst. C. A. 1930, **24**, 938; J. S. C. I. 1929, **48**, 645-B; Brit. Plastics, 1929, **1**, #4, 153.
3. E. P. 298888; abst. C. A. 1929, **23**, 3066.
4. E. P. 298423; abst. C. A. 1929, **23**, 2797.
5. H. Mallabar and Non-Inflammable Film Co., Ltd., E. P. 288782; abst. C. A. 1929, **23**, 679; Plastics, 1929, **5**, 636. F. P. 645111; abst. C. A. 1929, **23**, 2006.
6. L. Mascart, U. S. P. 1342267, 1342268.

hesion, J. Thornton[11] pretreats the glass with hydrofluoric acid or sodium silicate. The non-scatterable glass of A. Roosevelt[2] uses a gelatin dissolved in formic acid for initially coating the glass, while E. Hope[3] mixes cellulose acetate with dialkyl itaconates, places between glass panes, and then heats at 70° for 3 days, when an unsplinterable sheet is produced. A phenol-gelatin layer makes an excellent primary coating for glass, if a sheet of acetylcellulose is to be subsequently attached thereto[4]. A "soluble" gelatin has been described for amalgamating sheets of glass into a unitary structure[5].

Cellulose acetate as the intermediary layer, usually in sheet form and containing a relatively high percentage of plasticizant, often with a trace of blue dyes for increased whiteness and clarity, forms the subject matter of the processes of C. Dreyfus[6], British Celanese, Ltd.[7], W. Moss[8], H. Mallabar[9], O. and B. Hawkes[10], J. Newton[11], J. Jeffray[12], M. Colefax[13], C. Dreyfus[14], V. Edwards[15] and L. Schiff[16]. As a solvent and plastifier for the cellulose acetate intermediary layer, triacetin is used by Acetex Safety Glass, Ltd., and W. Johnston[17], British Celanese, Ltd., and

1. E. P. 308117; abst. C. A. 1930, **24**, 215.
2. U. S. P. 1210987.
3. U. S. P. 1644131; abst. C. A. 1927, **21**, 4040. F. Atack, D. R. P. 484146; abst. C. A. 1930, **24**, 938; Chem. Zentr. 1930, I, 1673. F. P. 657333; abst. Chem. Zentr. 1929, II, 2813.
4. J. Robertson, E. P. 321157; abst. J. S. C. I. 1930, **49**, 13-B; Brit. Plastics, 1930, **1**, #10, 447.
5. Non-Inflammable Film Co., Can. P. 291026.
6. Can. P. 323602.
7. E. P. 347648.
8. U. S. P. 1831462; abst. C. A. 1932, **26**, 822. Can. P. 317726; abst. C. A. 1932, **26**, 1409.
9. U. S. P. 1802213; abst. Plastics, 1931, **7**, #8, 469.
10. E. P. 365371; abst. J. S. C. I. 1932, **51**, 262-B.
11. E. P. 333242; abst. Chem. Zentr. 1930, II, 2817; Kunst. 1931, **21**, 93. F. P. 693919; abst. C. A. 1931, **25**, 1962.
12. E. P. 327949; abst. C. A. 1930, **24**, 5124; Chem. Zentr. 1930, II, 2940.
13. E. P. 323671; abst. C. A. 1930, **24**, 3095; J. S. C. I. 1930, **49**, 240-B; Brit. Plastics, 1930, **1**, #11, 498.
14. Can. P. 293732.
15. U. S. P. 1467030.
16. D. R. P. 547801; abst. C. A. 1932, **26**, 3637.
17. U. S. P. 1809276; abst. C. A. 1931, **25**, 4374. E. P. 330265; abst. C. A. 1930, **24**, 5958; Brit. Plastics, 1930, **2**, #16, 185; Kunst. 1931, **21**, 93. F. P. 677389; abst. C. A. 1930, **24**, 3095.

J. Rooney[1] and G. Heyl[2]; methylcyclohexanone by P. Head[3]; and methyl or ethyl acrylate by Röhm and Haas A. G.[4].

Cellulose acetate combined with synthetic resins obtained by condensing hydroxybenzyl alcohol with the reaction product of formaldehyde with glycerol or polyglycerol[5] is alleged to result in the formation of shatterless glass of unusually high stability against actinic rays. In order to remove all occluded bubbles from the acetylcellulose sheet before imprisonment between the glass panes, it is advised to expose the sheet for at least 6 hrs. at a temperature of 70° to a pressure of 12-20 mm.[6], benzyl alcohol being the prescribed solvent. The molding of acetylcellulose under pressure is said to be facilitated if it is pretreated with a liquid which is not a solvent for the acetate at room temperature, but becomes one when the temperature is raised[7]. Suitable compounds include the higher alcohols, butyl alcohol, amyl alcohol, cyclohexanol, and hydrocarbons as turpentine. It is advised to first press the glass and the plastic acetylcellulose together in the presence of an inert gas as air, and then by steam at a temperature below the boiling point of the solvent or plasticizer used[8].

The Newtex Safety Glass Co. and W. Dougan[9] assemble alternating sheets of cellulose acetate and glass in a solution of an initial glycerol-phthalic acid condensation

1. E. P. 320374; abst. J. S. C. I. 1929, **48**, 1011-B; Brit. Plastics, 1930, **1**, #8, 330.
2. U. S. P. 1867009. D. R. P. 519028; abst. C. A. 1931, **25**, 2827. Belg. P. 354051.
3. E. P. 299900; abst. C. A. 1929, **23**, 3553. E. P. 321977; abst. J. S. C. I. 1930, **49**, 103-B; Plastics, 1930, **1**, #10, 448.
4. E. P. 355712; abst. J. S. C. I. 1932, **51**, 72-B.
5. British Celanese, Ltd., E. P. 365094; abst. J. S. C. I. 1932, **51**, 357-B.
6. Soc. des Usines Chimiques Rhone-Poulenc, E. P. 361254; abst. J. S. C. I. 1932, **51**, 105-B. F. P. 690803; abst. C. A. 1931, **25**, 1351. See E. P. 316955, 345176. F. P. 688884 and F. P. Addn. 36863 to F. P. 658563.
7. British Celanese, Ltd., E. P. 357567; abst. J. S. C. I. 1931, **50**, 1135-B.
8. Acetex Safety Glass, Ltd., and W. Johnston, E. P. 330265; abst. C. A. 1930, **24**, 5958; Kunst. 1931, **21**, 93.
9. E. P. 355604; abst. J. S. C. I. 1931, **50**, 972-B.

product by means of a mixture of ethyl and butyl lactates and methylene chloride, and after removal from the bath, the sheets are consolidated by compression at 300 lbs. per sq. in., at 90-130°.

The utilization of the cellulose ethers as a central lamina in impact glass shows real advantages over the inorganic and organic esters which have been employed for this purpose in an augmented stability, wider range of less expensive solvent compositions, and greater facility of clarification by filtration. The appearance of "haze" so often noticeable in nitrocellulose mixtures and especially in cellulose acetate solutions is seldom observed in carefully clarified cellulose ether combinations with volatile solvents. Upon dissolving a cellulose ether in a solvent and allowing to stand quietly for several days before the final filtration, the microscopic particles appear to coalesce into larger aggregates or agglutinates, readily removable by the usual filtration methods.

The following described processes for cementing a plurality of glass panes into a unitary member all employ one or more of the etherified celluloses, usually an alkylcellulose of maximum etherification, and hence substantially unaffected by water. The I. G. Farbenindustrie[1] have described an invention relating to the manufacture of so-called safety glass, by interposing between layers of glass a product of reaction between maleic anhydride and a cellulose ether. There is used a product consisting of 30 parts of the reaction of maleic anhydride with castor oil or 1.3-butyleneglycol, and 70 parts alkylcellulose. The following example illustrates the working of the invention:

1. A mixture is prepared from 30 parts of the product from maleic anhydride and castor oil, 70 parts ethylcellulose and 60 parts acetone. Two glass plates are united by means of this mixture, to which a bleaching agent or dye-

1. E. P. 349283; abst. Brit. Plastics, 1931, **3**, #30, 271. E. P. 363933, 363940.

stuff may be added. By adding to this mixture an inorganic filler such as finely pulverized glass or mica, an opaque or translucent safety glass is obtained.

They have found that a mixed cellulose ether or a cellulose ether-ester such as ethylcellulose palmitate, or a cellulose ester of the fatty acids as cellulose acetolaurate, acetopalmitate, acetostearate, butyroricinoleate, butyrolaurate, laurate, naphthenate, butyronaphthenate or acetobutyrate may be employed, the cellulose ether-esters having a very high degree of both stability and thermoplasticity. Cellulose laurate dissolved in chloroform, cellulose laurate with polymerized vinyl acetate resin and resorcinol monoacetate, or cellulose acetobutyrate with polyvinyl acetate resin are some of the combinations recommended[1].

Investigations in the field of utilization of the cellulose ethers for compacting two sheets of glass into a unitary member have resulted in the issuance of eight patents to the British Celanese, Ltd., between 1928 and 1929, which processes involve the following points of interest. Sheets of pure quartz glass are united with intermediate sheets of cellulose ether under the combined action of heat and pressure[2], adhesion between ether and glass being heightened by distributing over the surface a suitable plasticizer in finely divided form. The whole is then pressed at 300-500 lb. per sq. in. at about 70° until the powder consolidates into a homogeneous and continuous layer between the surfaces of the glass. A sheet of trimethyl-, triethyl- or benzyl-cellulose is softened by the addition to or action thereon of triacetin and diphenylolpropane, the composition being rendered more plastic by the addition of 1-6% water thereto. After the plasticizer has uniformly intumesced the cellulose ether, the latter is inserted between glass panes, and pressed to a unitary appearing element[3].

1. M. Hagedorn and A. Jung, U. S. P. 1861915.
2. E. P. 306397; abst. C. A. 1929, **23**, 502; J. S. C. I. 1930, **49**, 714-B; Chem. Zentr. 1929, I, 3131.
3. British Celanese, Ltd., E. P. 317443; abst. C. A. 1930, **24**, 2292.

Adhesion is facilitated by the use either of phenol-furfural resin or aniline-furfural resin[1].

In order to minimize the action of ultra-violet light thereon, the cellulose ether used as the interior laminant is sheeted and exposed to direct sunlight or quartz light for a considerable period[2], then dissolved and meticulously filtered, after which it is poured into sheet form and used in the ordinary manner. This preliminary treatment, it is claimed, ensures the glass withstanding actinic rays for an almost indefinite period. In order to augment adhesion of an organic derivative of cellulose to glass[3], it has been found that if a relatively small amount of acetin be incorporated with the cellulose compound, they may be readily be caused to adhere to glass by means of adhesives prepared from polymerized vinyl compounds.

One form of apparatus for washing glass and applying ether thereto[4] is illustrated in Fig. 14, in which the scoured sheets of glass *1* are placed on and carried over the rollers. The glass is washed with water or steam issuing from the branch *7* and *8*, the surfaces being scrubbed by rotating brushes *9* and *10*. After being washed and scrubbed, the glass passes between the squeegees *12* to remove excess of water and is then dried benearth a casing *16* by means of heated air, introduced through pipe *13* through branches *14* and *15*. The clean dry panes now pass on the endless blanket *17* beneath a hopper *23* connected with *21* in which is the adhesive solution. A layer is spread on the glass by the hopper, is carried beneath the hood *27* where it is evaporated. The cellulose derivative solution is applied to the adhesive coated glass as shown in the lower drawing, being placed on the blanket *30* which carries the

1. H. Dreyfus, E. P. 326520; abst. C. A. 1930, **24**, 4910; J. S. C. I. 1930, **49**, 558-B.
2. British Celanese, Ltd., E. P. 341890; abst. C. A. 1931, **25**, 4997.
3. W. Moss, U. S. P. 1831462. British Celanese, Ltd., E. P. 341891; abst. C. A. 1932, **26**, 2838.
4. British Celanese, Ltd., E. P. 342458; abst. C. A. 1931, **25**, 4374. C. Dreyfus, Can. P. 315772.

glass beneath the hopper *37* supplied with the cellulose derivative solution from container *35*. The glass is now

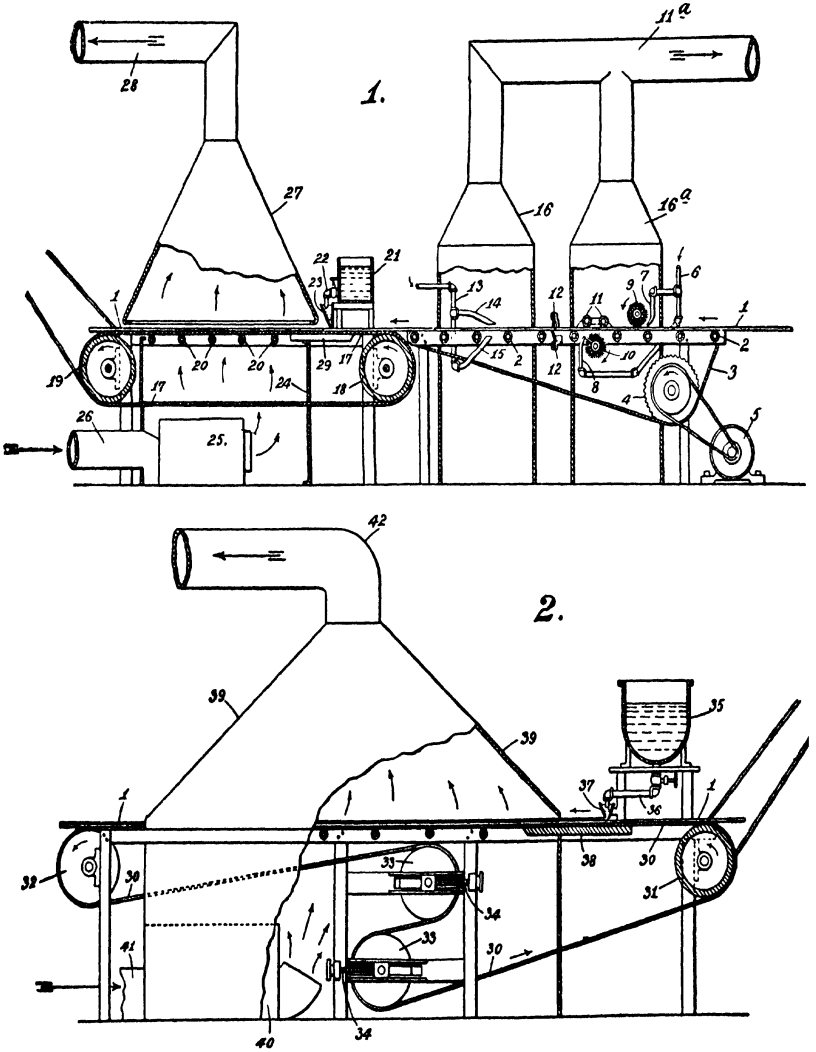


Fig. 14. Dreyfus Apparatus for Laminated Glass Manufacture.

placed within a casing *39* which connects by pipe *42* with a solvent recovery apparatus. The coated glass may now

be assembled and laminated by pressing at an elevated temperature[1]. It is claimed[2] that glass may be properly united by cellulose ether sheets less than 0.001 mm. in thickness.

Better and more uniform adhesion is said to result when the glass sheets and the intermediate cellulose ether layer are heated separately and then amalgamated by pressure before being allowed to cool[3]. J. Duclaux and Societe d'Etude des Verres et Glaces de Surete[4] prepare transparent, reinforced glass having the appearance of ordinary glass and not producing dangerous splinters by fracture owing to a violent shock, in which the central core is composed of methyl- or ethyl-cellulose or of caroubin (extracted from *Ceratonia Siliqua* seeds). The patentees claim that these substances, instead of acquiring a yellow color by the action of sunlight, are actually bleached thereby, in a manner similar to the bleaching of raw linen by the sun's rays, the armored glass being composed of two sheets of glass with an intermedullary layer of cellulose ether film.

The Du Pont Viscoloid Co.[5] claim as a non-discoloring plasticizing agent, a mixture of amyl acetate, ethyleneglycol diacetate or ethyl ether, triacetin and alkyl phthalates, with not more than 12% of camphor, and used for the manufacture of a plastic layer having a cellulose ether base[6].

In order to seal the edges of a laminated sheet such as described above[7], the edges may be coated with a thin metal, thus effectively sealing against the entrance and exit of

1. Brit. Celanese, Ltd., E. P. 347647; abst. C. A. 1932, **26**, 2838.
2. *Ibid.* E. P. 347648; abst. C. A. 1932, **26**, 2838.
3. C. Dreyfus, U. S. P. 1884624. British Celanese, Ltd., E. P. 347219.
4. E. P. 293052; abst. J. S. C. I. 1929, **48**, 323-B; Chem. Zentr. 1929, I, 282. E. P. 347219; abst. Brit. Plastics, 1931, **3**, #30, 272. F. P. 648990; abst. C. A. 1929, **23**, 2798. See F. P. 405881, 418251, 439644, 467303.
5. E. P. 310475; abst. C. A. 1930, **24**, 703; J. S. C. I. 1931, **50**, 158-B.
6. Soc. des Usines Chimiques Rhone-Poulenc, E. P. 316955.
7. F. Davis, U. S. P. 1845133.

vapors. F. Fraser has devised an appliance for sealing these edges[1]. Or[2], the sheets after adhesion may have their edges protected by attaching thereto U-shaped rubber strips by means of compressed air pressure, the under side of the rubber being made tacky for better adhesion. J. Sherts and R. Hamill[3] force a mixture of pyroxylin and tritolyl phosphate into the edges under pressure with heat, until the core softens and amalgamates with the sealing composition. F. Howe and M. Misener[4] have described a sensible process for sealing the edges of splinterless glass sheets. They apply a liquid to the edges which will convert the layer of colloidal reinforcing material into a gel for the required depth, remove the gel, and introduce sealing material into the groove so formed. A solution for use with cellulose acetate or nitrate reinforcing sheets consists of 80% commercial acetone and 20% water. This, it is stated, will produce a gel 2 mm. deep in a sheet 0.4 mm. thick in about 3 hrs. at 45° F. Methyl alcohol or methyl acetate may replace acetone. A hydrolyzing liquid may be used to facilitate penetration of the solvent, the sheet being preferably immersed in the solution, the gel when formed being removed by brushing with a suitable cleaning liquid, and the groove after drying being filled with sealing material.

Dioxane[5] and a mixture of cyclohexane and glycerol[6] have also been used as solvents and placticizers, both for duplex and triplex glass manufacture, and polybasic acid-polyhydric alcohols[7] have been described as plastifiants for

1. Can. P. 320833.
2. A. Johnson, E. P. 351257; abst. Brit. Plastics, 1931, **3**, #30, 272.
3. U. S. P. 1781084; abst. J. S. C. I. 1931, **50**, 633-B; Brit. Plastics, 1931, **3**, #30, 271.
4. E. P. 290144. D. R. P. 491726; abst. C. A. 1930, **24**, 2567. Can. P. 285240; abst. C. A. 1929, **23**, 682. Can. P. 320842.
5. British Celanese, Ltd., E. P. 347777; abst. Brit. Plastics, 1931, **2**, #30, 271; Chem. Zentr. 1931, II, 3244.
6. Triplex Safety Glass Co., Ltd., and J. Willson, E. P. 322551. See E. P. 221552, 279671, 316955, 321977, 326229, 328919.
7. I. G. Farbenindustrie, A.-G., E. P. 372579, Addn. to E. P. 363933; abst. J. S. C. I. 1932, **51**, 726-B. F. P. 715684; abst. C. A. 1932, **26**, 2029.

the same purpose. A small amount of Ponsol Blue may be added to whiten the appearance of the sheet[1]. The processes of J. Sherts[2], D. Adams[3], J. Brier and G. Watkins[4], B. Ayers[5] and W. Brown[6], in their essentials have been indicated by the processes epitomized above. Glycerol alone[7], formaldehyde-dicyanodiamide condensate[8], a mixture of ethyleneglycol and glycerol[9], or glycerol with acetic acid[10], represent some of the agglutinating and softening combinations which have been made the basis of patent protection. L. Pechin[11] has described a quadruplex glass, comprising four sheets compacted by three separated sheets of thermoplastic cellulose derivative material. Vinyl acetate may be employed as the adhesive[12], the glass and medullary film being subjected to pressure and polymerized *in situ.*

Those interested in the mechanical side of poly-sheet glass formation, which is outside the purview of this work, may consult the details as shown in the processes of J. Sherts[13], W. Bull[14], G. Watkins[15], R. Delloye[16], S. Barrett[17], W. Lytle[18], P. Lawson[19], Du Pont Viscoloid Co.[20], D. Adams[21] and J. Drake[22] which have been selected as

1. British Celanese, Ltd., E. P. 335878; abst. C. A. 1931, **25**, 1963; Brit. Plastics, 1931, **3**, #26, 82.
2. U. S. P. 1870693.
3. U. S. P. 1873248.
4. U. S. P. 1872663.
5. U. S. P. 1872553.
6. Can. P. 320832.
7. W. Brown, U. S. P. 1873280.
8. British Cyanides Co., Ltd., and E. Rossiter, E. P. 344047; abst. C. A. 1932, **26**, 3344.
9. F. Dehn, E. P. 358149; abst. J. S. C. I. 1931, **50**, 1095-B.
10. C. Lamberty, F. P. 722566; abst. C. A. 1932, **26**, 4147.
11. F. P. 721095; abst. C. A. 1932, **26**, 4147.
12. J. Walsh and A. Caprio, U. S. P. 1835619; abst. C. A. 1932, **26**, 1086. J. Walsh, U. S. P. 1875964. J. Walsh and A. Caprio, Can. P. 300366, 314576.
13. Can. P. 320381.
14. Can. P. 320241.
15. U. S. P. 1841689; abst. C. A. 1932, **26**, 1741. Can. P. 320837, 320838, 320839.
16. E. P. 360292; abst. J. S. C. I. 1932, **51**, 64-B. F. P. 711134; abst. C. A. 1932, **26**, 1741.
17. E. P. 336219.
18. U. S. P. 1844098; abst. C. A. 1932, **26**, 2029.
19. U. S. P. 1841745; abst. C. A. 1932, **26**, 1741.
20. D. R. P. 537489; abst. C. A. 1932, **26**, 1087. See E. P. 337547.
21. U. S. P. 1860067.
22. U. S. P. 1870284, 1872692, 1872693.

representing a composite picture of development of the art in this direction. T. Pesch and L. Lausberg[1] have discussed the advantages of various presses for this purpose.

Laminated and Composite Sheets. Plywood. In the process of J. Brüning and Sohn[2], plywood veneer having the thickness of paper is coated on one or both surfaces with thin layers of cellulose esters or ethers, and united by the simultaneous application of high pressure and increased temperature so as to form a unitary-appearing, and smooth-faced non-warpable wall covering which may be glued to the wall. The layer exterior to the wall may be of mahogany, satin wood or other beautiful wood in thin veneer.

British Celanese, Ltd.[3], produce paper, sheet and boards of laminated products by the use of methyl-, ethyl- and benzyl-cellulose, using as stock either rags, wood pulp, mineral wool, spun glass or leather fibers to a strong, water-resistant thermoplastic. It is advised to add the cellulose ether to the paper stock or other material while still in the beater, form the resultant stock into sheets, and thereafter fix the cellulose derivatives in the sheets. In order that the cellulose ethers shall be tenaciously held in admixture with the pulp or rag fibers, one expedient is to add the cellulose ether to the paper stock in the form of fibers (short staple filaments) whereby they intertwine with the pulp fibers to a more homogenously bound whole. As another expedient, a high boiling plasticizer or softener and the cellulose ether are added to the paper stock in the heater, whereby a more uniform product results. The presence of the high boilers and plasticizers enables a more thorough and uniform distribution of the cellulose ether throughout the stock. As suitable high boilers and plasticizers, diethyl phthalate, tricresyl phosphate, triphenyl phosphate, diacetin or triacetin may be added.

1. Kunst. 1932, **22**, 124; abst. C. A. 1932, **26**, 4146.
2. E. P. 283023; abst. C. A. 1928, **22**, 3972; Chem. Zentr. 1928, I, 1823. E. P. 283024; abst. Chem. Zentr. 1928, I, 1823.
3. E. P. 301428.

The adhesive of the I. G. Farbenindustrie[1] intended to cement wood or paper to wood, paper or metal, comprises thin sheets of highly plasticized cellulose ethers as ethylcellulose or cellulose naphtheneoleate, pressure being applied at a temperature just under the melting point of the cellulose compound. A somewhat similar adhesive[2] comprises a mixture of a celluose ether as the methyl, ethyl or benzylcellulose ether, and a soluble phenol-ketone resin (i.e., the condensation product of diphenylolpropane and acetone), with or without additions of other compatible natural or synthetic resins, and suitable solvents. The adhesive is said to be suitable for all materials, including especially glass, stone and asbestos.

In laminated board or paper production[3], cellulose ethers prepared and precipitated under such conditions that it assumes a fibrous character, are mixed with vegetable, animal or mineral fibers in a beating engine and the resulting stock run onto a paper or board machine. The sheets thus obtained are subjected to heat and pressure, or are brushed with a volatile solvent which is subsequently allowed to evaporate. The products find application as electrical insulators or in the manufacture of wheels and gears.

Composite sheets or films useful in making drawings or photographic reproductions[4] are made from layers of cellulose ethers, some of which swell in water and some of which do not. Thus, layers of cellulose acetate and cellulose ether, or layers of water-soluble and water-insoluble cellulose ethers may be employed. They are then pressed together by a glue rendered insoluble by water. A floor and wall covering has been described[5] composed of benzylcel-

1. F. P. 679607; abst. C. A. 1930, **24**, 3868. Can. P. 306972.
2. British Celanese, Ltd., E. P. 342674; abst. J. S. C. I. 1931, **50**, 452-B; Brit. Plastics, 1931, **3**, #28, 179.
3. *Ibid.* E. P. 301428; abst. C. A. 1929, **23**, 4072; J. S. C. I. 1930, **49**, 369-B; Chem. Zentr. 1929, I, 2493.
4. Wolff & Co. and R. Weingand, E. P. 304722; abst. C. A. 1929, **23**, 4819; J. S. C. I. 1930, **49**, 268-B; Chem. Zentr. 1929, I, 2719. F. P. 667942; abst. C. A. 1930, **24**, 1508; Cellulose, 1930, **1**, #4, 126.
5. H. Boernstein and N. V. Nederlandsche Linoleum Fabrik, Holl. P. 21183; abst. C. A. 1930, **24**, 2857.

lulose 20, mixed with tricresyl phosphate 27, to which wood meal, or china clay as fillers may be added, and the mass then pressed into sheets, or passed through rollers into long strips, or the mass in sheet form may be pressed onto jute as a backing.

The laminated film of R. Stinchfield[1], intended primarily for photographic purposes, involves the use of a base layer of cellulose ether upon which is laid a film of polymerized vinyl chloride as *b*-caoupren chloride, and on which is superimposed the photographically sensitive layer. The laminated sheet material of G. Richter[2] involves the production of a waterlaid ply of substantially unbeaten cellulose fibers in loosely felted condition, associated with a ply of cellulose fibers bonded together with gelatinized cellulose, one of the plies being impregnated with rubber and the other with a cellulose derivative as nitrocellulose.

The composite sheet material for making boxes and cartons as described by L. Rado[3] comprises coating pasteboard with a pellicle of organic cellulose derivatives, which is after-coated with a solution of celluloid or other water-repellent material, this latter coat being applied to paper by means of a solvent and heat, and then attached to the pasteboard backing. The J. McIntosh laminated fibrous sheets are prepared by passing paper, asbestos or textile fabric through an acetylcellulose solution[4], the solvent being afterwards evaporated and then the sheets superposed on each other to form the finished product of desired thickness, which is intended to be used for gears and radio panels.

Phonograph Records. While it is indisputable that the radio has made serious inroads in the phonograph (gramophone) industry in the past few years, yet it has and holds a distinct field of its own, for the only way to hear the

1. U. S. P. 1627935. See P. Seel, U. S. P. 1431900.
2. U. S. P. 1829157; abst. C. A. 1932, **26**, 847.
3. E. P. 305098; abst. C. A. 1929, **23**, 4785.
4. U. S. P. 1697077; abst. C. A. 1929, **23**, 1229.

Glee Club sing "Old Folks at Home" any time desired is by means of a phonograph record.

Pyroxylin has for many years in conjunction with shellac, formed the agglutinating basis for flat or sheet phonograph record material. The art in this respect is fairly covered by reference to the processes of M. Adom[1], C. Adams-Randall[2], Aeolian Co.[3], American Graphophone Co.[4], F. Applegate[5], G. Archer[6], F. Armbruster[7], J. Aylsworth[8], H. Ballard[9], A. Bawtree[10], A. Bacigalupi[11], E. Berliner[12], The Burt Co.[13], F. Capps[14], J. Challen[15], M. Claussen[16], F. Clay[17], W. Clifton and B. Oaksford[18], G. Clinchant, F. Desbriere and G. Vescier[19], Compagnie Francaise du Celluloid[20], Campagnie Generale de Phonographes, Cinematographes, et Appareils de Precision[21], Continental Royal Phone and Phonogram Co.[22], C. Cooke[23], J. Coombs[24],

1. U. S. P. 1202638, 1916; abst. C. A. 1917, **11**, 90.
2. E. P. 10357, 1891; 2690, 8248, 1893.
3. E. P. 24120, 24135, 1911.
4. E. P. 4052, 1900; 17767, 1906. D. R. P. 203685, 1909. Can. P. 108703, 1907.
5. U. S. P. 939119, 939120, 1909. E. P. 24723, 1909. D. R. P. 229412, 1909. Can. P. 123819, 1910.
6. E. P. 27283, 1912.
7. E. P. 28784, 1903. F. P. 328221, 1903. Belg. P. 174524, 1903.
8. U. S. P. 855555, 855556, 871554, 1907; 953454, 1910; 1024965, 1036416, 1043389, 1046137, 1912; Re-13531, 1913, thereto; 1146384, 1916; 1170391, 1916. E. P. 9559, 1911. F. P. 429292.
9. U. S. P. 985496, 1911.
10. E. P. 4680, 1905.
11. Ital. P. 87558, 1907; 91466, 1908; 104615, 1910; 112272, 1912.
12. U. S. P. 548623, 1895. See also S. Brown, E. P. 1157, 1911.
13. E. P. 16536, 1904; 7993, 1905. F. P. 347270, 1905; Addn. thereto 4701, 1905.
14. U. S. P. 666493, 689536.
15. U. S. P. 663011, 1900.
16. E. P. 3334, 1913.
17. U. S. P. 728867, 881664, 900706.
18. E. P. 2099, 1903.
19. E. P. 926, 1901. F. P. 296351, 1900; Addn. 1365, 1903. D. R. P. 112517, 1900.
20. F. P. 335240, 1903. D. R. P. 156413, 1902; abst. Chem. Ztg. 1904, **28**, 1158. See also A. Defavrie, E. P. 19163, 1903.
21. E. P. 12035, 1910. F. P. 391826, 1907.
22. U. S. P. 939119, 939120, 1909. E. P. 24693, 24723, 25342, 25361, 1909. D. R. P. 229379, 229412, 229715, 229837. Belg. P. 220478, 220479, 220854, 1909. Can. P. 114758, 1908; 123818, 123819, 123820, 1910; 131425, 1911.
23. E. P. 715, 1901.
24. E. P. 21087, 1907. F. P. 382260, 1907.

E. Cousens[1], J. Craig, Jr.[2], A. Defavrie[3], G. Downing[4], E. Dragoumis[5], W. Duddell[6], T. Edison[7], B. Edwards[8], A. Eichengrün[9], W. Elliott[10], T. Emery and W. Adkins[11], V. Emerson[12], J. Escamez and A. Moriones[13], H. Fairbrother[14], T. Flatau and F. Schellhorn[15], H. Framery and L. Pacaud[16], H. Godwin and A. Hoffman[17], B. Goldsmith[18], R. Grimoin-Sanson[19], R. Haines, J. Pletts and E. Lauste[20], V. Harris[21], R. Head[22], E. Heimerdinger[23], L. Helm[24], G. Herrington[25], G. Hogan[26], G. Holden[27], W. How[28], W. Hoyt[29], H. James[30], J. Jones[31], Cie Gen. des Phonographes

1. E. P. 1497, 1906.
2. U. S. P. 992169, 1911. E. P. 13064, 1909.
3. E. P. 19163, 1903; abst. J. S. C. I. 1904, **23**, 834.
4. E. P. 8840, 1907.
5. E. P. 19956, 1906. F. P. 382211, 1907.
6. E. P. 24546, 1902.
7. U. S. P. 713209, 713863, 1902; 1078265, 1913; 1119142, 1914; 1146413, 1146414, 1915; 1207383, 1916; 1234450, 1248468. D. R. P. 130033. Can. P. 82572. T. Edison and J. Aylsworth, E. P. 507, 1913. U. S. P. 1342326; abst. C. A. 1920, **14**, 2244.
8. E. P. 11945, 1890
9. E. P. 17574, 1912.
10. E. P. 11668, 11669, 1890.
11. U. S. P. 781137, 1905.
12. U. S. P. 838968, 1906; 1113973, 1183358, 1916; 1341740; abst. C. A. 1920, **14**, 2244. Can. P. 102043. J. Ellis, W. Eickstedt, E. P. 18519, 1911.
13. E. P. 17168, 21789, 21799, 1907. F. P. 370354, 375429, Addn. 7983, 8134, 375739, 375741, 1907. Belg. P. 202785, 1908. In this connection see E. P. 1644, 1878; 8248, 1893; 4680, 1905; 6220, 1906.
14. E. P. 17786, 1902.
15. E. P. 13428, 1906. F. P. 367026, 1906.
16. E. P. 8649, 1903. F. P. 336677, 1904. Belg. P. 167540, 1902.
17. U. S. P. 819058, 1906.
18. U. S. P. 840932, 1907. E. P. 14098-A, 1907. D. R. P. 203924.
19. Belg. P. 207073, 1908.
20. E. P. 18057, 1906.
21. U. S. P. 837061, 837927, 1906; 846411, 854886, 1907. Re-13067, 1910; 854887, 1907; 860320, 1910. E. P. 11908, 11909, 1903; 27952, 27953, 27954, 1906. F. P. 332336, 332337, 372538, 372539, 372540, 1906. D. R. P. 149297, 1904; 190964, 1907. Belg. P. 170552, 170553, 1903; 196777, 196778, 196779, 1906.
22. U. S. P. 805544, 1905; 820926, 1906.
23. E. P. 16446, 1903. F. P. 332181, 332184, 1903. D. R. P. 152822, 1904. Belg. P. 170379, 170380, 170381, 1903.
24. E. P. 25217, 1907.
25. U. S. P. 397856, 399264, 399265, 1889.
26. U. S. P. 673396, 1901. E. P. 7594, 1900. D. R. P. 128950, 1902.
27. E. P. 7543, 1905.
28. U. S. P. 709984, 1902.
29. U. S. P. 847338, 1907; 897254, 1908. E. P. 18250, 1907. W. Hoyt and W. Gaven, U. S. P. 808842.
30. E. P. 27382, 1908.
31. U. S. P. 763564, 1904.

Cinematographes et App. de Precision[1], C. Krieger and G. Burt[2], I. Kitsee[3], T. Lambert[4], H. Langston[5], M. Lefferts[6], S. Levin[7], H. Lioret[8], C. Loeschner[9], L. Ludwig and E. Pfefferkorn[10], L. Lumiere[11], T. Macdonald[12], F. von Madaler[13], American Graphophone Co.[14], G. Manwaring[15], F. Matthews[16], B. Philpot[17], F. Matthews and W. Messer[18], H. Mikorey[19], J. Milans[20], W. Miller and A. Pierman[21], J. Millet[22], E. Mobley[23], W. Morton[24], O. Multhaupt[25], F. Myers[26], F. Myers and H. Smythe[27], A. Neuman[28], Nicole Freres[29], W. Kaiser[30], T. Opel[31], S. Paxton and C. Shigley[32], L. Pacaud and H. Framery[33], W. Runge[34], A. Petit[35],

1. F. P. 358366, 1905; abst. J. S. C. I. 1906, **25**, 227.
2. E. P. 17163, 1902. 3. U. S. P. 903199, 1908.
4. U. S. P. 645920, 664223, 695159, 742454, 742455. E. P. 1560, 1561, 13344, 1900; 9906, 1902. F. P. 319469, 326174, 1902. D. R. P. 124752, 1901; 127119, 1902; 136447, 141268, 1903. Can. P. 67854, 1900. Belg. P. 164703, 1902. For litigation on above patents see Off. Gaz. 174, **8**, 31; Off. Gag. 174, 1220. 125 F. R. 922. 60 C. C. A. 632. In this connection see T. Edison, U. S. P. 382418, 1888; 414761, 1889.
5. E. P. 18318, 1905.
6. U. S. P. 672909, 1901. 7. U. S. P. 870300, 1907.
8. U. S. P. 528273, 1894; 629273, 1899. E. P. 23366, 1893. F. P. 230177, 1893.
9. D. R. P. 115466; abst. Jahr. Chem. 1900, **53**, 850; Wag. Jahr. 1900, **46**, II, 565. Aust. P. 7720, 1901.
10. E. P. 7624, 1889.
11. E. P. 11015, 1909. Aust. P. 16941, 1904. A. and L. Lumiere E. P. 15490, 1903. F. P. 338849; Addn. 2694, 2707, 1903.
12. U. S. P. 862407, 865716, 1907; 878547, 1908.
13. E. P. 23497, 1899; 19562, 1906. Belg. P. 146267, 1899.
14. E. P. 17767, 1906. 16. U. S. P. 951483, 1910.
15. U. S. P. 819072, 1906. 17. U. S. P. 892301, 1908.
18. U. S. P. 705772, 1902; 961980, 1910. E. P. 16833, 1902.
19. E. P. 24880, 1904. 22. U. S. P. 1047971, 1912.
20. U. S. P. 832403, 1906. 23. F. P. 359148, 1905.
21. U. S. P. 785510, 790516, 1905. 24. E. P. 3408, 1912.
25. E. P. 24183, 1901. Belg. P. 159971, 1901. Aust. P. 12113, 1903.
26. E. P. 18017, 1900.
27. U. S. P. 663194, 1900; 686321, 1901. E. P. 20710, 1900; 22709, 24509, 1901. D. R. P. 125469, 1902. Can. P. 79890, 1903.
28. E. P. 6220, 6613, 1906. F. P. 364222, 364414, 1906.
29. F. P. 326891, 1902.
30. Kunst, 1911, **1**, 122. 31. E. P. 12549, 1908.
32. U. S. P. 800331, 1905; 822485, 1906.
33. E. P. 8649, 1903. F. P. 336677, 1904. Belg. P. 167540, 1902.
34. U. S. P. 850256. E. P. 24382, 24382-A, 1903. F. P. 378304. See also G. Downing, E. P. 8840, 1907.
35. U. S. P. 657956, 662961, 1900; 666937, 683862, 683979,

B. Philpot[1], The Phonofilm Syndicate[2], J. Pletts[3], R. Revell and T. Barnard[4], N. Reif[5], V. Reko[6], J. Reynard[7], W. Runge[8], F. Russell and A. Jung[9], F. Seymour[10], C. Shigley and S. Paxton[11], D. Reed[12], Societe des Etablissements Gaumount[13], G. Stevens[14], F. Stock[15], Stollwerk Akt.-Ges. Gebr.[16], J. Szek and G. Schauli[17], W. Tyler[18], M. Thomas[19], G. Hogan[20], E. and B. Trenckmann[21], U. S. Phonograph Co.[22], E. Walker[23], C. Wickes[24], R. Winne[25], J. Whitman[26], H. Wolcott[27], C. Wurth[28], J. Young[29], W. Young[30], and Excelsiorwerk Fakrik für Feinmechanik[31].

In the field of cellulose acetate, a number of processes have been exploited using as an agglutinant acetylcellulose coupled with shellac, resins or colophony. The L. Rutstein

689117, 689118, 689408, 1901; 692337, 708828, 710299, 1902; 728607, 735579, 736773, 739713, 750118, 750119, 1903; 773978, 1904; 840932, 1907. E. P. 22867, 1899; 8930, 11469, 1900; 7146, 18917, 23386, 1902; 16283, 1903. D. R. P. 132732, 1901; 148682, 1904. Aust. P. 11697, 1902; 15112, 1903. Can. P. 68305, 1900; 70735, 1901.

1. U. S. P. 999183, 1911.
2. Can. P. 136378, 1911. Belg. P. 226126, 1910.
3. E. P. 15302, 1903.
4. U. S. P. 867836, 1907. R. Revell and T. Barnard, E. P. 5879, 1906. F. P. 371284, 1907.
5. U. S. P. 895197, 1908.
6. Kunst. 1914, **4**, 261; abst. C. A. 1914, **8**, 3236.
7. U. S. P. 666819, 1901.
8. U. S. P. 692363, 1902; 850256, 1907; 966771, 1910; 1018631, 1912. E. P. 9727, 22273, 1901; 1803, 24382, 24382-A, 1903. F. P. 321507. Belg. P. 163518, 1902. Can. P. 75281, 1902.
9. E. P. 14071, 14073, 1907.
10. E. P. 24552, 1910.
11. U. S. P. 800331, 1905; 822485, 1906.
12. E. P. 3542, 1867.
13. F. P. 394492, 1907; 400252, 1908.
14. U. S. P. 650431, 1900; Re-11917, 1901; 667600, 1901.
15. E. P. 23386, 1903.
16. E. P. 1992, 1903.
17. E. P. 8011, 1906.
18. U. S. P. 836417, 1906.
19. E. P. 16129, 1905.
20. E. P. 7594, 1900.
21. E. P. 4953, 1909. F. P. 400051, 1909. Belg. P. 214380, 1909.
22. E. P. 10319, 1910. D. R. P. 229715, 1911. Belg. P. 109692, 225343, 1910.
23. U. S. P. 805600, 1905. E. P. 24117, 1905. F. P. 360613, 1906.
24. U. S. P. 1213051, 1917; abst. C. A. 1917, **11**, 877.
25. U. S. P. 881644, 1908.
26. U. S. P. 1030364, 1912.
27. U. S. P. 649385, 650739, 1900. E. P. 15057, 1899.
28. U. S. P. 771758, 1904.
29. E. P. 1478, 1894.
30. U. S. P. 876035, 1908.
31. E. P. 17827, 1909. In this connection see G. Harrison, E. P. 10319, 1910. Londe, Mon. Phot. **20**, 74.

formula, which may be considered as representative, comprises rotten stone and finely ground record mass 100 each, china clay 75, mica 40, lamp black 5, cotton flock 10, orange shellac 10, and 80 of a plastic comprising cellulose acetate in a non-volatile solvent, such as a sulfonamide. The marked drop in the price of shellac in the past few years has caused a cutting down in the proportion of cellulose ester used in these records from price considerations[1]. The H. Laffon phonograph disk employs a cellulose ester with "resinic ether," ethyl phthalate or triphenyl phosphate as plastifier[2], while the G. Hilhouse invention unites facing disks of cellulose acetate with a central sheet of paper by combined heat and pressure[3]. The raw record material of A. Thomae[4] comprises gelatinized acetylcellulose with camphor or camphor substitute, and that of H. Sauget[5] adds 5% gum lac to the acetylcellulose to lower the temperature necessary for pressure.

As a representative example of a laminated phonograph record is the process of Gramophone Co., Ltd., and S. Whyte[6], who prepare core layers of paper covered with superposed layers of cellulose acetate, the core being previously impregnated with paraffin. "Surface noise" of the record is stated to be reduced by the use of different compositions. The J. Aylsworth disk sound record utilizes cellulose acetate in conjunction with a thin paper sheet, the disk being sufficiently flexible so that it may be rolled up without deterioration[7]. C. Bancarel[8] combines cellulose acetate with a phenol-aldehyde resin; F. Jones[9] places pow-

1. L. Rutstein, U. S. P. 1727039, 1727040; abst. Brit. Plastics, 1929, **1**, #7, 285. C. Dreyfus, W. Cameron and G. Schneider, U. S. P. 1843214; abst. C. A. 1932, **26**, 1731. C. Dreyfus, E. P. 222167. Can. P. 317959.
2. U. S. P. 1787484; abst. Plastics, 1931, **7**, #4, 236.
3. E. P. 353349, Addn. to E. P. 345875.
4. E. P. 337437; abst. C. A. 1931, **25**, 2255; J. S. C. I. 1931, **50**, 171-B; Brit. Plastics, 1931, **2**, #23, 531.
5. F. P. 670235; abst. C. A. 1930, **24**, 1948.
6. E. P. 320492; abst. C. A. 1930, **24**, 2563.
7. U. S. P. 1146387, 1146391, 1230816, 1347668.
8. E. P. 295228; abst. C. A. 1929, **23**, 2258; Chem. Zentr. 1928, II, 2207.
9. Can. P. 244972.

dered acetylcellulose in a mold and impresses the sound waves thereon; while combinations of cellulose acetate and rubber have been described as especially useful on account of superior tonal qualities produced[1].

Acetylcellulose with asphalt forms the record mass of Polyphonwerke A. G.[2], and acetylcellulose with acaroid resin constitutes the impressionable mass of F. Jones[3].

In the cellulose ether field, it has been found that a larger proportion of inert or filling material may be incorporated and still retain the desirable acoustic properties than by employing cellulose acetate or the pyroxylins, and it only remains to bring the cost of production of the etherized celluloses on a more nearly price competitive basis, for considerable quantities of these ethers to be used in this art.

C. Dreyfus and G. Schneider[4] have described the manufacture of molding powders of methyl-, ethyl- and benzyl-cellulose appropriate for phonograph record blanks, the cellulose ether being associated with sulfonamide compounds or other suitable plasticizing body. C. Dreyfus[5] has outlined a method for producing a sound record, in which the portion that contains the sound record track comprises a cellulose ether, specifically ethylcellulose. There is some evidence to support the statement that the use of the cellulose ethers in phonograph records improves the tonal qualities of the record over that of a similar record composition employing the cellulose esters.

The gramophone record as perfected by P. Balke and G. Leysieffer[6] associates ethylcellulose with methylurea or ethylurea as a gelatinizing agent with the usual fillers and black pigment, the composition being applied to paper or thin metal sheets to produce a finished article of about 0.3

1. F. Turner, J. Starck, J. Craig and P. Packman, E. P. 222177; abst. C. A. 1925, **19**, 1036.
2. F. P. 633790; abst. Chem. Zentr. 1928, I, 2464; Brit. Plastics, 1930, **1**, #11, 499.
3. U. S. P. 1558175; abst. C. A. 1926, **20**, 98.
4. U. S. P. 1732330. 5. E. P. 222167. Can. P. 288362.
6. U. S. P. 1456047; abst. C. A. 1923, **17**, 2482. E. P. 169232; abst. C. A. 1922, **16**, 803. E. P. 170568, Addn. to E. P. 169232.

mm. in diameter. No shellac is used. Either the coating material is produced in thin sheets and attached to the paper or metal backing, or a solution of the cellulose ether is applied to the backing and allowed to dry, when the sound wave undulations are then impressed by a combination of heat and pressure.

R. Pollak-Rudin[1] claims that the fragility of hardenable disks for recording sounds may be overcome by the addition of high-boiling compounds as glycol, butyleneglycol, glycol monoacetate, glycerol, acetin, *p*-methoxypyridine or oxalethylene, the viscosity being reduced by the addition of certain types of sugars and substituted saccharides as pentagalloylglucose. For hardening, a mixture of a bichromate and an aldehyde is recommended. An interesting and comprehensive paper on laminated gramophone records has been published by R. Jones[2]. To those whose "taste" runs in that direction, the edible chocolate phonograph record of E. Heimerdinger[3] is recommended.

Artificial Horn. The manufacture of artificial horn and similar corneous bodies from moldable nitrocellulose is based primarily upon the discoveries and patents of G. Davey[4], W. Harvey[5], A. and E. Bishop[6], Chemische Fabrik Heidenau[7], A. Rowe[8], T. Guilford[9], H. Blücher and E. Krause[10], Offenbacher Celluloid Fabrik[11], F. Nickerson[12], and Schreiner and Sievers[13], all of whom employ some form of

1. F. P. 725219; abst. C. A. 1932, **26**, 4927. See also J. Aylsworth, U. S. P. 1167468, 1283450. A. Hawerlander, U. S. P. 1842168. R. Chester, E. P. 335660. A. Little, Inc., and H. Billings, E. P. 340099. Compagnie Francaise pour l'Exploitation des Procedes Thomson-Houston, F. P. 680022.
2. British Plastics, 1932, **3**, 357.
3. E. P. 1992, 16445, 1903. F. P. 332181, 332182, 332183, 332184.
4. E. P. 1443, 1872.
5. U. S. P. 460086; abst. J. A. C. S. 1891, **13**, 242.
6. E. P. 24634, 1893.
7. D. R. P. 273958; abst. C. A. 1914, **8**, 3103.
8. E P. 21708, 1912.
9. U. S. P. 256476.
10. E. P. 11563, 1915; 106270, 1917; abst. C. A. 1917, **11**, 194, 2604. See E. P. 76, 1914; abst. C. A. 1916, **10**, 99.
11. D. R. P. 71204; abst. Ber. 1893, **26**, 1030.
12. U. S. P. 251924.
13. D. R. P. 67912; abst. Chem. Tech. Rep. 1893, **32**, I, 144.

cellulose nitrate in the completely plasticized condition[1].

In the cellulose acetate field, L. Lederer[2] has described an artificial horn prepared by combining acetylcellulose with organic compounds containing one or more hydroxyl groups or aldehyde, ketonic or amino groups, or with acid amides, with or without pressure, aminophenol and saligenin being claimed as especially suitable. W. Walker[3] associates cellulose acetate with a phenol as thymol and chloroform in the preparation of a corneous mass suitable for a succedaneum for horn.

In 1931 was published the process for the production of artificial horn of F. Schmidt[4], in which cellulose derivatives, as ethyl- and benzyl-cellulose, are combined with vegetable proteins as the protein from soy beans by virtue of a mixture of alcohol and water. The process limitations are indicated in the following examples:

1. 30 gms. ethylcellulose are mixed with 20 gms. alcohol; also mix 60 gms. vegetable protein (for instance soy bean protein) with 10 gms. each alcohol and water. The two mixtures are worked up in an open kneading machine or in rolls into a homogeneous mass and may thereupon be treated under pressure or in rolls.

2. 30 gms. benzylcellulose are mixed with 25 gms. alcohol; also mix 60 gms. size with 20 gms. of equal parts of alcohol and water, and manipulate as in Ex. 1.

3. 30 gms. ethylcellulose are mixed with 25 gms. alcohol, and 60 gms. casein with 12 gms. each alcohol and water. The further treatment of the masses is as in Ex. 1.

1. In this connection see H. Arledter, E. P. 16085, 1912. R. Dodd and H. Humphries, E. P. 15316, 1913; abst. C. A. 1915, **9**, 132. E. Jetter, U. S. P. 749297, 1904. Belg. P. 169302. F. Kleinsteuber, E. P. 14334, 1895. C. Lockwood, D. R. P. 27658. L. Nottelle and L. Leroux, E. P. 23619, 1904. R. Piogey, E. P. 106448, 1917; abst. C. A. 1917, **11**, 2604. W. Welling, U. S. P. 98272. G. Lincoln, U. S. P. 412398. J. Ind. Eng. Chem. 1913, **5**, 608. Kunst. 1912, **2**, 139.

2. U. S. P. 774677. E. P. 7088, 1902. F. P. 319724; abst. J. S. C. I. 1902, **21**, 1550. D. R. P. 145106, 151918, 152111.

3. U. S. P. 774713; abst. J. S. C. I. 1904, **23**, 1159.

4. U. S. P. 1811972; abst. C. A. 1931, **25**, 4983; J. S. C. I. 1932, **51**, 360-B. E. P. 230025; abst. Chem. Zentr. 1925, II, 624. Swiss P. 113925.

Artificial horn masses have also been described combining acetylcellulose with diphenylamine, trichlorphenol, triphenyl phosphate and phenol salicylate[1], and also with dioxydiphenyldimethylmethane[2].

Playing Cards. A variety of proposals have been made to produce opaque, washable playing cards using as a backing a cellulose derivative with the proper amount of opacity-inducing pigment therein. Celluloid has been a favorite material, as exemplified in the patented processes of J. Hyatt[3], N. Hart and R. Bacon[4], R. Hoh & Co.[5], J. France[6], M. Winkelströter, A. Leisegang and P. Simons[7], J. Kohn and S. Strauss[8], A. Liesegang, M. Winkelströter and P. Simons[9], A. Neumann and L. Zuckerbaecker[10] and S. Neugröschl[11]. Index cards have also been made from celluloid[12]. Notwithstanding numerous attempts, celluloid playing cards have been commercially successful but to a limited degree because they did not fulfill the most important requirement—preventing the markings on the cards from showing through. The great difficulty is to render the card sufficiently opaque so that the markings are not recognizable, even when a strong source of light falls on the card between the latter and the observer. This is due to the fact that the celluloid substance seems incapable of taking up more than a certain amount of filling ingredients, addi-

1. W. Lindsay, U. S. P. 1199798. U. S. P. 1245476; abst. C. A. 1918, **12**, 424. U. S. P. 1386576.
2. W. Beatty, U. S. P. 1158960, 1158961. F. P. 447645. U. S. P. 1188356; abst. J. S. C. I. 1916, **35**, 923. E. P. 18822, 18824, 1912; 18499, 1913.
3. U. S. P. 218122.
4. U. S. P. 241004.
5. E. P. 1286, 1905.
6. E. P. 17691, 1888; abst. J. S. C. I. 1889, **8**, 303.
7. E. P. 20197, 1895.
8. E. P. 3364, 1892.
9. E. P. 13773, 1896.
10. E. P. 15442, 1891.
11. E. P. 14977, 1891.
12. R. Lansing, U. S. P. 513791. Can. P. 48294. D. Allport, E. P. 21361, 1897. G. Brandt, E. P. 2895, 1905. E. Brown, Can. P. 66548. B. Cohn, U. S. P. 627392. W. Herren, U. S. P. 657217. J. Harcombe, E. P. 6210, 1913. F. Koskul, U. S. P. 289917. M. Lefferts, U. S. P. 238928. S. Pierce, U. S. P. 617119. See A. Becher, U. S. P. 788129. V. Roybier, F. P. 440485. J. Todd, U. S. P. 93924. J. Rand, U. S. P. 1218464, 1248910, 1248911.

tion of excess seriously impairing the strength of the card, causing it to become brittle and readily tearable.

On the other hand, the usual pigments as zinc oxide, lithopone, calcium sulfate, talc and magnesium carbonate, possess insufficient covering power. There may be little difficulty in rendering plates or sheets of one or more millimeters entirely opaque, but almost impossible to do so with the usual filling materials when the thickness is 0.25 mm., as is required in playing card manufacture. It is claimed the markings on a playing card are unrecognizable, even against a source of illumination as ordinarily prevails in the home or club if an alkylcellulose or alkylcellulose acetate (as ethylcellulose acetate) be used[1], in conjunction with such pigments as bismuth oxychloride, bismuth subnitrate, antimony oxide, mercurous chloride, titanium oxide or zinc sulfide. If a mixture of 4 parts zinc white and 1 part of titanium white be used with the cellulose ether, sheets are said to no longer allow light to pass through even from a strong source of illumination. A mixture of pigment and cellulose derivative is made, rolled out into sheet form or otherwise sheeted, and the surface of the card so produced preferably rendered a matt finish as by frictioning the surface before printing, whereby it takes the printing ink better. The ink used may be one which has a cellulose ether component therein (see Topic "Inks," p. 2474), especially multicolor impressions. After printing, if desired, the matt surface may be made glossy or semi-glossy by calendering or with the aid of a surfacing press.

Artificial and Imitation Pearls. Pearl Essence[2]. The value of pearls, their soft, velvety and nacreous appearance,

1. S. Klausner, A. Eichengruen and R. Roehm, U. S. P. 1811322. S. Klausner, Cellon Werke and A. Eichengruen, E. P. 304276; abst. C. A. 1929, **23**, 4819. Cellon Werke and A. Eichengruen, D. R. P. 468476.

2. W. Obst, Kunst. 1927, **17**, 80; Plastics, 1927, **3**, #7, 323; see J. C. S. 1926, 1381. H. Mattin, Industrial Finishing, Dec. 1930. M. Frued, Industrial Finishing, March, 1932. W. Miskella, Metal Cleaning and Finishing, 1932, **4**, 407; abst. C. A. 1932, **26**, 5389. H. Taylor, Bureau of Fisheries, Document #989, 1925; 16; abst. C. A. 1926, **20**, 802. R. Ellis, Du Pont Mag. 1932, 6; reprinted in Plastics,

changing in shimmering shade with conditions of the atmosphere, and hence (poetically) with the moods of the wearer, has furnished many a page of history of love, courtship, romance and tragedy, and many a fascinating theme for the historian and romanticist. A great deal of misinformation and exaggeration has been set to type concerning real pearls and the attempts made to synthesize them. The value of a pearl resides not in the material of which it is composed, but in the manner in which nature so cunningly arranges the material, for except in shape, the genuine pearl is identical with the shell or mother-of-pearl of the mollusk which produces it, and to which it is attached. Pearls are formed as a pathological process in a manner quite similar to the formation of gall stones in the human body, by the gradual accretion or building up of concentric or eccentric layers of material of varying light birefringence, which combined with a partial opacity, allows the partial penetration of light rays with a deflection and refraction into their primary colors, which produces that satiny sheen and alluring play of colors so much desired. And, like everything else that is much sought after and difficult to obtain, pearls are costly. The wearing of pearls is associated with the insignia of wealth, the aristocracy of breeding, the hall-mark of social prominence.

Both pearls and mother-of-pearl matrix from which pearls originate consist of layers of conchiolin, a corneous organic agglutinant, with bands of calcium carbonate, these two otherwise worthless materials being so disposed in relation to each other as to induce the pleasing and permanent optical effect that makes it one of the most sought after articles of commerce. To successfully imitate pearls man must make use of some substance that, when put into the shape of a pearl, exhibits that fascinating and ever-

1932, **8**, #3, 105. O. Parkert, Kunst. 1921, **11**, 183. The N. Y. Public Library has a bibliography on artificial pearls of 182 citations. Can. P. 150646, Ital. P. 133188. Hung. P. 59446. Norw. P. 24818. Span. P. 55263. Belg. P. 255253.

changing play of colors called "pearly luster," a problem stated in one sentence, but never successfully solved.

The older methods of attempted pearl synthesis involved the production of solid structures (for the pearl is a solid) by either a homogeneous composition, or at a later period by a built-up structure method of procedure. The methods of P. Castle[1], A. Muller-Schmoss[2], O. Parkert[3], P. Perdrizet[4], Pressloid Co.[5], A. Zand[6], D. Brewster[7], E. Higgins[8], and several other research investigators are of this nature and are composed of calcium carbonate, sulfate, phosphate or other salts in connection with glinting materials as mica. As adhesive, gelatin[9] or fish glue[10], with schist[11] or tin salts, alkaline silicate as water glass[12], or with casein[13] as a binder are usually pressed together into the shape and size desired. S. Itane[14] went a step further, specifying that the calcium carbonate used is to be extracted from fish scales. Bearing in mind that the lustrous versi-color and multitone changeable sheen of mother-of-pearl are dependent upon diffraction of light due to a grating-like structure of the terminal edges of successive laminae and also to light interference induced by reflection from numerous parallel laminae of sensibly equal thickness, it is obvious that any solid particle used to simu-

1. E. P. 24629, 1903.
2. D. R. P. 289142; abst. C. A. 1916, **10**, 2511.
3. Sprechsaal, 1910, **43**, 327; abst. C. A. 1910, **4**, 2194.
4. F. P. 339171. D. R. P. 164894.
5. Can. P. 182581. 6. E. P. 17827, 1903.
7. Phil. Trans. 1814, **104**, 397. See also Brugnatelli Gioranale, 1815, **8**, 253; Jour. de Phys. 1815, **81**, 181, 471; Thomsen, Amm. Phil. 1814, **3**, 190.
8. Can. P. 251634.
9. F. Alary-Ruelle and A. Choisy, F. P. 328357; abst. J. S. C. I. 1903, **22**, 957.
10. K. Wirth, D. R. P. 88442; abst. Wag. Jahr. 1892, **42**, 1086. D. R. P. 119118.
11. E. Douzal, L. Davion and E. Deloume, F. P. 475760.
12. J. Rosen, E. P. 17953, 1912; abst. J. S. C. I. 1913, **32**, 790; Kunst. 1913, **3**, 396.
13. E. Jasset, C. Bernadac and F. Kowachiche, F. P. 458036, 1912; abst. Kunst. 1913, **3**, 476. D. R. P. 258370; abst. C. A. 1913, **7**, 2999.
14. Jap. P. 30572; abst. C. A. 1917, **11**, 2393.

late a pearly appearance in a composition, must comprise lamellae, plates or blades in order to induce the optical effect desired, and that these blades must not all lie in the same plane.

Pearl Essence, essence d'Orient, Triple X paste, is a departure from the older methods of endeavoring to build up solid structures in the synthesis of pearls, but applying to a built-up mass, either by incorporation, impregnation or superficial coating, of a solution or suspension, to induce the effect desired. The experimentation leading up to the discovery and isolation of the product which has proven satisfactory in this respect is an intriguing story. It appears that the discovery which first led to real success was made by Jacquin, a French rosary maker, who on the banks of a stream near his home in Passy, France, noticed about 1656, that the water in which a small fish of the *Ablette* family had been washed contained a highly lustrous substance, which when concentrated by sedimentation, suggested in a remarkable degree pearl, and he applied this sediment to small globules of alabaster and wax, producing in time, and for the first time, merchantable imitations of pearls. His pearls gained a reputation and apparently an extensive distribution. Reaumur—who combined speculation with real work and close observation—in 1716 seems to have been the first to discover, or at least to record, that the "fish essence" is not a homogeneous liquid but a suspension of a multitudinous number of particles, shaped like blades, which float around changing in countour. His method was to agitate the scales of the ablette with water and elutriate off the finer particles, together with particles of tissue, blood and similar protein detritus.

C. Ehrenberg[1] in 1833 conducted an investigation on the formation of crystals in the tissues of living animals, this being followed by similar work of others, which finally led to the preparation of a compound of barium and guanin by A. Strecker[2] and the work of A. Bethe[3], who

1. Ann. 1838, **28**, 465. 2. Ann. 1861, **108**, 154.
3. Zts. Physiol. Chem. 1895, **20**, 472.

demonstrated that pearl essence is merely a suspension of crystals of guanin in the pure state. Guanin is one of the end products of protein metabolism in the animal body, a derivative of nucleic acid, and occurs in all cell tissues. In fishes guanin occurs mostly on the white or belly side of the fish as a camouflage, producing a bright silvery appearance to blend with the bright sky as seen from below by enemies of the fish. Similarly when seen from above, the back of the fish is a greenish-gray, to blend with the color of the water. It is not sufficient to say that pearl essence is a suspension of guanin, it is absolutely essential for purposes of making pearl essence that the guanin must be in a definite crystalline state.

Pearl essence, then, is a suspension of the natural crystals of guanin in a liquid, water, ammoniated water, amyl acetate, acetone or other liquid, in which a cellulose derivative may be dissolved to give increased body and adhesion. The natural crystals of guanin obtained from fish scales are usually much broken by virtue of the washing and purifying treatments to which it has been subjected. While the size of the crystals varies somewhat on a single fish, those from the shad, which are representative, have dimensions of about 0.1x0.02x0.001 mm., a surface of 0.0000424 sq. cm., and a weight of thirty-two-millionths of a milligram. The sp. gr. of the crystals is slightly over 1.6, 1 gm. of the crystals having an aggregate surface of about 12575 sq. ccm.—somewhat more than a square yard, and contains about 312,500,000 individual crystals. The large amount of surface accounts for some of the properties of the essence, for the crystals absorb substances from solution and hold them on their surfaces.

To understand the beautiful and peculiar appearance of pearl essence, one may visualize very thin, light blades floating in a liquid, and turning over and over like narrow strips of paper falling in air, their narrow surfaces throwing brilliant flashes of light in all directions. The light emanating from them is doubly refracted and polarized,

and when it passes through two of these crystals successively, is broken into colors by a twisting or other deflection of the polarized beam. The crystals show their maximum luster when orientated parallel to each other, which condition takes place when a current is set up in the liquid containing them. If the crystals happen to lie across stream, the velociety gradient perpendicular to the direction of the flow causes one end of it to move faster than the other, and it is therefore steered around until its long axis is parallel to the direction of flow of the stream. This accounts for the whirly effect in the liquid essence, especially when in suspension in a cellulose derivative lacquer. It also indicates that in applying such lacquers the maximum effect is obtainable if the fluid is caused to flow until solidification takes place. If the coat is applied as a uniform film with the crystals pointing promiscously in all directions, the effect will be a metallic or dull pearly luster.

Guanin (2-amino-6-oxypurin) belongs to the group of purin bases. It is insoluble in water, alcohol, ether, chloroform, ethyl or amyl acetate or any neutral solvent, dilute or glacial acetic acid, acetaldehyde, acetic anhydride, formic or lactic acids or solutions of salicylic or citric acids. Upon the property of this high insolubility its commercial value depends, otherwise it would be impossible to incorporate it in a cellulose ether or cellulose ester lacquer while preserving its crystallographic form, upon which its value depends. Guanin was synthesized by E. Fischer[1] in 1897, and while it may sometime substitute the guanin obtained from fishes, the manufacture of guanin of the delicate crystalline form necessary for pearl essence appears to present such an array of difficulties as to indicate continued dependence on the natural supply from fish scales, especially as there appears to be no real scarcity of the latter, once the collection is organized.

When guanin crystals are suspended in a non-aqueous liquid, that itself is not miscible in all proportions with

1. Ber. 1897, **30**, 2251.

water, the liquid must be strictly anhydrous. If a trace of water is dissolved, the crystals refuse to subside into a compact silvery mass, but hold apart from each other in a feathery aggregation or agglomerate. If more water is present they will flocculate in large masses which become impossible to again break up. If crystals of guanin are boiled in amyl acetate or other volatile solvents used in the lacquer industry, they lose their crystalline form and become amorphous.

In reality, fish scales do not enter in any manner into the manufacture of pearl essence, the luster being guanin crystals which are not found in the scales but are deposited in the epidermis of the fish, parts of which adhere to the scales when they are removed from the fish. It is this epidermis that is the source of the shiny crystals, the removal of which from the scales is the first operation in the manufacture of the essence. C. Dreyfus[1] dissolves this albuminous matter from the guanin by means of the peptonizing action of an enzyme. The particles of guanin should be neither too coarse nor too fine. The finest particles consisting of minute crystal fragments, appear, when separated from the coarser ones, chalky white or yellowish, while the larger crystals, such as those from the larger species of fish, give a grainy coating. For bead pearls, the larger particles give too great a brilliancy, approaching metallic luster, while those too small make dull pearls. Intermediate sizes produce the most desirable pearly luster.

Once having obtained the guanin crystals, the next problem is the most desirable vehicle for incorporation, in order to induce the effect desired. Nitrocellulose in solution has long been used for this purpose, being neutral, water-insoluble and dissolving in a line of solvents which do not attack guanin. The processes of C. de Vere[2], S. Sakane[3],

1. C. Dreyfus and G. Miles, Can. P. 312025.
2. F. P. 473382. See also F. P. 407092.
3. U. S. P. 1264979; abst. C. A. 1918, **12**, 1692; J. S. C. I. 1919, **38**, 265-A.

C. Claessen[1], J. Bock[2], S. Itane[3], L. Haudricourt[4], G. Le Roy & Co.[5], V. & H. Horschler[6], A. Zand[7], and G. Keil and K. Plischke[8] are of this order. Methods have been described for utilization of goldfish scales[9] and also the eyeball[10], but they appear to have no specific merit.

Variations in procedure of the general type method of incorporation in a nitrocellulose or celluloid solution of guanin crystals for the preparations of pearl essence have been pointed out by Sachse & Co.[11], E. Mauvillin and V. Guillet[12], Compagnie Francaise du Celluloid[13], P. Castle[14], Erste Offenbacher Gelatin-Folien u. Flitter-Fabrik Kock & Liebmann[15], Gesellschaft f. Gelatinierungen[16], J. de Jong[17], E. Maalouf[18], M. Junghans[19] and by E. Heusch[20]. In the production of substantially spherical artificial pearls, the methods of J. Meyer Bros.[21] and A. Potiez[22] may be

1. E. P. 6893, 1914. D. R. P. 278933; abst. C. A. 1915, **9**, 1377, 2435. F. P. 469694.
2. F. P. 469017.
3. Jap. P. 30572; abst. C. A. 1917, **11**, 2393.
4. Belg. P. 256116. See E. P. 23137, 1914.
5. F. P. 473662, Addn. 20258; abst. C. A. 1918, **12**, 1112.
6. D. R. P. 201914; abst. Zts. ang. Chem. 1908, **21**, 2287.
7. U. S. P. 746909. E. P. 17827, 1903. Zapon Lack. Ges., D. R. P. 281265; abst. J. S. C. I. 1915, **34**, 500.
8. D. R. P. 215672; abst. C. A. 1910, **4**, 682; Zts. ang. Chem. 1909, **22**, 2342; Chem. Zentr. 1909, II, 2054; Chem. Tech. Rep. 1909, **33**, 624; Chem. Ind. 1909, **32**, 759; Wag. Jahr. 1909, **55**, II, 557.
9. P. Perdrizet, F. P. 382603. A. Sachse & Co., Aust. P. 11204, 1903.
10. A. Lecocq, F. P. 361562; abst. C. A. 1907, **1**, 2956.
11. D. R. P. 140521; abst. Wag. Jahr. 1903, **50**, II, 571.
12. E. P. 10983, 1914; abst. C. A. 1915, **9**, 2806. D. R. P. 278084; abst. Kunst. 1914, **4**, 336.
13. F. P. 324894.
14. E. P. 246629, 1903.
15. F. P. 437876.
16. F. P. 268570; abst. C. A. 1914, **8**, 2041; Kunst. 1914, **4**, 20.
17. U. S. P. 494255. The Pressloid Co. (Can. P. 182581, 182582) combine powdered pearl shell, milk, calcium chloride, or resin, shellac or stearin.
18. F. P. 360545. See J. Rosen, E. P. 17953, 1912, for collodion containing artificial pearl manufacturing process.
19. E. P. 10896, 1902; abst. J. S. C. I. 1903, **22**, 287. F. P. 321821, 1902; 443406, 1912.
21. D. R. P. 113114; abst. Wag. Jahr. 1900, **46**, II, 585. E. Heusch and J. Paisseau, F. P. 471581; abst. J. S. C. I. 1915, **34**, 419.
21. E. P. 114619, 1918; abst. C. A. 1918, **12**, 1591. Can. P. 184065.
22. F. P. 463060; abst. Kunst. 1914, **4**, 195.

followed. The luminosity and desirability is said to be enhanced by a combination of rhodamine and zinc sulfide[1], but rhodamine is a fugitive dyestuff to light .

J. Paisseau has made an intensive study of the extraction of guanin from fish scales, and has worked out several processes. In one process[2], the raw material (fish scales, swimming bladders, teguments, bird excrement or insects) is treated with a reagent as soap or saponin which is capable of rapidly removing the protoplasm in which the crystaloids are embedded, the latter being separated from the reagents before they are acted upon. Proteolytic enzymes as pancreatin or pepsin may be used to dissolve away the albuminous material[3]. Or[4], there may be used as detersive agents substances which cause the surface tension of the treating liquid to assume such value that the liquid moistens the crystals constituting the pearl essence, bile, biliary salts and derivatives, sulforicinoleates or a dilute alcoholic saponin solution being recommended for this purpose. Formic, acetic or tartaric acids, especially in association with saponin and pepsin[5], form the basis of another extraction method. These all are aimed at separating the albuminous matrix in which the crystals of guanin are *individually* embedded, so the latter may be released in a free state in which the crystals have been broken as little as possible, for upon the crystallographic perfec-

1. S. Saubermann, U. S. P. 1096644; abst. C. A. 1914, **8**, 2228.
2. U. S. P. 1525317; abst. C. A. 1925, **19**, 1036; J. S. C. I. 1925, **44**, 207-B. U. S. P. 1737943; abst. Plastics, 1930, **6**, #4, 204. E. P. 23137, 1914. E. P. 188774; abst. J. S. C. I. 1923, **42**, 55-A. E. P. 222881. F. P. 407092, 420885. Can. P. 218608.
3. J. Paisseau, U. S. P. 1576454; abst. Plastics, 1926, 287; C. A. 1926, **20**, 1499; J. S. C. I. 1926, **45**, 323-B. Can. P. 258982.
4. *Ibid.* U. S. P. 1615770; abst. C. A. 1927, **21**, 806. E. P. 229585; abst. C. A. 1925, **19**, 3150; J. S. C. I. 1925, **44**, 316-B. F. P. 549806, 549807; abst. Chem. Ztg. 1923, **47**, 191. D. R. P. 334236; abst. Chem. Ztg. 1921, **45**, 105. Can. P. 256509.
5. *Ibid.* U. S. P. 1865703; abst. C. A. 1932, **26**, 4427. E. P. 213743; abst. C. A. 1924, **18**, 2412; J. S. C. I. 1924, **43**, 507-B. F. P. 473533, 416696, 521126. F. P. 599834; abst. Chem. Zentr. 1926, I, 2860. D. R. P. 334236; abst. Chem. Ztg. 1921, **45**, 105. Can. P. 240207.

tion of the crystals depends the degree of desirable pearly luster.

J. Bock[1] adds formaldehyde to the nitrocellulose solution to increase the solubility and hence increase the hardness and wearing qualities of the pearl essence layer. C. Durocher[2] adds tetrachlorethane to the lacquer to diminish inflammability, while A. Gaston[3] prepares the pearl base in wood and varnishes over this the pearl essence in a cellulose derivative lacquer. The methods of E. Maalouf[4], C. Paisseau-Feil[5], M. de Keghel[6], and E. Jasset, C. Bernadac and F. Kowachiche[7] are similar. K. Murakami[8] utilizes the crystalline lens of fishes.

Other methods of combining pearl essence or other products showing nacreous and iridescent properties are contained in the inventions of R. Liesegang[9], E. Higgins[10], P. Ganzinotti[11], P. Schreurs and G. Metz[12], K. Wirth[13], F. Alary-Ruelle and A. Choisy[14], W. Bowker and J. Walsh[15], E. Cadoret[16], Compagnie Francaise du Celluloid[17], L. Clement and C. Riviere[18], T. Didier[19], W. Felix[20], S. Hahn[21], D. Haig[22], E. Heusch and J. Paisseau[23], R. Himmel[24], J. Jacobson[25], Raison sociale Jasset, Bernadac, Firma &

1. F. P. 469017.
2. La Nature 1926, **54**, i, 161; abst. C. A. 1926, **20**, 1695.
3. F. P. 463060.
4. F. P. 360545.
5. U. S. P. 978394. E. P. 22420, 1909. Can. P. 252108.
6. Rev. Chim. Ind. 1913, **24**, 193; abst. C. A. 1913, **7**, 3585.
7. F. P. 458036.
8. E. P. 152914; abst. C. A. 1921, **15**, 932; J. S. C. I. 1920, **39**, 819-A.
9. Sprechsaal, 1915, **48**, 2; abst. C. A. 1915, **9**, 2135.
10. U. S. P. 1529084; abst. C. A. 1925, **19**, 2264. U. S. P. 1606030, 1607623. E. P. 243558, 247717. Can. P. 259103. Belg. P. 323116, 323117.
11. U. S. P. 1254791.
12. U. S. P. 1252849.
13. D. R. P. 119118; abst. Bied. 1900, **23**, 596.
14. F. P. 328357; abst. J. S. C. I. 1903, **22**, 957.
15. U. S. P. 1864794.
16. E. P. 12451, 1896.
17. F. P. 324894.
18. Chim. et Ind. 1922, **8**, 782.
19. E. P. 22245, 1904.
20. Neueste Erfindungen, **46**, 345; abst. Chem. Zentr. 1919, IV, 932.
21. E. P. 13139, 1894.
22. E. P. 23196, 1906.
23. F. P. 471581.
24. E. P. 18413, 1891.
25. E. P. 1566, 1892.

Kowachiche[1], A. Kraus[2], G. Le Roy & Co.[3], G. Lippincott[4], C. Marx[5], H. Mattin[6], E. Mauvillin and V. Guillet[7], O. Parket[8], O. Reinsch[9], J. Rosen[10] and the Rheinische Hartgummiwaaren-Fabrik[11], which contain manipulative details for various phases of the subject. Likewise are the contributions of A. Schahse & Co.[12], J. Echonwanek[13], C. Schuster[14], Societe Industrielle du Celluloid[15], O. Thiele[16], and the general review of the subject by A. v. Unruh[17].

In the employment of cellulose acetate as the solid adhesive for admixture with pearl essence for imitation pearl objects, J. Paisseau[18] employs cellulose acetate 7 parts, ethyl acetate and ethyl lactate 25 each and methyl alcohol 50. J. Camoin and A. Passerieu add a small amount of sugar (reason not clear) to fish scale essence and then incorporate with an acetylcellulose solution[19]. C. Claessen[20] employs Cellon, a cellulose acetate with plasticizers added thereto, while E. Higgins[21] produces the chatoyant aspect by the use of either of cellulose acetate or nitrocellulose. A method has been described by E. Jaks[22] of lacquering and irridescing a cellulose acetate mass in such a way that the optical properties of mother-of-pearl are accurately simulated. A similar effect is said to be induced by combining

1. D. R. P. 258370. Belg. P. 247933.
2. Farbe und Lack, 1932, 110; abst. Chem. Zentr. 1932, I, 3000.
3. F. P. 473662.
4. U. S. P. 1812885; abst. Plastics, 1932, **8**, #8, 317.
5. Plastics, 1926, **2**, #6, 195.
6. Ind. Finishing, 1932, **8**, #3, 13; abst. C. A. 1932, **26**, 1458.
7. U. S. P. 1351529.
8. Kunst, 1920, **10**, 129.
9. Chem. Tech. Rept. 1867, **6**, I, 62.
10. E. P. 17953, 1912.
11. D. R. P. 32874.
12. D. R. P. 140521.
13. D. R. P. 292370; abst. Kunst. 1916, **6**, 174.
14. U. S. P. 1434157.
15. F. P. 527236; abst. Chim. et Ind. 1922, **8**, 879.
16. E. P. 13823, 1894.
17. Kunst. 1918, **8**, 49.
18. U. S. P. 1438395, 1808372. E. P. 207144. F. P. 473533, 649019.
19. F. P. 521473; abst. Chim. et Ind. 1922, **7**, 756.
20. Aust. P. 70059; abst. Kunst. 1918, **6**, 287.
21. E. P. 247717.
22. D. R. P. 488151; abst. C. A. 1930, **24**, 2250.

rubber and cellulose acetate with an overlying coating of a pearly substance[1].

The cellulose ethers appear equally applicable in those older processes based upon the application of cellulose acetate in the menstruum containing the pearl essence. J. Paisseau[2] has specified the use of the cellulose ethers for this purpose, the etherized cellulose being dissolved in a suitable solvent combination and associated with the required amount of pearl essence.

Much research has been expended upon the problem of a successful substitute for fish scale essence, which is a fairly expensive commodity. W. Lindsay[3] has found that certain salts of mercury and bismuth in an exceedingly fine state of subdivision, when incorporated in a cellulose ether lacquer induce an appearance very closely simulating that of pearl. A white, silvery variety of mercurous chloride, or a precipitate of mercurous chloride-stannous chloride has been found suitable, the particles of mercurous chloride being about 0.02 mm. or less in size. It is said that sheets of cellulose derivative plastic 0.03-0.04 inch in thickness present a pearl-like, satiny and scintillating effect. A. Stiebel depends entirely for the pearly effect by the use of bismuth oxychloride finely divided by precipitation, for incorporation with a cellulose ether or ester to induce the same effect, a product of soft, lustrous beauty being obtained, indistinguishable from natural pearl to the novitiate[4]. The formation of a "metallic mirror" in cellulose derivative solutions is said to result by the use of the W. Wickel process[5], employing antimony oxychloride or bismuth oxychloride.

1. Regensburger & Co., Komm.-Ges., E. P. 315385; abst. C. A. 1930, **24**, 1712.
2. U. S. P. 1438395; abst. C. A. 1923, **17**, 1860. E. P. 23137, 1914; abst. J. S. C. I. 1919, **38**, 473-A. F. P. 473533. Belg. P. 293417, 313237, 320301.
3. U. S. P. 1809449; abst. C. A. 1931, **25**, 4403.
4. D. R. P. 267370, Addn. to D. R. P. 231030.
5. E. P. 347888; abst. Brit. Plastics, 1931, **3**, #30, 271.

A. Caprio[1] in aiming at duplicating the luster-producing property of guanin, has found that oxanilid when combined in a cellulose ether or ester lacquer, the oxanilid particles "show such a remarkable reflective or refractive action on light that the celluloidal solutions gleam with positive pearly effect." The preferred amount to use based on the weight of the cellulose ether or ester is 3-5%. It will be remembered that oxanilid has been patented as a nitrostarch stabilizer[2]. The plastic sheets of H. Smith and W. Bowker having imitation pearl appearance[3], comprises relatively thin sheets of cellulose derivatives containing mercurous chloride therein, the sheets being built up into block form, compacted by heat and pressure into a unitary mass, sheets or foils of the desired thickness being shaved or planed from the consolidated structure at any angle desired.

Recent Cellulose Ether Data. *Methylcellulose.* In a study of the preparation of acetone-soluble acetylcellulose capable of undergoing complete substitution by methyl groups in an almost homogeneous medium after one treatment only with methyl sulfate and alkali at comparatively low temperatures, W. Haworth and H. Machemer[4] find that hydrolysis of this methylcellulose at a low temperature with saturated aqueous HCl effected complete cleavage into the methylated glucose components. The latter were converted into the methylglucosides and submitted to an exhaustive separation by fractional distillation, the distillates yielding tetramethylmethylglucoside. By the methylation of cellobiosan[5], a product was obtained of m. pt. 226-229°, of apparent mol. wt. of 2100. J. Frydlender[6] published a description of the manufacture and properties of methyl-,

1. U. S. P. 1848158; abst. C. A. 1932, **26**, 2862.
2. F. Holmes, U. S. P. 875924. Aust. P. 73001.
3. U. S. P. 1814641; abst. Plastics, 1932, **8**, 175.
4. J. C. S. 1932, **135**, 2270.
5. W. Haworth, E. Hirst and O. Ant-Wuorinen, J. C. S. 1932, **135**, 2368.
6. Rev. Prod. chim. 1932, **35**, 225, 289; abst. C. A. 1932, **26**, 6122.

ethyl- and benzyl-cellulose, and A. Lautenberg[1] methods of production (see p. 1548, n. 1).

In an investigation of the methylation of *α*-cellulose as obtained from wood, D. Bell[2] determined that the maximum methoxyl contents which will effect the complete etherification of cotton cellulose lie between 36.3-39.1%, and that cleavage of methylated wood cellulose reveals the presence of "resistant portions." The non-resistant portions are constructed entirely of glucose residues having free hydroxyl groups in positions 2, 3 and 6. Acetylation of different wood *α*-celluloses produce triacetates of specific rotations varying from —19 to inactivity. Simultaneous deacetylation and methylation of the acetate leads to the formation of fully methylated depolymerized cellulose (methoxyl 39.2%), completely soluble in most organic solvents. Cleavage of the methylate yields 2.3.6-trimethylmethylglucoside (see pp. 37, 81, 123, 125, 1164, 1306, 1313), and a resistant portion with 29.9% methoxyl. The molecular weight of hendecamethylcellotriose has been determined[3], and the X-ray diagram of hendecamethyltriose from cellulose studied[4]. On examining the crystal aggregates of this body it was found to consist of parallel needles, a "fiber" period of 4.8 A. U. being found, the lattice plane distance perpendicular to fiber axis being unexpectedly long. It is stated that if methylcellulose is kept at the m. pt. a new X-ray diagram is obtained[5], which is ascribed to a double compound, but heating at a higher temperature restores the original lattice. Summation of

1. E. P. 358803; abst. C. A. 1932, **26**, 6134. F. P. 708181; abst. C. A. 1932, **26**, 1119.
2. Biochem. J. 1932, **26**, 590; abst. C. A. 1932, **26**, 5414; J. S. C. I. 1932, **51**, 934-A.
3. K. Hess and M. Ulmann, Ann. 1932, **498**, 77; abst. J. S. C. I. 1932, **51**, 1117-A.
4. C. Trogus, Naturwissenschaften, 1932, **20**, 317; abst. C. A. 1932, **26**, 5257.
5. K. Hess, E. Garthe and C. Trogus, Cellulosechem. 1932, **13**, 156; abst. J. S. C. I. 1932, **51**, 1117-A.

most recent knowledge on the cellulose alkyl ethers has been recorded by C. Stark[1] and by E. Dörr[2].

Methylene Cellulose. Previous results (p. 1621, n. 1) confirm that the maximum content of methylene cellulose is 8%, corresponding with the formula $(C_6H_{10}O_5)_2CH_2O$, but most of the immunity to swelling and adsorption of alkali is conferred by the first 1.5-2% formaldehyde introduced, the importance of regarding this and other cellulose reactions as taking place on the surface of the micelles being emphasized[3]. See p. 212, n. 4; 253, n. 1.

Butylcellulose is obtainable by treatment of alkalicellulose from linters with butyl bromide[4], a yield of 6-18% butylcellulose being obtained in one stage. Butyl chloride does not react. The yield may be increased to 95% by adding powdered NaOH from time to time until an aqueous layer containing NaOH and NaBr separates below the mixture. The composition of this ether lies below those of a di- and a tri-ether, the product being soluble in benzene, toluene, chloroform and dichlorethylene. The ether has a fairly high plasticity and is strongly hydrophobic. See p. 1339.

Allylcellulose may be prepared by the introduction of an unsaturated radical into cellulose by treating it with a salt or an ester of an unsaturated alcohol (as allyl alcohol) in the presence of a base[5], the ether formed being used in making threads, plastic masses and coating compositions. See pp. 99, 163, 298, 910, 1291.

Benzylcellulose may be purified by treating the reaction mass[6], optionally after washing with water, by

1. Kunststoffe, 1932, **22**, 107. See Rev. gen. mat. plastiques, 1932, **8**, 133.
2. Cellulosechem. 1932, **13**, 85; abst. C. A. 1932, **26**, 6123.
3. M. Schenk, Helv. Chim. Acta, 1932, **15**, 1088; abst. J. S. C. I. 1932, **51**, 1117-A.
4. A. Nowakowski, Cellulosechem. 1932, **13**, 105; abst. J. S. C. I. 1932, **51**, 717-B.
5. C. Dreyfus, F. P. 724584; abst. C. A. 1932, **26**, 4950.
6. Imperial Chem. Industries, Ltd., and A. Levesley, E. P. 375399; abst. J. S. C. I. 1932, **51**, 881-B.

treatment with organic solvents (p. 1546, n. 1), without the use of water-soluble wetting agents, and may be prepared by treating alkalicellulose with benzyl chloride[1], the alkali concentration being rendered constant during the benzylation process by addition of fresh material. In this manner a more uniform benzyl ether is said to be obtained[2]. See Chap IX.

Mixed Cellulose Ethers and Ether-Esters. Ethylbenzylcellulose (pp. 39, 190, 236, 241, 257, 278, 282, 286, 287, 290, 1342, 1345) is formed when 1 mol. of colloidal carbohydrate as cellulose[3] is caused to react with a mixture of 10 or more mols. of ethylating agent and 2 or more mols. aralkylating agent in the presence of alkali, as a mixture of ethyl and benzyl chlorides. The product is said to produce an excellent lacquer of unusually high stability. Where cellulose containing free hydroxyl groups are esterified with organic acid halides in absence of acid-binders under non-hydrolyzing conditions (exclusion of water and removal of the halohydric acid formed either by vacuum or a current of gas or a solvent)[4], cellulose ether-esters result. Thus hydroxypropylcellulose or *b*-hydroxyethylcellulose kept for several days with acetyl chloride in light petroleum at 15°, gives hydroxypropylcellulose acetate or *b*-hydroxyethylcellulose acetate.

Hydroxyalkylcellulose esters result when anhydrides of monobasic organic acids are caused to react on hydroxyalkylcellulose at high temperatures[5], and in the presence of catalyzers or diluents. Thus, alkalicellulose and ethylene oxide are allowed to react to produce hydroxyethylcellulose, which is treated with acetic anhydride in the presence of

1. G. Frank and K. Mienes, D. R. P. 555930; abst. C. A. 1932, **26**, 6134.
2. Anon., Chem. Age, 1932, **26**, 156; Silk J. 1932, **8**, #94, 39; Chem. Trade J. 1932, **90**, 152; abst. Chem. Zentr. 1932, I, 2403.
3. O. Leuchs and E. Dörr, D. R. P. 554877; abst. C. A. 1932, **26**, 6134. G. Balle and K. Ost, U. S. P. 1867050; abst. C. A. 1932, **26**, 4718.
4. I. G. Farbenind., A.-G., E. P. 372122; abst. J. S. C. I. 1932, **51**, 796-B.
5. M. Hagedorn, D. R. P. 549648; abst. C. A. 1932, **26**, 4825.

benzene to give the acetate. Similarily hydroxypropyl- and hydroxybutyl-cellulose may be transformed into hydroxypropylcellulose acetate and hydroxybutylcellulose acetate. These products are rendered readily soluble by after-treating them with cellulose ester catalysts such as acids, acid halides or salts of strong acids or weak bases, in the presence of diluents[1]. Thus, hydroxypropyl laurate is boiled with trichloracetic acid in the presence of tetrachlorethane. Hydroxyethyl (or butyl) laurate, palmitate or stearate may be similarly treated.

In an improvement over a previous process (p. 1385, n. 2; 1614, n. 1) cellulose or starch are caused to react with mixtures of alkylene oxides and other alkylating agents under reduced pressure or in admixture with indifferent gases under a low partial pressure of the reaction gases[2]. Alkoxyalkyl ethers as hydroxymethyl(or ethyl or propyl)-ethyl(or propyl or butyl)cellulose being produced. Partial hydroxyalkylcelluloses (see p. 978, n. 2) are acylated in the presence of a solvent comprising a chlorinated hydrocarbon as methylene chloride and in the absence of free fatty acid[3]. The preparation of the hydroxyalkylcellulose from cellulose and an alkylene oxide may also be effected in the presence of a chlorinated hydrocarbon.

In the preparation of non-inflammable coatings[4], as for aviation purposes, first is deposited an under layer such as methyl(or ethyl or propyl)benzyl crotonate and then a finished layer containing cellulose ethers with the usual plastifiants as butyl phthalate. Ethylbenzylcrotylcellulose may also be used. In restricting discoloration of cellulose ethers by iron or other metals[5], the products are treated

1. I. G. Farbenind., A.-G., D. R. P. 554233, Addn. to D. R. P. 549648; abst. C. A. 1932, **26**, 6136.
2. *Ibid.* F. P. 39765, Addn. to F. P. 700880; abst. C. A. 1932, **26**, 4951.
3. R. Hofmann and G. Balle, D. R. P. 550702, Addn. to D. R. P. 526479; abst. C. A. 1932, **26**, 5207.
4. Soc. Française Duco, F. P. 727309; abst. C. A. 1932, **26**, 5221.
5. British Celanese, Ltd., E. P. 353075; abst. C. A. 1932, **26**, 5418.

with dilute, aqueous solutions of acids such as oxalic, tartaric and citric, or their mono- or di- sodium or potassium salts at temperatures under 100°.

Cellulose Glycollate, prepared according to the method of I. Sakurada[1], may be rendered ash-free by dialysis[2], re-precipitating several times from ethyl alcohol and neutralizing with NaOH. The viscosity of an aqueous solution of this ester with the addition of NaOH or neutral salts has been determined, and the relationship between viscosity and concentration plotted.

It has been found that whereas cellulose glycollic acid in which 1 mol. chloracetic acid has been brought to reaction with 1 mol. C_6 cellulose is insoluble in alcohol, ether, acetone or benzene, by the use of practically saturated (50%) NaOH solution products may be formed in which two or more ether groups are introduced into the cellulose molecule, and which are soluble in organic solvents[3]. The process is indicated by the following examples:

1. 162 parts cotton or purified wood pulp are treated with 300 parts 50% NaOH, and the whole kneaded for about 2 hrs. During this period a further 180 parts powdered NaOH are incorporated, and at the end of the operation 200 parts chloracetic acid are introduced gradually, and temperature maintained below 40°. After 6 hrs. 250 parts NaOH and 200-300 parts chloracetic acid are worked in, and this operation repeated after another 6 hrs., the temperature meanwhile being allowed to rise to 55°. On addition of water to the reaction product the cellulose glycollic acid goes into solution and may be separated by addition of a mixture of aqueous HCl and alcohol, and may be purified by cautious washing with hot, aqueous alcohol. The chloracetic acid may be replaced by chlorpropionic or

1. Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 96; abst. J. S. C. I. 1929, **48**, 430-A.
2. T. Nakashima, J. S. C. I. Japan, 1932, **35**, 352; abst. J. S. C. I. 1932, **51**, 1086-A.
3. H. Dreyfus, U. S. P. 1884629.

chlormalonic acid, the corresponding cellulose lactic acid or cellulose tartronic acid being formed.

2. To the product produced as above are added 200-300 parts 50% NaOH solution and 50-100 parts powdered NaOH worked in afterwards, when 500 parts methyl sulfate are gradually added and the whole kneaded from time to time. An almost complete methylation of cellulose glycollic acid results. Further esterification may be effected by adding an additional 80-100 parts powdered NaOH and 200-300 parts methyl sulfate. The methylcellulose glycollate is washed with water to neutrality, and may then be dissolved in acetone, acetic or chloracetic acids. Ethyl- or propyl-cellulose glycollates, lactates or tartronates may likewise be similarly produced.

Manufacture of Cellulose Ethers. The process of C. F. Burgess Laboratories, Inc., involves treatment of cellulose with a solution of NaOH to form a moist alkali carbohydrate and then etherifying with olefine oxides or halohydrins to produce the particular cellulose ether desired[1]. L. Lilienfeld[2] treats cellulose with one or more alkylating agents (alkyl sulfates) without heating or while cooling, in presence of an amount of alkali smaller than the weight of water; the resulting alkylcellulose, which is soluble in alkali but insoluble in water, is dissolved in alkali, brought to the desired form, and coagulated in a bath containing 35-80% sulfuric acid. O. Leuchs and E. Dörr[3] alkylate cellulose in the vapor phase, a small pressure vessel containing a liquid alkylating agent being put into communication with a larger pressure vessel containing alkalicellulose under such conditions that the vapor of the alkylating agent reacts with the alkalicellulose.

New cellulose ethers have been described of indefinitely characterized composition[4], obtained by treating cellulose simultaneously or successively with alkali and with methyl,

1. F. P. 725935; abst. C. A. 1932, **26**, 4951.
2. E. P. 374964; abst. J. S. C. I. 1932, **51**, 796-B.
3. D. R. P. 554309; abst. C. A. 1932, **26**, 5207.
4. L. Lilienfeld, E. P. 357080; abst. C. A. 1932, **26**, 5753.

ethyl or propyl isothiocyanates, in the presence of a small quantity of copper, nickel or iron salt as catalyst. The products are generally soluble in aqueous alkali solutions, and insoluble or but slightly soluble in water or organic solvents. They are suitable for artificial silk and films. Another class of etherized celluloses have been patented, of obscure composition[1], obtained by reacting upon cellulose xanthates with alkylating or aralkylating agents, the products being then treated with aliphatic diamines. Aqueous solutions of products soluble in water are obtained by treating alkalicellulose with CS_2 and etherifying agents, to produce the same derivatives. The original process gives examples using piperazine and diethylethylenediamine as the diamines applicable.

Cellulose containing at least one free OH group may be etherified with alkylene oxides containing a replaceable halogen atom, optionally in the presence of catalysts, and the product treated with ammonia or its derivatives. Thus, mercerized cotton is treated with a solution of the chlorhydrin ester of sulfuric acid in epichlorhydrin at 130-140°, the product obtained being pure white[2]. Or[3], cellulose ethers result upon treatment of cellulose in the presence of an alkali metal hydroxide with mono-, di- or trichlor (or brom or iodo) ethylene, suitable for the film or filament manufacture. For the formation of methyl- or ethyl-cellulose in which a gaseous etherifying agent is used[4], a raised temperature and redced or augmented pressure is advised. Thus, methyl chloride is led over alkalicellulose at 125°, for the formation of a substantially maximum methylated cellulose.

Cellulose ether xanthates result when an alkali-soluble alkylcellulose or an alkali-soluble or insoluble aralkylcellu-

1. Soc. Anon. pour L'Ind. Chim. a Bale, F. P. 39740, Addn. to F. P. 686575; abst. C. A. 1932, **26**, 4950.
2. *Ibid.* D. R. P. 549839; abst. C. A. 1932, **26**, 4950. D. R. P. 550760; abst. C. A. 1932, **26**, 4950.
3. L. Lilienfeld, E. P. 356776; abst. C. A. 1932, **26**, 5752.
4. M. Luther and E. Ober, D. R. P. 556063; abst. C. A. 1932, **26**, 5752.

lose, or a cellulose ether or hydroxyaryl monocarboxylic acid as hydroxyacetic acid, is treated with CS_2 in the presence of alkali, the product obtained being purified by precipitation by methyl or ethyl alcohols and washed with alcohol or ether. Solutions of the cellulose ether in NaOH are precipitated by dilute inorganic acids, salts or alcohols[1]. Cellulose ethers have been described[2] resulting from the treatment of alkalicellulose with alcoholic NaOH and dimethylaniline-, diethylaniline-, quinoline-8-, aniline-, dimethyl-1-naphthylamine-, or 1-methyl-4-aminobenzene-3-sulfochloride in toluene or benzene. The products obtained are very resistant to heat.

Cellulose Ether Solvents and Plastifiants. Dihydrodioxoles carrying hydroxylated substituents are used as plasticizers for cellulose derivatives[3], being of assistance in the incorporation of caoutchouc with cellulose esters or ethers. Suitable dioxoles are 3.3-pentamethylene-5-hydroxymethyldioxole (from cyclohexanone and glycerol) and methyl 3.3-pentamethyl-5-hydroxymethyldioxole. Coating compositions which present a crystalline surface comprise a cellulose ether with a water-insoluble urea derivative as diethyldiphenylurea[4], or a water-insoluble urethane such as fenchyl, isobornyl, phenyl or *iso*butyl phenylcarbamates, in a quantity at least equal to that of the cellulose derivative. Monoethylin phthalate forms 15% by weight of the W. Lawson coating composition[5], and *iso*propyl ether[6] has been recommended for the solvent extraction and concentration of acetic and other acids.

In the manufacture of substances the bases of which are cellulose derivatives[7], use is made of *N*-hydroxy-

1. L. Lilienfeld, E. P. 357167; abst. C. A. 1932, **26**, 5752.
2. I. G. Farbenind., A.-G., E. P. 322556.
3. Deuts. Hydrierwerke, A.-G., E. P. 375067; abst. J. S. C. I. 1932, **51**, 948-B.
4. I. G. Farbenind., A.-G., E. P. 358761; abst. C. A. 1932, **26**, 4969.
5. Can. P. 324955; abst. C. A. 1932, **26**, 5439.
6. J. Davidson and J. Schaefer, Can. P. 324125; abst. C. A. 1932, **26**, 4610.
7. Soc. des Usines Chim. Rhone-Poulenc, E. P. 373704; abst. J. S. C. I. 1932, **51**, 902-B.

alkylated arylsulfonamides of the benzene series, which are used as plasticizers with the cellulose ethers. Examples are products from benzene- or toluene-*p*-sulfonamide or their *N*-ethyl derivatives and ethylene chlorhydrin or ethylene oxide. The A. Jaeger coating composition contains cellulose ethers, natural or artificial resins, and are plasticized by the use of non-resinophoric esters of keto-aromatic acids such as butyl or amyl benzoates, or methylnaphthoyl or butylnaphthoyl benzoates[1]. New acetals solvents have been detailed[2], formed by treating *ab*-unsaturated aldehydes with orthoformic ester or a formimido ether, or a mercury derivative thereof, in the presence of a catalyst as ammonium chloride or potassium acid sulfate. A solvent not capable of forming addition products with the aldehydes may be present, but the presence of any substantial amount of hydroxylated solvent should be avoided.

Cellulose Ether Filaments and Films. In the fabrication of hollow or voluminous artificial filaments and threads[3], a solution of an organic derivative of cellulose which may contain the coagulant, is dry-spun and a coagulant (hydrocarbons b. pt. 60-120°) less volatile than the solvent in the spinning solution is applied to the filaments immediately after their extrusion, or to the spinning nozzle itself. The solvent is subsequently rapidly evaporated at a temperature above the b. pt. of the solvent, but below that of the coagulant. In a variant of this general method, dry-spinning solutions have been described[4] of cellulose ethers in solvent mixtures comprising a volatile substance, a non-solvent of higher b. pt. than the volatile substance, and at least one solvent of still higher b. pt. in specified proportions.

In preparing hollow bodies from cellulose ethers[5], sheets composed of an organic cellulose derivative are

1. E. P. 359164; abst. C. A. 1932, **26**, 4969.
2. R. Schmidt, D. R. P. 553177; abst. C. A. 1932, **26**, 4611.
3. H. Dreyfus, E. P. 372835; abst. J. S. C. I. 1932, **51**, 796-B.
4. *Ibid.* E. P. 353956; abst. C. A. 1932, **26**, 5421.
5. British Celanese, Ltd., E. P. 373037; abst. J. S. C. I. 1932, **51**, 795-B.

wound on a mandrel and made to unite by means of a softening or swelling agent applied by spreading or immersion. The tubes so formed are subsequently subjected to heat and pressure. In preparing cellulose ether films and yarns[1], a suspension of white or colored pigment in some of the spinning solution is introduced into the main spinning solution during its direct passage from the filters to the spinning jets. In increasing the heat-resistance of the cellulose ether or cellulose ester textiles[2], the safe ironing temperature is increased by deposition therein of a comparatively small quantity of an insoluble metal compound by double decomposition, with or without further impregnation with fireproofing substances such as ammonium tetraborate, phosphate or chloride. Formation of the insoluble compound is effected at a temperature of 75-95°, so that it is present in the fibers in a voluminous form. Salts of tin, aluminum, calcium, barium iron, magnesium and chromium are used for this purpose.

Cellulose ether filaments with a granular core and therefore of low density and good covering power[3] are obtained by incorporating with the spinning solution such a quantity of non-solvent for the cellulose ether that ordinary dry-spinning would give a precipitated product, and directing a stream of solvent vapor (preferably the same solvent as that used in the spinning solution) onto the filaments close to the spinning jets. The vapor pressure of the non-solvent at the spinning temperature should be substantially lower than that of the solvent. When acetone is the solvent, suitable non-solvents are toluene, xylene, kerosene, carbon tetrachloride and alcohols. Filaments of organic cellulose derivatives while still plastic[4] are stretched,

1. Brit. Celanese, Ltd., E. P. 374356; abst. J. S. C. I. 1932, **51**, 767-B.
2. British Celanese, Ltd., G. Ellis and R. Storey, E. P. 374049; abst. J. S. C. I. 1932, **51**, 839-B.
3. British Celanese, Ltd., R. Roberts, E. Johnson and L. Gregory, E. P. 377712; abst. J. S. C. I. 1932, **51**, 930-B.
4. British Celanese, Ltd., W. Dickie and P. Sowter, E. P. 375423; abst. J. S. C. I. 1932, **51**, 881-B. H. Dreyfus, E. P. 375424;

only a portion or none of the stretching force being applied immediately after extrusion into the precipitating bath, or drawn through the liquid coagulant, of which at least a portion is moved so as to exert a drag upon them, or drawn against a tension exerted by a gaseous stream opposing their travel. To maintain the plasticity of the products during treatment, the solution of the cellulose derivative, the coagulating bath and the gaseous stream may contain high-boiling solvents or plasticizers.

The properties of cellulose ether filaments or films may be improved by treating them with a solvent or softening body, applied at a concentration such that the action is exercised to a limited degree[1]. Effects may be obtained on cellulose ether materials as textiles[2] by distributing on the material, locally or uniformly, a paste containing an effect material, a water-insoluble thickener incorporated with or dissolved in an agent having an appreciable solvent action on the cellulose derivative, and a direct solvent for the same. The thickener may be a cellulose ether.

Films and threads have been described[3] made from cellulose ethers containing a natural or synthetic resin which is soluble in the cellulose derivative. Resins of the phenol-aldehyde or formaldehyde-urea type are preferred, the size of the resin particles coming with 0.0005-0.0001 mm. When making sheets or films of cellulose ethers[4], they are subjected to a maturing treatment with water vapor at a raised temperature, and then wound in a space maintained at a temperature considerably below the maturing temperature. In this manner, it is said their elasticity and tensile strength are increased. To further fortify the film, thickened portions are formed near the margins, in particular to prevent tearing of edges of the film

abst. J. S. C. I. 1932, **51**, 881-B. British Celanese, Ltd., and W. Taylor, E. P. 375425; abst. J. S. C. I. 1932, **51**, 881-B.

1. H. Dreyfus, F. P. 718018; abst. C. A. 1932, **26**, 2863.
2. *Ibid.* F. P. 718019; abst. C. A. 1932, **25**, 2863.
3. *Ibid.* F. P. 39028, Addn. to F. P. 702174; abst. C. A. 1932, **26**, 1784.
4. Spicers, Ltd., and A. Wickham, E. P. 369610.

as the latter is stripped from the casting surface. When the film is to be cut longitudinally into narrow strips such as are to be used for cinematograph films, additional ridges spaced apart the width of the strips may be formed on the film[1]. To avoid the entry of bubbles of air into the solution in the casting box of a machine for casting sheets of cellulose ethers[2], the valve controlling the supply of solution from the storage tank is arranged beneath the surface of the liquid in the box so that the presence of airpockets adjacent to the valve is avoided.

Dyeing of Cellulose Ethers. Cellulose ether or acetate silk may be dyed with dispersions of indigoid dyes comprising an indole or thionaphthene group attached in position 2 or 3 to a benzene or naphthalene residue[3]; dyes from isatin, *a*-anil and *a*-naphthol (blue), thioisatin *a*-bromide and *b*-naphthol (red), isatin *a*-chloride and *m*-hydroxydiphenylamine (grey-violet), and 5.7-dibromisatin *a*-chloride and 5-hydroxyacenaphthene (blue). Textile materials containing cellulose ethers are treated by printing, stencilling, padding or spraying[4] with dyes and discharging agents having little affinity for the cellulose derivatives composing them, in conjunction with a cellulose ether solvent as ethyl lactate, the color or discharge effects being fixed in the material by drying without steaming. If thiocarbamide is applied before, during or after dyeing[5], it is retained in the material, and dyeings fast to light and acid are thus obtained with 1.4-di(methylamino)anthraquinone and other aminoanthraquinones.

Textiles composed of or containing cellulose ethers are colored by dyes of the indigo type in which an indole or thiophene residue is joined to a residue by a different kind[6], i.e., the residue of an aromatic hydroxy compound

1. Spicers, Ltd., and A. Wickham, E. P. 369609.
2. *Ibid.* E. P. 369608.
3. British Celanese, Ltd., and G. Ellis, E. P. 374884; abst. J. S. C. I. 1932, **51**, 931-B.
4. C. Dreyfus, E. P. 376797; abst. J. S. C. I. 1932, **51**, 932-B
5. British Celanese, Ltd., E. P. 373628; abst. J. S. C. I. 1932, **51**, 839-B.
6. H. Dreyfus, F. P. 728926; abst. C. A. 1932, **26**, 6156.

such as *a*-naphthol or *a*-anthrol. Suitable dyes are 2-indole 2′-(5′-phenylamine)benzene indigo (from isatin *a*-chloride and *m*-hydroxydiphenylamine), 2-thionaphthene-2′-naphthalene indigo (from thioindoxylcarboxylid acid and *b*-naphthoquinone), 2-thionaphtheneacenaphthylene indigo (from hydroxynaphthene and acenaphthoquinone), and dyes obtained from 5.7-dibromisatin *a*-chloride and 4-hydroxyacenaphthene, from 5.7-dibromisatin *a*-chloride and *a*-anthrol, and from isatin anilide and *a*-hydroxyanthranol.

Blue to violet shades are formed on cellulose ethers from aminoanthraquinonecarboxylic acid and derivatives (as the chloride) by conversion into carboxylic acidamides, or by a conversion of nitriles of aminoanthraquinones into carboxylic acid amides[1]. If aminoanthraquinones containing at least three amino groups are alkylated in such a manner that alkyl groups do not enter all the amino groups[2], deep blue colors on cellulose ethers are formed, an example being the partial alkylation of 1.4.5.8-tetraaminoanthraquinone. Or[3], cellulose ether textiles may be colored by a dye containing a single anthraquinone ring joined to a second cyclic system, as the anthraquinoneacridones or anthraquinonethioxanthones. Two or more color effects are produced on cellulose ethers and their derivatives dyed with nitroanthraquinones or their substitution products[4], by treating the dyed fiber with a reducing paste. Thus, 1-amino-4-nitroanthraquinone is produced by printing with a sodium hydrosulfide paste, giving an orange shade.

Azo dyes containing a di- or tri-sulfide grouping, dyes cellulose ether fibers in full shades from a sulfide bath below 65°, preferably at 15°. Examples are, 2.2′-dinitro-4.4′-diaminodiphenyl sulfide + *b*-naphthol, gives orange, or with

1. P. Nawiasky and A. Krause, U. S. P. 1871821; abst. C. A. 1932, **26**, 6153.
2. I. G. Farbenind., A.-G., F. P. 728659; abst. C. A. 1932, **26**, 6154.
3. H. Dreyfus, F. P. 728815; abst. C. A. 1932, **26**, 6156.
4. H. Berthold, D. R. P. 551775; abst. C. A. 1932, **26**, 4962.

m-phenylenediamine, brown-yellow; 4.4′-diaminodiphenyl disulfide + its bis-2.3-hydroxynaphthoyl derivative, blue-red, or with *b*-naphthol, red after chroming; or 4-nitro-*o*-aminophenol + 6.6′-dihydroxy-2.2′-dinaphthyl disulfide, violet after being coppered[1].

A uniform color screen may be prepared by applying dyes or other reagents to a film comprising a permeable base as cellulose acetate, an intermediate permeable colloid layer, and a cellulose ether base[2].

New Uses for Cellulose Ethers. Elastic masses for binding gypsum have been described[3], formed by mixing burnt gypsum with ethylcellulose dissolved in anhydrous solvents. An artificial plaster-of-Paris results. According to H. Frederking[4], the most satisfactory procedure for preserving paper documents is with solutions of cellulose ethers which cannot liberate acid from decomposition on standing, and cellulose acetate which may do so. The F. Heynert and F. Lucius[5] composition for use in ornamentation of fabrics, yarns and solid materials consists of 15-60% of cellulose ethers and 85-40% of the syrupy condensation product of urea or thiourea with formaldehyde, to which fillers as china clay or zinc oxide, or 1-2% of phosphoric or boric acids may be added.

O. Leuchs[6] has described the manufacture of plastic masses obtained by treating cellulose ethers with the amount of a mixture of carbon tetrachloride and methylene chloride required to impart the desired consistency, a small amount of ethyl alcohol being sometimes beneficial, especially where triphenyl phosphate is incorporated in the mass. For producing flexible electrical insulation materials[7], cel-

1. Soc. Anon. des Mat. Col. et Prod. Chim. de St.-Denis and R. Lantz, E. P. 377348; abst. J. S. C. I. 1932, **51**, 979-B.
2. G. Whitfield and Ilford, Ltd., E. P. 367028.
3. C. Mienes, D. R. P. 554969; abst. C. A. 1932, **26**, 6082.
4. Papierfabr. 1931, **29**, Tech. wiss. Teil 117; Mitt. deut. Materialprüfungsanstalt, 1932, #12, 188; abst. C. A. 1932, **26**, 5206.
5. E. P. 376540; abst. J. S. C. I. 1932, **51**, 932-B.
6. D. R. P. 554802; abst. C. A. 1932, **26**, 6134.
7. D. Traill and Imperial Chem. Industries, Ltd., E. P. 377688; abst. J. S. C. I. 1932, **51**, 945-B.

lulose ethers insoluble in and which do not swell in water are worked up with known plasticizers, especially aromatic polyethers of polyhydric alcohols, to which the usual volatile solvents and fillers may be added. In preparing windowglass substitutes[1], a fabric insertion (wire warp, and weft of textile threads which have previously been freed from air by heating in a lacquer solvent with a suitable lacquer solution), is conducted through a thin solution of lacquer or glue so that the meshes are not filled up. After drying, the whole is coated with a cellulose ether lacquer, and finally dried. G. Watkins[2] unites glass sheets with an intervening sheet of material such as celluloid or a cellulose ether, which is then treated with a mixture of a synthetic resin and a polyglycol derivative as diethyleneglycol monobutyl ether. W. Brown[3] uses glycerol for bonding together layers of glass with cellulose derivatives compositions.

J. Cooper and A. Lever[4] have described a plastic composition intended for use as a leather substitute, formed by the use of a mixture of ethylcellulose and rubber in a suitable solvent medium, and C. Dreyfus[5] has devised a method of manufacturing hollow articles such as toys, in which a closed hollow article is made of a cellulose ether thermoplastic combination, which is placed in a closed mold, the temperature being then raised so that the composition is softened, the gas confined within it causing expansion against the walls of the mold. The difficultly burnable composition of A. Daly[6] comprises a cellulose ether containing a tri-brom derivative of an acetylated benzene amine.

In the waterproofing of cellulose sheets[7], paper, film or fabric made from cellulose ethers is impregnated with

1. Kalle & Co., A.-G., E. P. 367288; abst. J. S. C. I. 1932, **51**, 462-B.
2. U. S. P. 1867787; abst. C. A. 1932, **26**, 5189.
3. U. S. P. 1873280; abst. C. A. 1932, **26**, 6090.
4. E. P. 380964; abst. J. S. C. I. 1932, **51**, 1042-B.
5. U. S. P. 1872912; abst. C. A. 1932, **26**, 6136.
6. Can. P. 321715. Belg. P. 361052.
7. Courtaulds, Ltd., and W. Glover, E. P. 375451; abst. J. S. C. I. 1932, **51**, 798-B.

a wax-free organic solution (see p. 841, n. 6; 2053, n. 8) containing a cellulose ether, petroleum jelly, a gum or resin and preferably a plasticizer. A suitable solution consists of butyl acetate 374, nitrocellulose 52, methylated spirit 26, ester gum 34, butyl phthalate 10 and petroleum jelly (vaseline) 4 parts. In the formulation of varnishes[1], nitrocellulose and an alkyl or aralkylcellulose ether are dissolved in a mixture comprising one or more aliphatic or aromatic hydrocarbons, an aliphatic alcohol of high b. pt., and a softening agent. Xylene, *iso*propyl alcohol, tetrahydronaphthalene and tricresyl phosphate is a combination recommended for varnish purposes. Or[2], a cellulose ether may be admixed with a drying, or semi-drying oil-modified "alkyd" resin[3], for varnishes intended primarily for application outdoors.

The Bakelite Corp.[4] prepare varnishes by treating phenol with a fatty acid in the presence of a converting agent such as phosphoric acid or aluminum chloride with aqueous formaldehyde in the presence of a high-boiling solvent which retards gelation, such as butyl alcohol, amyl alcohol or ethylglycol, water being removed from the product at a temperature substantially higher than 120°. The phenol and fatty acid may be replaced by a mixture of urea and thiourea[5], or mono- or di-methylol derivatives of urea or thiourea or their anhydrides. The products are incorporated in cellulose ether solutions to produce varnishes or enamels.

B. Maxorov[6] has described the new artificial resin "Alkalit," obtained by heating the sodium salt of phenolphthalein with toluoyl chloride, which, when dissolved in oil, yields an almost colorless, glossy, transparent film, un-

1. T. Ward and J. Hand, F. P. 727303, 727336; abst. C. A. 1932, **26**, 5220.
2. R. Kienle, E. P. 376332; abst. J. S. C. I. 1932, **51**, 948-B.
3. P. Schlingman, E. P. 370440; abst. J. S. C. I. 1932, **51**, 614-B.
4. E. P. 358603; abst. C. A. 1932, **26**, 4970.
5. Bakelite Corp., E. P. 357140; abst. C. A. 1932, **26**, 4726. I. G. Farbenindustrie, A.-G., E. P. 359147; abst. C. A. 1932, **26**, 4970.
6. Bull. Plastmasstroj, 1931, #1-2; Farbe u. Lack, 1932, 223; abst. C. A. 1932, **26**, 5220.

usually resistant to mineral acids and alkalis, and which is miscible with cellulose ether solutions to produce lacquers and enamels. In producing discharge effects on cellulose ether material[1], the textile is printed with a zinc or other water-insoluble metal derivative of a leuco-vat dye, or with the free leuco-compound and zinc oxide or carbonate.

Fast marine blue to black shades are obtained on cellulose ethers and esters by dyeing with 4.4'-diamine-3-methoxy-6-methylazobenzene[2], treating with nitrous acid and developing in an acid or neutral bath with 2.3-hydroxynaphthoic acid. Cellulose ethers may be weighted by treatment with a solution of an alkali metal stannate (sodium stannate), and then may be dyed[3]. Alkaline zincate solutions (potassium zincate) may be used for the same purpose[4].

Fabrics with crepe effects are prepared by taking highly twisted cellulose ether threads which have been provided with coatings of cellulosic material or cellulose derivative capable of being swollen by treatment of water or other liquid[5]. L. Lilienfeld[6] imparts a silk-like luster to cotton yarn or fabrics by treatment with solutions of cellulose ethers, cellulose xanthic esters or of *N*-substituted thiourethanes of cellulose, and then subjecting to a shrinkage treatment with sodium hydroxide or sulfide. The solutions may also contain mercaptans or sulfides of di- or poly-hydric alcohols or a sulfur derivative such as 2-hydroxy-1.3-trimethylene sulfide[7].

The manufacture of cellulose ethers of hydroxycarboxylic acids[8] which are soluble in organic solvents is con-

1. British Celanese, Ltd., G. Ellis and J. Allan, E. P. 378917; abst. J. S. C. I. 1932, **51**, 1076-B.
2. Soc. Anon pour L'Ind. a Bale, D. R. P. 554632; abst. C. A. 1932, **26**, 6157.
3. G. Ellis, U. S. P. 1874176; abst. C. A. 1932, **26**, 6159.
4. *Ibid.* U. S. P. 1874177; abst. C. A. 1932, **26**, 6159.
5. British Celanese, Ltd., H. Dreyfus, W. Dickie and C. North, E. P. 357169; abst. C. A. 1932, **26**, 5771.
6. E. P. 357120; abst. C. A. 1932, **26**, 5771.
7. L. Lilienfeld, E. P. 357190; abst. C. A. 1932, **26**, 5771.
8. H. Dreyfus, Can. P. 328388.

ducted by etherifying cellulose with sufficient halogenated acid as chloracetic acid to introduce substantially more than one ether group into the cellulose molecule, and in the presence of sufficient alkali metal hydroxide to form with any water present a solution of at least 45% concentration.

A new type of artificial yarn has been described[1] comprising an organic cellulose derivative containing about 5% glucose pentacetate. H. Dreyfus[2] has detailed methods for producing a series of cellulose ethers obtained by reacting upon cellulose with an amino- or nitro-aralkylating agent. The properties of the product may be improved by treatment with a softening agent as ethanolamine[3], and may be sized in the filament or fabric form by the use of a synthetic resin in emulsion[4], said to be easily removable by merely wetting out and submitting to a scouring operation[5]. In fabric form, organic cellulose derivatives may be embossed by treating the fabric with a dilute acetone solution sufficient to induce incipient swelling[6], and then embossing in the usual manner under heat and pressure. Or[7], if embossing a circular knit fabric with an all-over design in a single embossing step, the fabric is first treated with a softening agent for the thermoplastic derivative, and then embossed while still in double thickness. Or a design may be locally imprinted[8] by solvent wetting the fabric and

1. C. Diamond, U. S. P. 1891146. Matt effects are said to be readily obtained on this type of cellulose compound by treating with soap solution at or near the boiling point.
2. H. Dreyfus, Can. P. 328389. See R. Roberts and L. Gregory, Can. P. 326631. They improve the properties of cellulose ethers which have been coagulated by aqueous media, by subjecting the products to heat.
3. C. Dreyfus and G. Schneider, Can. P. 326248.
4. H. Dreyfus, Can. P. 325891. See H. Dreyfus, Can. P. 326441, 328162.
5. H. Dreyfus and W. Taylor, Can. P. 328949.
6. C. Dreyfus, U. S. P. 1889045. See C. Dreyfus, U. S. P. 1872700; abst. C. A. 1932, **26**, 5963. C. Dreyfus and C. Haney, Can. P. 328948. C. Dreyfus, G. Miles and G. Schneider, Can. P. 326818. C. Dreyfus, Can. P. 328384. C. Dreyfus and K. Loughlin, Can. P. 327718.
7. *Ibid.* U. S. P. 1889062.
8. W. Dickie and H. Halkyard, U. S. P. 1889061.

applying heat and pressure locally only. The fabric may be conditioned in the same manner[1].

The fabric of W. Dickie and H. Halkyard[2] prepared wholly or partially from yarns of cellulose ethers, is obtained by dampening the fabric with a wetting liquid which is not a solvent but exerts a softening or swelling action such as benzene, toluene, gasolene, together with a cellulose ether solvent as acetone, cyclohexanone or diacetone alcohol, in proportion so that the structure or strength is not impaired, and then embossing in the usual manner. A crepe effect is obtainable which is permanent to washing by pressing against sheets of woven Monel metal gauze as by passing through a plain heated roller. In the coloration of dry spun yarns of organic cellulose derivatives[3], there is applied to the filaments as they leave the spinning apparatus, but prior to winding, a dyestuff dissolved in a polyhydric alcohol. If it is desired to produce colors of substantially equal fastness to light where organic cellulose fibers with other fibers are to be treated[4], an insoluble vat dyestuff is applied, and non-diazotizable dispersed insoluble dyestuffs, then applying to the other fiber a color obtained by diazotization and development on the fiber of diazotizable cotton or acid wool dyes. The fabric may be processed by the application thereto of an albuminous substance followed by submission to the vapors of formaldehyde[5].

The C. Malm photographic film with antihalation coating[6] makes use of water soluble salts of cellulose dicar-

1. C. Dreyfus and W. Whitehead, Can. P. 328542. See C. Dreyfus and J. Dean, Can. P. 327533.
2. U. S. P. 1889061.
3. C. Dreyfus and W. Whitehead, Can. P. 327931, 327933. See C. Dreyfus, Can. P. 326847.
4. H. Dreyfus, G. Ellis and H. Olpin, Can. P. 327929.
5. H. Dreyfus, G. Langdon, A. Flower and S. Fulton, Can. P. 327007. Cf. H. Barthelemy, U. S. P. 1876130.
6. U. S. P. 1884035. A representative formula is given as sodium cellulose phthalate, 5 parts, Crystal Violet 6B, 4.5, Tartrazine 2, Glycerol 0.2, Saponin 0.1 and water to 100 parts. The following dyes are stated as especially applicable: Rhodamine B, Nigrosine, Bismark Brown, Metanil Yellow and Auramine.

boxylic acid esters in the base or anti-halation layer, such as sodium, potassium or ammonium cellulose phthalates or cellulose aceto-hydrogen-phthalates or aceto-hydrogen-succinates, the available dyes being practically unlimited. When benzanthrone is condensed with formaldehyde in sulfuric acid and then caused to react with an organic acid halide such as acetyl chloride or benzoyl chloride in the presence of aluminum chloride[1], intermediates or dyes are formed suitable for use as pigments or from the vat, or direct dyes for cellulose ether materials, being especially applicable for the production of yellow dyes. Material sensitized with diazo compounds alone, or in conjunction with azo components[2], is protected by applying with adhesive on the sensitive face or on both faces, a transparent sheet of cellulose ether, or a sheet of cellulose hydrate lacquered with a solution of a cellulose ether.

Carbohydrate ethers readily soluble in organic solvents and even in water[3], are obtainable by causing an alkylene oxide and caustic alkali to act simultaneously on the carbohydrate in the presence of water at normal temperature and without application of pressure. As carbohydrate may be used potato flour, cotton, α-cellulose and wood pulp, and as an alkylene oxide may be used ethylene, propylene or butylene oxides. Hydroxyethylcellulose, hydroxypropylcellulose and hydroxybutylcellulose have been described and their corresponding acetates, propionates, butyrates, laurates, stearates, palmitates and oleates specified. Of the

1. Imperial Chemical Industries, Ltd., D. Jones, R. Thomson and J. Thomas, E. P. 358420. The British Celanese, Ltd., and G. Ellis (E. P. 380061; abst. J. S. C. I. 1932, **51**, 115) make dyes giving yellow shades on organic cellulose derivatives by couplings (free from sulfonic groups) of diazotized aminophenols with 1-aryl-3-methyl-5-pyrazolones which are acetylated. Acetylation of *p*-aminophenol with phenylmethylpyrazolone gives pure yellow.

2. Kalle & Co., E. P. 371153.

3. M. Hagedorn, W. Ziese, B. Reyle and R. Bauer, E. P. 365110. U. S. P. 1876920; abst. C. A. 1933, **27**, 101. These acylating processes may be carried out without difficulties with a corresponding acid anhydride in the presence of an acylating catalyst or with a corresponding acid chloride, if necessary in the presence of a tertiary amine, as pyridine, triethylamine or trihydroxyethylamine. Refer to Soc. Anon. pour L'Ind. a Bale, F. P. 711513. Swiss P. 149995.

ten separate examples given, an illustrative method is to steep α-cellulose for 4.5 hrs. at room temperature in 50% strength NaOH solution, then pressing until an alkalicellulose is obtained containing about 71% alkali. While cooling with ice, the alkalicellulose is treated while stirring, with sufficient alkylene oxide that it is always covered by the treating liquor. After 42 hrs. a water-soluble hydroxyethylcellulose is obtained containing 7-8 OH-groups per C_{24} cellulose. It may be freed from alkali by extraction with methyl alcohol. The hydroxyethylcellulose may be acetylated by being introduced into a mixture of glacial acetic acid 16, acetic anhydride 8, and zinc chloride 1. The mixture is treated 6 hrs. at 50-60° in a kneading machine, precipitated by water and dried. A film produced from the hydroxyethylcellulose acetate shows a lengthening by water of 0.4-0.5%.

Water-soluble compounds of xantho-fatty acids have been described[1], obtainable in concentrated solutions, by using as solvents aqueous solutions or suspensions of phenylamine compounds as monomethyl-, dimethyl-, monoethyl- and diethyl-aniline, -toluidine or -xylidine. A method of dyeing the cellulose ethers has been described[2], specially applicable to water-insoluble alkylcellulose with direct, acid, vat or sulfur dyes, where the cellulose ether is of the type which is insoluble in water at 16° and above, but which swells or is soluble in water below this temperature, particularly below 10°. In dyeing, water is allowed to act upon the cellulose ether at a temperature at which they incipiently swell but do not disintegrate or dissolve, and the swollen material then treated with aqueous solutions of direct dyes in the usual manner. Thus, if an ethylcellulose which swells in water at 5-8°, but which dissolves in water below 5° is to be dyed, then water at 5-8° is used for

1. L. Lilienfeld, U. S. P. 1890393. Can. P. 327192. F. P. 724045; abst. C. A. 1932, **26**, 4952. Either water, or a mixture of water with methyl or ethyl alcohols or acetone may be used for dissolving the cellulose-xantho-fatty acids.
2. L. Lilienfeld, U. S. P. 1890392.

swelling. An opalescent effect may be produced on paper which has been gelatinized or rendered translucent[1], by treatment of the paper with a cellulose ether lacquer in which has been incorporated waxy materials or natural or synthetic resins, in conjunction with dyestuffs if desired, by a variation of the solvent power of the liquids used to dissolve the materials. The paper is intended for covering cartons and artificial masses.

Esters of fatty acids and ethyleneglycol alkyl-ethers have been detailed[2], being excellent solvents for ethyl- and benzyl-cellulose. They are obtained by heating ethylglycol with stearic, margaric, palmitic or oleic acids in the presence of a small amount of sulfuric acid. Ethylglycol stearate (ethyleneglycol monoethylether ester of stearic acid) is an example. C. Gränacher[3] has described new cellulose compounds obtained by treating cellulose or viscose with aromatic compounds containing a NO_2 group capable of being reduced to an NH_2 group, and a substituent capable of double decomposition in the presence of an acid-binding agent, and reducing the products. The products may be colored by diazotizing and coupling with appropriate components. Thus, cotton treated with 10% NaOH and then in a bath of molten 1-chlor-2.4-dinitrobenzene in the presence of lithium carbonate, is colored brown with diazo-*p*-dinitrobenzene.

The literature does not appear clear upon the nomenclature of combinations of cellulose with crotonic acid, and hence confusion exists in the designation of the crotonic ethers of cellulose (crotylcellulose) in contradistinction to the cellulose crotonates (cellulose crotonic esters, crotonylcellulose). Both classes have been stated as crotonylcellulose in both literary contributions and patent disclosures.

1. I. G. Farbenindustrie, F. P. 725069; abst. Chem. Zentr. 1932, II, 3978.
2. J. Buckley, U. S. P. 1869660; abst. Chem. Zentr. 1932, II, 3980.
3. F. P. 687298; abst. C. A. 1931, **25**, 812. D. R. P. 551863; abst. C. A. 1932, **26**, 4950.

As coagulant for filaments of organic cellulose derivatives, neutral oils or oily liquids have been disclosed as superior[1], irrespective as to whether the filaments have or have not been subjected to a stretching operation[2]. A new method of filament stretching has been patented[3], comprising drawing the plastic filaments through a body of liquid moving so as to exert a drag upon them. The viscosity of cellulose derivatives may be reduced[4] by incorporating them in a solvent which has an electrolyte dissolved therein. Plastic derivatives result when the cellulose ether is admixed with higher fatty acids by means of a harmonious solvent or solvent combination[5]. If it is desired to produce a pattern effect on cellulose compounds[6], a reducing discharge is first applied, incorporating in the discharge an unsulfonated pyrazolone dye. The abrasive composition of J. Walsh and A. Steinberger[7] comprises incorporating an organic cellulose derivative with a plasticizer and a fire-retardant, adding an abrasive substance, and molding to the desired shape by means of heat and pressure. Fabrics showing crepe effects[8] are obtained by weaving in highly twisted threads of organic cellulose derivatives in which are incorporated substances having high affinity for water as glycerol, and thereafter treating the fabrics with water. Such fabrics may be printed with a thickened paste containing agents which accelerate the dulling, being afterwards dried, and the dull effects produced by a passage of short duration through a hot solution[9], at a temperature near the boiling point, containing small quantities of neu-

1. C. Dreyfus and W. Whitehead, Can. P. 326816.
2. British Celanese, Ltd., W. Dickie and P. Sowter, E. P. 375423; abst. Text. Mfr. 1932, **58**, 505.
3. H. Dreyfus, E. P. 375424; abst. Text. Mfr. 1932, **58**, 505.
4. C. Dreyfus and W. Whitehead, Can. P. 328945.
5. *Ibid.* Can. P. 326817.
6. H. Dreyfus and G. Ellis, Can. P. 327006. See British Celanese, Ltd., E. P. 373406, 375313.
7. Can. P. 327255.
8. Societe Pour la Fabrication de la Soie Rhodiaseta, E. P. 368110; abst. Silk J. & Rayon World, 1932, **9**, #100, 45.
9. Heberlein & Co., A. G., E. P. 376097; abst. Text. Mfr. 1932, **58**, 505.

tral or slightly alkaline inorganic salts, which act as protectors against the delustring action on the unprinted parts. The fabric may be printed with a composition containing glycolchlorhydrin and tragacanth, dried and passed through a 1% solution of sodium sulfate at 90°.

In producing delustered or diminished luster filaments of organic cellulose derivatives[1], the spinning solution contains finely divided titanium dioxide, ammonium stearate or glucose pentacetate being also components. Or[2], the filaments may be spun directly from a solution containing glucose pentacetate. A solution of a cellulose ether may be colored by a mineral pigment[3] by incorporating therewith a solvent which has but little dissolving action upon the etherized cellulose. In conditioning and softening cellulose ether and cellulose acetate filaments[4], it is advocated to treat with the higher polyhydric alcohols in conjunction with oils.

A. Jaeger[5] and also A. Jones[6] have contributed general articles on ethyl- and benzyl-cellulose, the contribution of the latter having special reference to the technical applications of the benzylcelluloses.

In preparing articles of cellulose ethers[7] especially applicable in dentistry (see p. 2536), and for the manufacture of artificial limbs, foot supporters, acid-proof receptacles and wall-coverings, the dissolved etherified cellulose is in-

1. H. Dreyfus, R. Riley, R. Parkinson and H. Sims, E. P. 352611. Can. P. 326441.
2. Courtaulds, Ltd., and C. Diamond, E. P. 352610; abst. C. A. 1932, **26**, 5435.
3. L. Clement and C. Riviere, E. P. 350894; abst. C. A. 1932, **26**, 5421.
4. British Celanese, Ltd., E. P. 351084; abst. C. A. 1932, **26**, 5434. See Can. P. 326818.
5. Kunstseide, 1932, **14**, 332; abst. C. A. 1933, **27**, 188.
6. Brit. Plastics, 1932, **4**, 292. He gives as a typical type molding powder, asbestos 300, chalk 300, clay 300 and benzylcellulose 125 parts, with a molding pressure of 30-60 lbs. per square inch, the sp. gr. of the benzylcellulose being 1.20. On account of the excellent flowing properties of benzylcellulose, it is especially applicable for the injection process.
7. W. Hengstmann, E. P. 357100, 359077; abst. C. A. 1933, **27**, 413, 414.

corporated with synthetic resins, and methyl or ethyl adipate. The composition may be vulcanized with sulfur in a manner similar to rubber. M. Hagedorn and E. Rossbach[1] form mixed cellulose ethers as propylhydroxyethylcellulose, by reacting upon alkalicellulose with an alkyl halide as propyl chloride or benzyl chloride, in the presence of an unsubstituted alkylene oxide such as ethylene oxide. G. Henkel[2] precipitates cellulose derivatives from solution in a flocculent and readily filterable form by effecting the precipitation in the presence of a finely divided auxiliary substance capable of decomposing the mixture of cellulose derivative and solvent formed at the beginning of the precipitation. Water, and aqueous solutions of salts, acids and alkalis are suitable auxiliary substances.

In making threads and films from cellulose derivatives[3], stretch spinning is effected by allowing the filaments while still in the plastic condition, to impinge on a force offering a resistance to the movement of the materials by means of a mobile mass of gas.

1. U. S. P. 1877856; abst. C. A. 1933, **27**, 413.
2. D. R. P. 557244; abst. C. A. 1933, **27**, 413.
3. H. Dreyfus, F. P. 730725; abst. C. A. 1933, **27**, 415.

CHAPTER XV

ANALYTICAL DETERMINATIONS

The analytical determinations in connection with the cellulose ethers are but few in number, and comprise a determination of the purity of the cellulose base material from the viewpoint of suitability for etherification purposes, an examination as to the composition of the alkalicellulose necessarily formed as a step preliminary to etherification, and the usual physical constants of the cellulose ethers, with methods for the determination of the alkyl or aralkyl groups united to the cellulose complex.

Moisture and Ash in Cellulose. The cellulose usually employed for etherification purposes at the present time, on account of the small cost factor difference between purified wood pulp and cotton linters pulp, both in sheet form, is the latter. The normal moisture in the sheets averages 5.6-6.8% as received from the car. By means of a cork borer or shot-gun wad cutter, a number of circles is obtained from different portions of individual bales constituting the shipment, a total of 10-15 gms. being dried in a Petrie dish or watch glass at 105° for 4 hrs., or until successive half hour dryings show not greater than a 2% deviation in moisture. If a moisture-free balance is not available, the drying is conducted in a wide-mouth weighing bottle, glass-stoppered.

Ash is determined by gently sintering a 5-10 gm. sample in an open porcelain or platinum crucible to a dull red heat so as not to volatilize possible chlorides. The ash should not exceed 0.22%. The ash content of typical cottons of the world has been given by R. Fargher and M. Probert[1] as varying from 1-1.3%, these results being of the natural cotton and in the unpurified state.

1. J. Text. Inst. 1926, **17**, 46-T; abst. C. A. 1926, **20**, 1326.

Fat and Resinous Matter. Wood pulp usually give a detectable amount of resinous matter. In the production of viscose rayon from wood pulp sheets, this trace is sometimes observable as a scum forming on the top of the acidifying liquor in the bleaching step of purifying the viscose rayon in hank form. A 20-30 gm. sample obtained as above, and without previous moisture elimination to the "bone dry" stage, is placed in an ordinary Soxhlet extraction apparatus, and extracted with purified ether or crystallizable benzene, the extractive being slowly evaporated off from the receiving thimble at the bottom, then the thimble dried at 105° for about 2 hrs. and weighed. For cotton the ether-extract should not exceed 0.12%. For purified wood pulp, the maximum should be 0.2% by weight. R. Fargher and L. Higginbotham[1] have described delicate methods for fat and wax determination in cotton.

Determination of Alpha-Cellulose. This method is the result of the labors of Sub-Committee 2 of the Division of Cellulose Chemistry of the American Chemical Society, and gives closely duplicable results when applied to wood pulp or cotton pulp sheets of high purity as used for technical etherification purposes[2]. The pulp is given no preliminary treatment, being cut into 0.5 inch (1.25 cm.) squares, placed in a glass-stoppered container for 48 hrs. to attain a uniform moisture content throughout the sample.

Approximately a 3 gm. sample is accurately weighed in a weighing bottle, and placed in a 250 cc. Pyrex beaker, 35 cc. of 17.5% carbonate-free sodium hydroxide solution being added[3], temperature of the solution being 20°, and the solution allowed to stand 5 min. With a short glass rod, the end of which has been flattened out to form a disk

1. J. Text. Inst. 1924, **15**, 75; 1926, **17**, 233-T; abst. C. A. 1924, **18**, 1752; J. S. C. I. 1926, **45**, 529.

2. Jour. Ind. Eng. Chem. Anal. Soc. 1929, **1**, 52.

3. The sodium hydroxide solution is prepared by dissolving sticks of alkali in an equal weight of water, and allowing to stand 10 days for the sodium carbonate and impurities to settle. The clear, supernatant liquid is decanted and diluted with carbon dioxide-free water until the density at 15° is 1.197. Such a solution contains 17.4-17.6% NaOH per 100 gms. solution.

1 cm. in diameter, the pulp is macerated 10 min., adding intermittently in 10 cc. portions, a total of 40 cc. sodium hydroxide solution at 20° during this interval[1]. The beaker is covered with a watch glass. After 30 min. additional mercerizing treatment in a water bath at 20° (total mercerization time 45 min.), 75 cc. distilled water at 20° are added to the alkalicellulose mixture followed by thorough stirring. The contents of the beaker are filtered immediately by means of suction in a 40 cc. Gooch crucible[2] having a finely perforated bottom, allowing the cellulose to form its own mat. The filtrate is poured through the mat a second and a third time if necessary, to catch any fine material.

The residue in the Gooch crucible is washed with 750 cc. distilled water at 20° by means of suction. The suction tube is disconnected, 40 cc. of 10% acetic acid added at 20°, and allowed to soak 5 min. Then the suction is applied to remove the acid. The alphacellulose is washed with distilled water at 20° until free from acid, litmus being used to test the filtrate. The alphacellulose is carefully removed from the Gooch to a tared, flat, glass-stoppered weighing bottle. The alphacellulose is opened and dried at 105° to a constant weight, that is, the first consecutive constant weights obtained after 1 hr. heating intervals fol-

1. An interval of 15 min. should elapse between the times of starting the alkaline treatment of the individual triplicate samples. Such a procedure allows time before proceeding to the next sample in the triplicate determination for the various steps in the procedure, such as impregnation, maceration, filtration, and partial washing. If 5 min. are allowed between the addition of a part of the alkali and the beginning of maceration, it will be found that sulfite pulp swells to 5-6 times its original volume, and the fibers can be much more easily macerated. The remaining 10 min. interval, during which the remaining 40 cc. portion of the alkali is added, making a total of 75 cc., has been found ample time for the maceration of pulps. With such a scheme, for example, one would add the alkali to the samples at 9:00, 9:15 and 9:30 o'clock respectively, and filtering would begin at 9:45, 10:00 and 10:15.

2. Coarse Jena glass filter crucibles may be used in the place of Gooch crucibles specified in the directions.

3. To test the acidity of the wash water on litmus paper, the last few drops removed after the addition of water should be used. As a result of a careful study of the method by a number of chemists

lowing an initial drying of at least 6 hrs. The weighing bottle and its contents are allowed to cool in a desiccator for 30 min. and then re-weighed.

The alphacellulose yield is calculated on the oven-dry weight of the material. Duplicate 3 gm. samples for moisture determination should be weighed out at the same time that the samples for the alphacellulose determination are taken.

Moisture and Ash in Cellulose Ethers. A representative sample is selected and quickly powdered in a mortar. A 2-3 gm. portion is then weighed out in a wide mouth glass-stoppered weighing bottle and dried at 105° for 3 hrs., cooled and weighed. The material is then re-heated at 105° for a further period of one-half hour, cooled in a desiccator and weighed again. The loss upon second drying should not exceed 2%. The normal moisture content varies from 6-9% for methylcellulose to a minimum of 4.5-6.5% for benzylcellulose, varying within rather wide limits depending upon whether the inside of the individual lumps as received are corneous and semi-transparent and hard, or whether they are uniformly yellowish-white and free from horny particles.

A 5-7 gm. sample of the powder obtained by grinding is placed in a porcelain or platinum crucible and very gently heated until the mass melts to a limpid liquid. Heating is continued cautiously to prevent loss by spirting until after decomposition sets in and the clear liquid liberates gas and becomes opaque. Heating is continued to a maximum of low red heat until all carbonaceous matter has been volatilized when the crucible is cooled in the desiccator and

working independently it was found that (1) dilution of the sodium hydroxide-cellulose solution with an equal volume of water and stirring immediately before filtering does not precipitate *b*-cellulose and facilitates filtration. (2) The yield of alphacellulose is not affected by washing with water at temperatures above 20°. (3) Cellulose is more soluble in NaOH solution alone than in a similar solution containing dissolved cellulose. (4) Mercerization in air and in nitrogen gives the same yields of *a*-cellulose.

weighed. The ash found is usually within the limits of 0.1-0.4%.

Determination of Solubility. In commercial work, the solubility characteristic is usually satisfactory in a unitary or mixed solvent or solvent combination, if the results are within 3% of each other in duplicate determinations. A fairly accurate and quick method which has been used in the Author's laboratory for some time comprises making a 200 cc. sample of the desired percentage composition of cellulose ether and solvent in a 250 cc. salt mouth bottle, with foil covered cork stopper, in which is placed several steel balls of about half-inch diameter. If a rotating wheel is available, the bottle is attached thereto and allowed to slowly rotate several hours until a homogeneous mixture appears to have been formed. Otherwise, the bottle is shaken at intervals until the same effect is produced. Immediately at the close of agitation, two clinical centrifuge tubes of 50 mm. capacity and graduated to 0.5 mm. the first 10 mm. from the bottom and in 1 mm. intervals from 10-50 mm., are filled to the 50 mm. mark with the solution, placed in the centrifugal and rotated for at least 20 min., or until the supernatant liquid appears clear but for traces of haze. The two tubes are removed and the amount of sediment read off. Each 0.5 mm. represents 1% of undissolved residue. In more delicate work, the supernatant liquid may be nearly all poured off, replaced by fresh solvent, the tube stoppered, then shaken frequently for several hours, re-centrifuged, and a reading again taken. It is recommended to make the solubility determination upon the previously dried sample for most concordant results.

Determination of Viscosity. As previously stated, the viscosity of a solution of a cellulose ether or ester is an important commercial means of evaluating its suitability for a given purpose and a criterion of its applicability for a particular use. Theoretically, the viscosity is measured by the shearing stress in dynes per square centimeter required to move either of two parallel planes, 1 ccm. apart

relative to each other, with a velocity of 1 ccm. per second, the space between the planes being filled with the fluid under examination. It is measured in poises or centipoises, the centipoise being the approximate velocity of water at 20° (1.005 centipoises). For rough work a 50 cc. glass burette or separatory funnel with the aperture in the stopcock made quite small may be used for the more fluid solutions, the time required to empty from one mark to the other (usually a 50 cc. range) being recorded and compared against an arbitrarily set up standard, the determinations being taken always at a given temperature, usually 20°. The results, of course, are but comparative.

The two methods in general use for more accurate work are the "ball fall" or "falling ball" method, and measurements made with a viscometer as that of Cochius or of Ostwald, both being constructed on the same general principle.

The Ball Fall Method of Viscosity Estimation. This has been worked out carefully by the Hercules Powder Co., primarily as applied to nitrocellulose solutions, and is used extensively for this purpose in the United States and elsewhere. The falling ball viscometer has been developed from Stokes' mathematical derivation of the relation between the viscosity of a liquid and the rate of fall of a small sphere through the liquid. In this derivation the assumption is made that the ball falls through liquid of infinite extent. The resulting formula calls for correction factors as one is unable to employ an infinite length of liquid in a practical test. Ladenburg has developed an equation for these corrections. The Hercules Powder Co. has determined the correction factors for the following described apparatus, and the tolerances necessary to maintain an accuracy of 3.8% (exclusive of stop watch errors) with the instrument standardized.

The method comprises in noting the length of time required for a ball to fall a definite distance through the liquid being tested and which is contained in a glass tube

of definite uniform internal diameter, the whole being maintained at a definite temperature. The parts used in the instrument have the following specifications: The glass tube is 355 mm. (14 inches) long, of uniform internal diameter of 25.0 mm., ± 0.5 mm. (0.984, ± 0.02 inch). This specification should be closely followed, as small variations in tube diameter cause large errors in results. A tolerance, for instance, of ± 0.5 mm. allows for a variation in results of 2.2%. Two marks, 254 mm., ± 0.8 mm. (10 in., ± 1/32 inch) apart are to be etched on the tube, so that each mark is approximately 50 mm. (2 inches) from an end of the tube. One end of the tube is closed by means of a cork stopper wrapped with tin foil. The balls, of steel, are 7.938 mm., ± 0.01 mm. (0.3125 in., ± 0.0005 in.) diameter, and weigh 2.0385 gm. ± 0.007 gm. A large percentage of 5/16th inch ball bearings on the market will pass these specifications. The time is to be noted by means of a good stop watch reading to 0.2 sec., the temperature to be noted by a thermometer graduated to 0.1°.

The apparatus used to maintain the proper temperature will depend on the number of tests to be made, and the accuracy required. If a large number of tests of high accuracy are to be made, a constant temperature water bath should be provided capable of maintaining a temperature of 25°, within 0.1°. If less accurate results are satisfactory, the temperature should be accurately noted and the reading obtained corrected by the use of suitable factors. The time in seconds multiplied by 3.77 gives the viscosity in poises at the temperature specified of the standard test solution, this factor differing for any instrument not within the above specifications. Any standard test solution may be used. That of the Hercules Powder Co., upon which the above factors are based, consists of the following formula:

Nitrocellulose (dry)	12.2% by wt.
No. 1 Denatured alcohol	22.0% by wt.

Ethyl acetate, 85-88% ester, sp. gr. 0.887-0.893
at 15.5°/15.5° . . . . . 17.5% by wt.
Toluene, sp. gr. 0.864-0.874 at 15.5°/15.5°,
b. pt. 108.4-112.4° . . . . . 48.3% by wt.

200 grams of the above solution are required, the ingredients to be weighed to 0.02 gm. accuracy. The nitrocellulose must be thoroughly dried before dissolving. With the above as standard, or the operator may prepare his own standard from a cellulose ether in a known solvent combination, the unknown to be tested is made up to the same percentage by weight on a dry basis with the same solvent proportions and of the same purity as the solvents employed in preparing the standard. The solution thus prepared with attention given to the solution being complete and without the presence of an undissolved or partially dissolved particle, is placed in the tube, and the time noted for the passing of the bottom of a ball from the upper to the lower mark. The method, although comparative, admits of close duplicate determinations being made.

Viscosity Determination by Ostwald Viscometer. This apparatus (Fig. 15) consists of the cylindrical bulb *a*, which tapers uniformly to the capillary tube *cd*. At *d*, the tube widens gradually and is bent into a U-shape, the other limb of the U being the wide tube *bc;* the spherical bulb *b* is at the lower end. At *gg'*, above and below *a*, lines are engraved on the glass. The regularity of the taper from bulb *a* to *c* is very important.

A definite volume of liquid is introduced into *b e* by means of a pipette and sucked up the capillary to fill the first bulb. The time occupied by the liquid in flowing from the mark above the bulb to the other below the bulb is noted.

Then if t_0 = time for standard liquid of known viscosity, p_0 = specific gravity, n_0 = viscosity, and t, p, are the corresponding values for another liquid

$$\frac{n}{n_0} = \frac{p\,t}{p_0 t_0}.$$

There has been much controversy concerning the sources of error in this instrument, and different experimenters have used apparatus of varying dimensions when seeking extreme accuracy in their determination.

Its dimensions are:

fh—Length, 8 cm.; external diameter, 0.5 cm.; internal diameter, 0.3 cm.
gh—Length, 8 cm.
gg'—Length, 8 cm.
Bulb *a*—Capacity, 3.5 to 4.0 c. c.; internal diameter, 1 cm.
cd—Length, 12 cm.; external diameter, 0.5 cm.; internal diameter, 0.5 cm. to 0.06 cm. (uniform bore).
Bulb *b*—Diameter, 3 cm.
be—Length from *e* to top of bulb, 22 cm.; external diameter, 1 cm.; internal diameter, 0.8 cm.

The other pieces of apparatus required for the determinations are:

A 10 c.c. standard pipette.
A thermometer 0° to 50°, graduated in fifths of a degree, corrected against a standard thermometer.
A 2 liter beaker, height 23 cm., diameter 11 cm.
A stand and clamp.
A stop-watch reading 1/5th seconds.
A 100 c.c. pipette.
Six 250 c.c. cylinders.

The 2-liter beaker is completely filled with water, and brought to a temperature of 20 ± 0.1°. The viscometer is clamped in position within the beaker, so that *cd* is vertical and the bulb *a* is immersed, the upper mark *g*, just projecting above the surface; 10 c.c. of the liquid, the viscosity of which is to be measured, are taken by means of the pipette and run into bulb *b*, through *be*, the pipette being drained for 30 seconds. The liquid is then carefully drawn up by suction to fill the bulb *a*, and its level adjusted to the mark *g*. It is then released and allowed to flow back through *cd*, the time taken for the level to fall from *g* to *g'*, being accurately measured by the stop-watch.

If the absolute viscosity is required, the time of flow for another liquid, the viscosity of which at 20° is known,

is measured in the same way; the density of each liquid at 20° must be known.

The formula $\frac{n}{n_0} = \frac{p\,t}{p_0 t_0}$ is then applied.

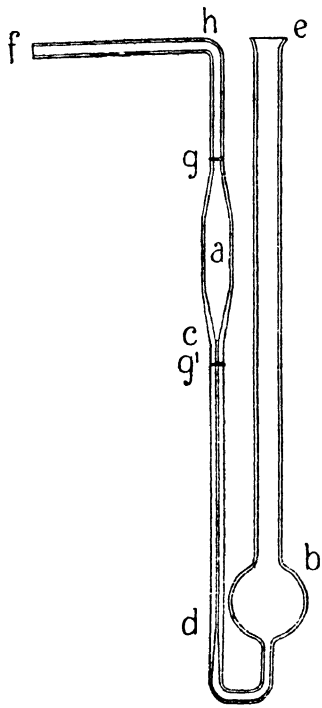


Fig. 15. Ostwald Viscometer.

Determination of Alkoxyl Groups. The ready cleavage of compounds of organic compounds containing methoxyl and ethoxyl by means of boiling hydriodic acid, first quantitatively determined by S. Zeisel[1], has been utilized as the basis of a quantitative method for the estimation of these groups, saponification of the resulting vapors of methyl iodide or ethyl iodide being conducted into alcoholic silver

1. S. Zeisel, Monats. 1886, **7**, 406.

nitrate solution with the precipitation of silver iodide or the double compound $AgI.2AgNO_3$, the latter being readily decomposed by water. From the amount of silver iodide formed, the equivalent amount of CH_3O or C_2H_5O may be calculated, it being remembered that both methoxyl and ethoxyl groups yield the same amount of silver iodide, so that the nature of the alkoxyl group must be previously determined, or the proportion of the two when both are present, as in methylethylcellulose. The amount of AgI from 100 gms. of compound has been designated by Zeisel as the "silver iodide number."

The original method of Zeisel has been modified in many particulars, and for the determination of alkyl groups in conjunction with the carbohydrates, the arrangement of M. Stritar[1] has been found satisfactory. This apparatus (Fig. 16) comprises a boiling flask *A* of about 40 cc. capacity, carrying a fused-in bent side tube narrowed to 1 mm. diameter for the introduction of a current of CO_2, the constriction being near the juncture of the tube with the flask as indicated in the illustration. The washing apparatus consists of a mantle *B*, surrounding the top of the reflux tube and having a tubular stopper reaching close to the bottom of the mantle. The size of the mantle is chosen so that it contains at least 5 cc. of washing fluid. The mantle is provided with a side tube, bent, and then enlarged at *C* in the form of a stopper, through which the vapors are led into the absorption flask *D* and the guard flask *E*, containing respectively 45 cc. and 5 cc. of an alcoholic solution of silver nitrate. The lower end of the outlet tube is of greater diameter at the bottom, so that the precipitate formed will not be liable to clog the opening. The glass stoppers should all be made tight by means of water or syrupy phosphoric acid. The receiver *D* is a wide-neck Erlenmeyr flask, marked at about half its height to indicate a capacity of 45 cc. The second receiver is simi-

1. M. Stritar, Zeits. anal. Chem. 1903, **42**, 579; abst. J. S. C. I. 1903, **22**, 1211.

larly marked at a point to indicate a capacity of not over 5 cc.

The boiling is effected by means of a bath of phosphoric acid, at such a rate that the zone of condensation is situated about half way up the reflux tube. The author has also described a device for the filtration of the silver iodide. The operation is conducted as follows: Place 0.2-0.3 gm. of the substance to be determined in flask *A* with

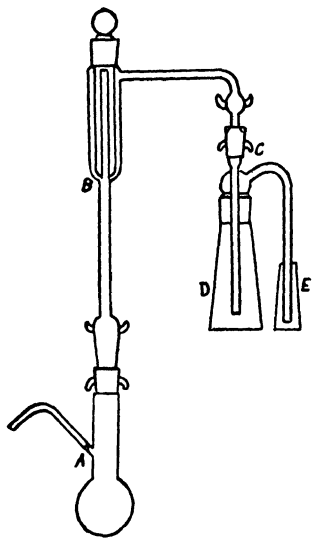


Fig. 16. Stritar Apparatus for Alkoxyl Estimation.

10 cc. HI sp. gr. 1.7, b. pt. 127°, and slowly heat until the acid begins to boil. An unglazed porcelain fragment serves to prevent bumping. The HI should boil gently so that the boiling liquid reaches about half the height of the ascending tube. Violent boiling long continued should be avoided since too much HI would then distill into the head, and this, as well as the ascending tube become coated with sub-

limed iodide and other distillation products which hold back small amounts of alkyl iodide.

The head *B* is charged with a layer of 0.25 gm. red phosphorus which serves to free the methyl or ethyl iodides in vapor form from associated HI. A slow stream of CO_2 is led in through the side tube of the reaction flask which serves to lead the alkyl iodide vapors through the wash apparatus, which frees it from HI and I vapors, and into the receivers *D* and *E*, containing 50 cc. and 5 cc. respectively of alcoholic $AgNO_3$ solution. The first turbidity is observable in the first receiver in 10-15 min. after boiling of the HI begins, and this quickly increases by the formation of the white precipitate of $AgI.2AgNO_3$. The operation is generally completed in 1-1.5 hrs., and is recognized by the sudden clearing of the liquid standing above the now crystalline precipitate. The second receiver nearly always remains clear, and if it does not become opalescent in several minutes after adding several volumes of water thereto, it may be disregarded. The contents of the receiving flask are now washed into a 600 cc. beaker and diluted with water to 500 cc., the adhering precipitate being usually somewhat dark colored from adhering silver phosphide, is removed from the inlet tube by means of a small brush and wash bottle. Then acidulate with 5-10 drops of dilute nitric acid and let stand 0.5-1 hr. on a boiling water bath. By this treatment the double salt $AgI.2AgNO_3$ is decomposed to readily filterable AgI, which after cooling, is filtered and weighed in the usual manner. Or, the silver iodide may be volumetrically determined, but on account of the fact that the titer of alcoholic silver nitrate quickly changes, this method of procedure is not as accurate.

The calculation is very simple. 100 parts by weight of AgI are equivalent to 13.20 parts CH_3O or 19.21 parts C_2H_5O.

In the preparation of the reagents care must be exercised, especially to determine that the HI is free from sulfur and phosphorous compounds, and hence not prepared from

H_2S and iodine. In a blank test, it should not cause a turbidity of AgI in the silver nitrate upon the addition of water. However, the formation of a slight brownish deposit at the mouth of the lead-in tube is seldom avoidable and results from red phosphorus used for the purification of alkyl iodide vapors. The HI may be obtained of suitable quality, and especially purified for this purpose, or may be made from red phosphorus and iodine, running a blank to assure its suitability.

The alcoholic silver nitrate solution is prepared by dissolving 20 gms. $AgNO_3$ in 50 cc. water and adding 450 cc. pure alcohol which has been distilled over caustic alkali or lime. It keeps clear for a considerable period in the dark. In event of turbidity, simple filtration is all that is necessary to restore its usefulness. The red phosphorus for the wash vessel is purified by digesting a half hour on the water bath with ammoniacal water, then washing with water and alcohol and drying in the air. Several times purification in this manner eliminates certain volatile impurities. According to Stritar, a longer boiling with 10% NaOH is beneficial. One filling of the apparatus suffices for several determinations.

THE END

ADDENDA

Page	*Add*
39, n. 3,	Ital. P. 190222.
49, n. 1,	Austrian P. 107289.
59, n. 2,	Ital. P. 209183.
107, n. 1,	Ital. P. 240422.
108, n. 2,	Can. P. 276359.
113, n. 2,	Ital. P. 242584 (Same as U. S. P. 1618413).
115, n. 4,	Can. P. 275953.
126, n. 4,	Swiss P. 119678.
129, n. 1,	Swiss P. 127542.
129, n. 2,	Swiss P. 127543.
129, n. 4,	U. S. P. 1793390.
134, n. 1,	Can. P. 285048.
138, n. 2,	Ital. P. 228814. Belg. P. 352382.
142, n. 2,	Can. P. 276555. Belg. P. 348213.
142, n. 3,	Can. P. 276553. Ital. P. 228813. Belg. P. 350777.
143, n. 1,	Can. P. 276554. Belg. P. 344887.
145, n. 3,	Belg. P. 351703. See E. P. 171432.
147, n. 2,	U. S. P. 1850929.
147, n. 4,	Belg. P. 353739.
165, n. 3,	D. R. P. 543463.
165, n. 5,	U. S. P. 1811689.
169, n. 2,	Can. P. 285979.
186, n. 2,	F. Addn. 40247 to F. P. 666897.
194, n, 3,	D. R. P. 539367.
203, n. 3,	U. S. P. 1824961.
215, n. 5,	Can. P. 319755. D. R. P. 531221.
225, n. 2,	Can. P. 297694. Ital. P. 275773.
229, n. 2,	Addn. 38319 to F. P. 690432.
248, n. 3,	Belg. P. 364521.
277, n. 3,	Can. P. 315497.
302, n. 6,	E. P. 362523, Addn. to E. P. 357169.
576, n. 5,	F. P. 493658.
596, n. 2,	Ital. P. 222794.
596, n. 6,	U. S. P. 1805919.
607, n. 6,	Ital. P. 241182 (Same as E. P. 244143).
625, n. 7,	U. S. P. 1817318.
626, n. 5,	U. S. P. 1792113.
631, n. 5,	U. S. P. 1851665.
680, n. 2,	Ital. P. 240761.
720, n. 5,	F. P. Addn. 39297 to 597922.
747, n. 1,	Can. P. 317331.
762, n. 6,	U. S. P. 1835997.
820, n. 8,	D. R. P. 551754.
995, n. 6,	Can. P. 287094.
1385, n. 1,	D. R. P. 554698.
1696, n. 1,	F. P. 692604.

ERRATA

Page	*Line from top*	*Change*	*To read*
39	note 3, line 2	remove 493	
41	note 4, line 1	1920	1921
41	note 4, line 2	1919	1920
42	note 5, line 3	J. S. C. I.	Bull. Soc. Chim.
51	note 12, line 1	1444351	1444331
71	note 2, line 1	Seidel	Speidel
72	note 3, line 2	Weltzein	Weltzien
73	note 1, line 1	Weltzein	Weltzien
85	note 3, line 1	1923	1924
93	3rd	Olsen	Olson
95	2nd	R. Becker	B. Becker
116	note 2, line 2	Weltzein	Weltzien
118	note 1, line 2	860-8	860-B
139	note 1, line 1	C. Olpin	H. Olpin
145	1st	stilbine	stilbene
148	note 3, line 1	1828	1928
164	note 4, line 4	**15**	**25**
164	note 5	add	F. P. 638448
173	16th	thiocarbanalide	thiocarbanilide
179	24th	753	576
180	25th	2.5-di(phenylamino) benzoquinone	2.5-di(*p*-aminophenyl-amino)-benzoquinone
183	note 1, line 1	British Celanese, Ltd.	S. Carroll
188	note 6, line 2	198-B	198-A
194	11th	reder	dered
202	note 1, line 1	Hahn	Hann
205	note 5, line 3	F. P. 522931	F. P. 523931
207	note 2, line 3	**8**	**48**
230	note 5, line 2	Richtmayer	Richtmyer
253	4th	benzyl-*p*-sulfonate	benzene-*p*-sulfonate
264	4th	thiocynanate	thiocyanate
265	2nd	thiocyannate	thiocyanate
269	17th	Souter	Sowter
275	note 1, line 1	E. P.	F. P.
286	28th	monoethylcellulose	monoethylbenzyl-cellulose
298	4th	1-amino-4-*p*-acetamidoanili-	1-amino-4-anili-
301	18th	chlormethoxylsulfonyl	chlormethoxysulfonyl
301	29th	W. Spiers	F. Spiers
303	8th	droxybenhenic	droxybehenic
304	5th	producable	producible
357	note 1, line **14**	Acetoylsis	Acetolysis
361	note 2, line 21	Aust. P.	Aust. Appl.
364	note 3, line 1	1912, **31**	1909, **28**
378	footnotes	note number 21	note number 3
378	footnotes	note number 3	note number 4
378	footnotes	note number 4	note number 5
398	note 1, line 12	**8**	**4**
402	note 1, line 1	G. Lutz	O. Schmidt, G. Lutz and T. Eichler
402	note 1, line 2	1912, **6**	1913, **7**
414	line 8, notes	F. P. 452347	F. P. 452374
421	line 14	Jaquet	Jacquet

Page	*Line from top*	*Change*	*To read*
438	note 3, line 1	**12**	**11**
467	note 6, line 1	Pimental	Pimentel
529	note 2	insert Kunst. before journal reference	
587	note 1, line 4	Lervux	Leroux
588	18th	Walcott	Wolcott
606	6th	stilbine	stilbene
611	note 4, line 1	G. Bate	S. Bate
612	note 1, line 1	G. Bate	C. Hollins
626	note 5, line 1	H. Mugdan	M. Mugdan
648	note 6, line 1	E. Gault	H. Gault
677	12th	Sedacyl	Setacyl
690	note 6, line 1	M. Mattingley	N. Mattingley
720	note 2, line 2	Hougoniot	Hugoniot
739	11th	B. Brigl	P. Brigl
770	12th	cyclohexylyamine	cyclohexylamine
791	28th	Engleman's	Engelmann's
837	8th	spectograms	spectrograms
853	8th	Durinodone	Durindone
941	note 8, line 1	F. Chiverton	F. M., Ltd.
944	2nd	nitrosine	nigrosine
977	13th	boryl	bornyl
994	note 3, line 1	Mattingly and Lancegays	Mattingley and Lancegaye
1041	note 4, line 1	Livesey	Livsey
1105	note 1, line 2	1280	280
1107	note 1, line 2	1280	280
1114	note 3, line 1	C. Wid	G. Wid
1121	5th	R. Andress	K. Andress
1130	note 4, line 1	C. Stein-	G. Stein-
1134	17th	Erdman	Erdmann
1134	18th	man	mann
1137	note 6, line 1	Herzog	A. Herzog
1162	note 3, line 5	**-4**	**43**
1164	15th	R. Becker	B. Becker
1177	13th	Andersen	Anderson
1177	note 5	2489	2469
1200	22nd	B. Londberg	G. Londberg
1208	25th	Tomahisa	Tomihisa
1219	29th	Willows and R.	Willows and A.
1345	1st col., line 21	acetoproprionate	acetopropionate
1568	note 2, line 1	Hahn	Hann
1574	note 3, line 1	Olsen	Olson
1812	note 3, line 1	A. Carter	C. Carter
1856	note 7, line 1	T. Cathelineau	H. Cathelineau
1886	14th	*2-Methylpentan-*	*2-Methylpenten-*
1886	note 1	A. Lorenz	L. Ach
1899	28th	H. Theumann	M. Theumann
1943	19th	K.	B.
2001	18th	ply	pyl