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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 fur 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 (Koninclijk 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'Etudes 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. Micrógr.	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 Natural History
Ann. Surg.	Annals of Surgery
Ann. Storia Natur.	Annali di Storia Naturale
Ann. Telegr.	Annales Telegraphiques
Annab.-Buchh. Ver. Naturk. Ber.	Bericht über 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 Központ 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 Universität 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 Hermbstädt
Archiv. Anat. Micro.	Archives d'Anatomie Microscopique
Archiv. Anat. Physiol.	Archiv. für Anatomie, Physiologie und wissenschaftliche Medicin
Archiv. Anthropol.	Archiv. für Anthropologie...Organ der deutschen Gesellschaft für Anthropologie, Ethnologie und Urgeschichte
Archiv. Anthropol. Etnol.	Archivio per l'Anthropologia e la Etnologia
Archiv. Augenheilk.	Archiv. für Augenheilkunde
Archiv. Augen-. Ohrenheilk.	Archiv. für 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. für Entwicklungsmechanik der Organismen
Archiv exper. Path. Pharm.	Archiv. für 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. für die gesammte Physiologie des Menschen und der Thiere (Pflüger)
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 für 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. für 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. für Verdauungs-krankheiten
Archiv. Wiss. Heilk.	Archiv. des Vereins für gemeinschaftliche Arbeiten zur Förderung 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 för Kemi, Mineralogi och Geologi
Arkiv. Math. Astron. Fysik	Arkiv för 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 für okonomische Chemie, etc.
Artus, Vierteljahresschrift	Vierteljahresschrift für 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

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. Künst. 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 Münchener Gesellschaft für 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 für 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. Sächs. Ges. Wiss.	Berichte über die Verhandlungen der Königl. Sächs. Gesellschaft der Wissenschaften zu Leipzig
Ber. Veter. König. Sach.	Berichte über das Veterinärwesen im Königreich Sachsen
Berg. Hüttenm. Jahr.	Berg- und hüttenmannisches Jahrbuch
Berg. Hüttenm. 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 Blätter für Blecharbeiter
Blätter Kunstgew.	Blätter für Kunstgewerbe
Blätter Zuckerrüb.	Blätter für Zuckerrübenbau
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.	Memoires de la Société des Sciences Physiques et

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 Jahrbücher, 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 für die Provinz Brandenburg
Brass World	Brass World and Platers Guide, The
Braunk.	Braunkohle
Braunschw. Ver. Naturwiss. Jahr.	Jahresbericht des Vereins für 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, Evkönyvei	A' Magyar Tudos Tarsasag' Evkonyvei (Year Books of the Hungarian Scientific Association)
Buda, Palyamunkak.	Termeszettudomanyi Palyamunkak
Buda, Tudomanytar.	Tudomanytar Közre 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 für 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 Kärnten
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 für gerichtliche und öffentliche Medicin
Casper Wochensch	Wochenschrift für die gesammte Heilkunde
Cassel Jahr	Jahresbericht, dann Bericht, über die Thätigkeit 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 für die medicinischen Wissenschaften
Centr. Mineral.	Centralblatt für Mineralogie, Geologie und Palaeontologie
Centr. Papierfabr.	Centralblatt für Papierfabrikation
Centr. Path.	Centralblatt für 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 für 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 über 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 1e (-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.	Correspondénzblatt für 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.	Beiträge zur Geologie des Grossherzogthums Hessen und der angrenzenden Gegenden
Darmst. Ver. Erdk. Notiz.	Notizblatt des Vereins für 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 Beiträge 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 für 1858–60 v. d. Gesellschaft für Natur- und Heilkunde in Dresden
Dresden, Mitth. Poly. Schule	Mittheilungen der K. Sächs. 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 für 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
Földt. Közlön	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. Röntgenstr.	Fortschritte auf dem Gebiete der Röntgenstrahlen
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 fur Pathologie
Französ. Ann.	Französische Annalen für die allgemeine Naturgeschichte, Physik, &c.
Freiberg, Jahr. Berg Hütt.	Jahrbuch fur den Berg- und Hüttenmann. Herausg. von der Königl. Berg-Akademie zu Freiberg
Freiburg, Beitr	Beiträge zur Rheinischen Naturgeschichte
Freiburg, Ber	Berichte über die Verhandlungen der Naturforschenden Gesellschaft zu Freiburg i. B.
Freie K.	Freie Künste
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.	Fühlings 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 über den Naturwissenschaftlichen Verein in Schleiz
Gerber	Der Gerber
Germar, Mag Entom.	Magazin der Entomologie
Germar, Zts. Entom.	Zeitschrift für 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 Württemberg
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	Glashütte, Die
Glas-Ind.	Glas-Industrie, Die
Gleanings Sci.	Gleanings in Science
Globe	See Geneve Soc. Geogr. Mem.
Glückauf	Glückauf; Berg- und Hüttenmannische-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 Götheborg
Göttingen, Abh.	Abhandlungen der Koniglichen Gesellschaft der Wissenschaften zu Göttingen
Göttingen, Comment.	Commentationes recentiores Societatis, etc.
Göttingen, Nachr.	Nachrichten von der Georg-Augusts Universitat und der Königl. 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 Graubündens
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 für 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 für 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 für (Kryptogamische) Literatur.
Heidelb. Jahr. Lit.	Jahrbücher der Literatur. Verhandlungen des Naturhistorisch-Medicinischen Vereins zu Heidelberg
Heidelb. Naturhist. Med. Festschr.	Festchrift zur Feier des fünfhundertjährigen 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 für 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 Förhandlingar
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 für Naturwissenschaften in Hermannstadt

Hermbstätt, Archiv.	Archiv der Agriculturchemie für denkende Landwirthe
Hermstädt, Bull.	Bulletin des Neuesten und Wissenwürdigsten aus der Naturwissenschaft, etc.
Hermbstädt, 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 bürgerlichen 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 fur 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. Blätt.	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. fur 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 fur 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 für 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 Ernährungsstörungen, 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 Yozk
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 fur 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 für 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. Gahr. 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 über der Fortschritte der Tier-Chemie
Jahr. wiss. Bot.	Jahrbücher 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 für die gesammte Mineralogie zu Jena
Jena Denkschr.	Denkschriften der Medicinisch-Naturwissenschaftlichen Gesellschaft zu Jena
Jena Geogr. Ges. Mitth.	Mittheilungen der geographischen Gesellschaft (für Thüringen) zu Jena
Jena Sitzber	Sitzungsberichte der Jenaischen. Gesellschaft für Medicin und Naturwissenschaft
Jena Zts.	Jenaische Zeitschrift für 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 für Kärnten
Karsten	See Botan. Untersuch.
Karsten, Archiv.	Archiv für 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 Fünfzigjährigen 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)
Kiöbenh., Reg. Soc. Med. Acta.	Acta Regiae Societatis Medicae Havniensis
Kiöbenh., Vidensk. Forh.	Videnskabelige Forhandlinger ved Sioelland Stifts Landemde
Kiöbenh, Vidensk. Meddel.	Videnskabelige Meddelelser fra den Naturhistoriske Forening i Kjöbenhavn
K. K. Ges. Aerzte	See Med. Jahr.
Klausenburg	See Kolozsvar
Kliniek	Kliniek
Klug, Jahr. Insect.	Jahrbücher 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
Königsb. Archiv.	Konigsberger Archiv fur Naturwissenschafften und Mathematik
Königsb. Med. Jahr.	Konigsberger medicinische Jahrbücher; herausgegeben von dem Verein fur wissenschaftliche Heilkunde zu Konigsberg
Königsb. Schr.	Schriften der physikalisch-ökonomischen 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.	Kuhn-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. selbstandigen 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 Ze tschrift fur wissenschaftliche Landwirthschaft und Archiv des Koniglich 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 Wissen. schaften
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 Sachsischen Gesellschaft der Wissenschaften zu Leipzig
Leipz. Färb. Ztg.	Leipziger Farber- und Zeugdrucker-Zeitung
Leipzig Jablon. Preisschr.	Preisschriften gekrönt 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 für Mineralogie, Geognosie, Geologie, und Petrefaktenkunde
Leonhard Bronn, Neu. Jahr.	Neues Jahrbuch für 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 für 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 för Mathematik och Naturvetenskap
Lund Bot. För.	See Bot. Centrbl.; Bot. Notiser
Lund, Phys. Sällsk. Tidskr	Physiografiska Sallskapets Tidskrift
Lüneb., Denkschr.	Denkschriften des naturwissenschaftlichen Vereins für das Füsrtenthum Luneburg
Lüneb., Jahr. Naturwiss. Ver.	Jahresbericht über die Thatigkeit des naturwissenschaftlichen Vereins in Lüneburg
Lüneb. Jheft. Naturwiss. Ver.	Jahreshefte des Naturwissenschaftlichen Vereins für das Fürstentum Lüneburg
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 für 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 jährigen 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 közlönye. (Report of the Hungarian Academy. Communications of the Mathematical and Natural Science Sections)
Magyar Böripar	Magyar Böripar
Magyar Nemzeti Muzeum	See Termr. Füz.
Magyar Termt. Tars.	See Termt. Közlön.
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 köreböl. Kiadja a Magyar Tudomanyos Akademia. (Memoirs in the Mathematical Sciences. Published by the Hungarian Academy of Science)

Magyar Tud. Akad. Ertek. (Termt.)	Ertekezesek a Termeszettudomanyok körebol. 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'Lle 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 für 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 Tübingen
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 für die gesammten Naturwissenschaften
Meisner, Anzeiger	Naturwissenschaftlicher Anzeiger der Allgemeinen Schweizerischen Gesellschaft für 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. könig. 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 Hüttenkunde
Moll, Jahr. Berg.	Jahrbücher 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 für 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.
München, Sitzber.	Sitzungsberichte der Königl. Baierischen Akademie der Wissenschaften zu München
München Thierarznei-Schule Jahr.	Jahresbericht der k. Central-Thierarznei-Schule in München
München Thierärztl. Hochschule Jahr.	Jahresbericht der k. Thierärztlichen Hochschule in München
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 (Färberei 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 für 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 für 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 für Wissenschaft, Kunst, und öffentliches Leben
Oesterr. Zts. Berg. Hüttenw.	Oesterreichsche Zeitschrift fur Berg- und Hüttenwesen
Oesterr.-ung. Zts. Zuckerind.	Oesterreichisch-ungarische Zeitschrift für Zuckerindustrie und Landwirtschaft
Off. Gaz.	Official Gazette, United States Patent Office
Offenbach. Ver. Naturk. Ber.	Bericht des Offenbacher Vereins für Naturkunde über seine Thätigkeit
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 Rübenzuckerindustrie
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 Ertesitö a Kolozsvari Orvos-Termeszettudomanyi Tarsulat es az Erdelyi Museum-Egylet Termeszettudomanyi Szakosztalyanak az..szaküleseiröl..(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 Societa 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 für...
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 für populäre 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
Pflüger, 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 für 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. Medd'el.	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
Plön Biol. Sta. Forschungsber.	Forschungsberichte aus der Biologischen Station zu Plön
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 Beiblätter
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 für 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.	Jahrbücher des Bohmischen Museums für Natur- und Länderkunde
Prag, Jahr. Realschule	Jahresbericht der k. k. Böhmischen 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. Böhmischen 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 für 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 Königl. Preuss. Geodätischen Instituts
Preuss. Geod. Inst. Veroff.	Veroffentlichung des Konigl. Preussischen Geodatischen Instituts
Preuss. Landes-Oekon.-Kolleg. Archiv.	See Landw. Jbüch.
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.	Jahrbücher 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 für 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 Färberzeitung
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 Fünfzigjährigen 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. Ver.	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 für 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.	Rüssisches 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 für 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.	Tran sactions 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.	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 für 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 für 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 königlich preussischen Akademie der Wissenschaften zu Berlin
Sitzber. konig. preuss. Akad.	Sitzungsberichte der königlich preussischen Akademie der Wissenschaften
Skand. Archiv Physiol.	Skandinavisches Archiv für Physiologie
Skand. Naturf. Forh.	Förhandlingar vid det af Skandinaviska Naturforskare och Lakare hallna Möte i Götheborg
Skand. Naturf. Mod. Forh.	Forhandlingerne ved de Skandinaviske Naturforskeres 11te Mode i Kjobenhavn fra den 3die til den 9de Juli, 1873
Skand. Natur Möt. Förh.	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 Meidçhe
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 für Steiermark
Steiermark. Mont. Lehranst. Jahr.	Die Steiermarkisch ständische montanistische Lehranstalt zu Vordernberg
Stein, Ann.	Annalen der Geburtshülfe überhaupt 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. Sällsk Handl.	Handlingar ved Svenska Läkare-Sällskapet
Stockholm, Vet. Akad. Lefnadsteckn.	Lefnadsteckningar öfver Kongl. Svenska Vetenskaps-Akademiens efter ar 1854 aflidna Ledamöter
Stockholm, Ymer	Ymer. Tidskrift utgifven af Svenska Sällskapet 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 Läk. Sällsk. Forh.	Forhandlingar ved Svenska Läkare-Sällskapets 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-österreichischen 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 Füzetek...Kiadja a Magyar Nemzeti Muzeum. (Natural History Magazine...published by the Hungarian National Museum)
Termt. Közlön.	Termeszettudomanyi Közlony...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. Farb. Ztg.	Textil und Färberei-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 Tübingen
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 för Vetenskap och Konst
Upsala Läkaref̈or. Förh.	Upsala Läkareförenings Förhandlingar
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 für 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 Hülfswissenschaften
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 Elèctrical 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 Provinciäl-Blätter. Verhandlungen der Gesellschaft zur Beförderung der vaterländischen Cultur in Minden
Westphäl, Ver. Jahr.	Jahres-Bericht des Westfälichen Provinzial-Vereins für 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 Blätter
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 fünfundzwanzigjährigen 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
Württemberg, Jahresh.	Jahreshefte des Vereins für vaterländische Naturkunde in Wurttemberg
Würzburg, Arb. Bot. Inst.	Arbeiten des Botanischen Instituts in Würzburg
Würzburg, Arb. Phys. Lab.	Arbeiten aus dem Physiologischen Laboratorium der Würzburger Hochschule
Würzburg. Med. Zts.	Würzburger medicinische Zeitschrift
Würzburg. Naturwiss. Zts.	Würzburger Naturwissenschaftliche Zeitschrift; Herausgegeben von der Physikalisch-Medicinischen Gesellschaft
Würzburg Phys. Med. Festschr.	Festschrift zur Feier ihres fünfzigjähreign Bestehens herausgegeben von der Physikalisch-Medizinischen Gesellschaft zu Würzburg
Würzburg, Phys. Med. Sitzber.	Sitzungsberichte der Physikalisch-Medicinischen Gesellschaft zu Würzburg
Wurzburg, 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 tür 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 Berücksichtigung 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 für deutsche Landwirthe
Zts. Dreschler	Zeitschrift für Dreschsler, Elfenbeingraveure und Holzbildhauer
Zts. Düngerw.	Zeitschrift für Düngerwesen
Zts. Electrochem.	Zeitschrift fur Electrochemie
Zts. Entom. (Breslau)	Zeitschrift für Entomologie im Auftrage des Vereins für schlesische Insektenkunde zu Breslau
Zts. Ethnol.	Zeitschrift für Ethnologie
Zts. exper. Path. Therap.	Zeitschrift für experimentelle Pathologie und Therapie, Berlin
Zts. Farben-Ind.	Zeitschrift für Farben-Industrie
Zts. Feuerwehr.	Illustrirte Zeitschrift für die deutsche Feuerwehr
Zts. Fischerei	Zeitschrift für Fischerei
Zts. Fleisch. Milchhyg.	Zeitschrift fur Fleisch- und Milchhygiene
Zts. Geburtsh.	Zeitschrift für Geburtshülfe und Frauenkrankheiten
Zts. Geburtsh. Gynäkol	Zeitshrift für Geburtshülfe und Gynäkologie
Zts. ges. Brauw.	Illustrirte Zeitschrift das gesammte Brauwesen
Zts. ges. Getreidew.	Zeitschrift für das gesamte Getreidewesen
Zts. ges. Naturwiss.	Zeitshrift fur die Gesammten Naturwissenschaften
Zts. Ges. Ornith.	Zeitschrift für die gesammte Ornithologie
Zts. ges. Textilind.	Zeitschrift fur die gesamte Textilindustrie
Zts. ges. Wasserwirts.	Zeitschrift für die gesamte Wasserwirtschaft
Zts. Heilk.	Zeitschrift für Heilkunde, als Fortsetzung der Prager Vierteljahrsschrift für praktische Heilkunde
Zts. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten
Zts. Immunit. Abt. I. 13. Abt. Ref.	Zeitschrift für Immunitätsforschung und experimentelle. Therapie. Abteilung I. 13. Abteilung II. or Ref. 1 vol.
Zts. Induk. Abst. Vererbungslehre	Zeitschrift für Induktive Abstammungs- und Vererbungslehre
Zts. Instrumentenk.	Zeitschrift für Instrumentenkunde
Zts. Klin. Med.	Zeitschrift für Klinische Medizin
Zts. Krebsforsch.	Zeitschrift für 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 Unterrricht
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 für Parafin Industrie
Zts. Parasit.	Zeitschrift für Parasitenkunde
Zts. Pflanzenkrankheiten	Zeitschrift für Pflanzenkrankheiten
Zts. physik. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandschaftslehre
Zts. Physik. Chem. Unterr.	Zeitschrift für dem physikalischen und chemischen Unterricht
Zts. Physiol. Chem.	Zeitschrift für physiologische Chemie (Hoppe-Seylers)
Zts. prakt. Geol.	Zeitschrift fur praktische Geologie
Zts. Psychol.	Zeitschrift für Psychologie und Physiologie der Sinnesorgane
Zts. ration. Med.	Zeitschrift für rationelle Medicin
Zts. Reprodukt.	Zeitschrift für Reproduktiontechnik
Zts. Rübenzuckerind.	Neue Zeitschrift für Rübenzuckerindustrie
Zts. Schiess Spreng.	Zeitschrift für das gesammte Schiess- und Sprengstoffwesen
Zts. Spiritusind.	Zeitschrift für Spiritusindustrie
Zts. Telegr. Ver.	Zeitschrift des deutsch-osterreichischen Telegraphen-Vereins
Zts. Thiermed.	Zeitschrift für Thiermedicin
Zts. Tuberkulose	Zeitschrift für Tuberkulose und Heilstättenwesen
Zts. Ver. deut. Ingen.	Zeitschrift des Vereins deutscher Ingenieure
Zts. Ver. Rübenzuckerind.	Zeitschrift des Vereins für die Rübenzucker-Industrie des deutschen Reichs
Zts. Ver. Zuckerind.	Zeitschrift des Vereins der deutschen Zuckerindustrie
Zts. Wiss. Geogr.	Zeitschrift für wissenschaftliche Geographie
Zts. wiss. Mikro.	Zeitschrift fur 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 für die gesammten Naturwissenschaften
Zürich, Soc. Entom.	Societas Entomologica. Organ für den internationalen Entomologenverein. Zürich
Zürich, Unters. Physiol. Lab.	Untersuchungen aus dem Physiologischen Laboratorium der Züricher 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

CHAPTER II

RISE AND DEVELOPMENT OF THE CELLULOSE ESTER INDUSTRY

The etherified carbohydrate compounds are so intimately—yes inextricably—bound up with the older and broader carbohydrate carboxylate art best known by the cellulose acetates that any serious attempt to indicate the theoretical possibilities of the cellulose ethers without a fundamental knowledge of the history, development and industrial trend of the organic cellulose esters would be incomplete in showing but *one* side of the picture.

The technical development of the cellulose acetate industry has been built up in no small degree by cumulative observations and practical experience developed from that portion of the field of nitrocellulose usefulness having to do with the peaceful arts in contradistinction to the warlike pursuits. Especially is this obvious in the application of solvents, non-solvents, diluents, flexilizers, extensifiers and thermoplastic-inducing bodies both volatile and non-volatile, liquid and solid, which had (or had not) been found useful in connection with nitrocellulose utilization. This fundamental fact is to be remembered, that the cellulose ethers as well as the cellulose esters have little or no value in the dry or undissolved state, and hence solvents play a basically important part.

The experience accumulated in both the nitrated cellulose and acetylated cellulose fields have and are being investigated in order to open up new possibilities of usefulness for the etherified carbohydrates, especially the alkyl and arylcelluloses. The rise and expansion of the inorganic and organic cellulose esters rest primarily upon the ability to induce new and valuable properties by the manipulation of solvents and solvent combinations. The control and modification of solubility, viscosity, evaporative speed and

non-hygroscopic effects with low-boiling and inexpensive dissolvants, and the ratio of evaporable to fixed components in solution with these carbohydrate derivatives, appears to be the most promising and lucrative field for present investigation and exploitation of technical usefulness.

Because of this, the industry of etherified cellulose is being builded upon disclosures previously made in connection with nitro- and acetylated-cellulose, and primarily in the dissolved condition, and this is the reason for the inclusion of this Chapter in this work. No such generalization aiming at completeness has heretofore been published. The development of the carbohydrate carboxylates is given in historical sequence in the following pages, with a maximum brevity compatible with clarity, as pointing to an aggregation or association of ideas, methods and products which may possibly be found applicable in connection with the cellulose *ethers* to augment their usefulness, extend their field of applicability, and render more easily available and widespread, certain products which up to the present have been generally classified with the luxuries of life.

In order to more clearly point out the primary advancements, the art has been divided into periods, and in each period, the data has been segregated under the name of the individual or firm, arranged alphabetically. In this manner, not only is the general trend of development unfolded, but the theoretical and inventive progress of any one person is apparent, his contributions being epitomized together in each period. While, from the viewpoint of continuity of presentation the subject matter may seem disjointed, from an historical survey, the art can be traced during its logical expansion from the chronological angle, which is the purpose of this Chapter.

Premiere Memoir of Schuetzenberger. An interesting prelude to the investigations of this chemist on the acetation of various carbohydrates and glucosides, was his seven contributions in 1858 in the *Comptes rendus* on various plant

alkaloids, in which glacial acetic acid and acetic anhydride were used in many of the researches[1], and his memoirs in 1862 upon the acetation of cyanogen and of iodine[2]. Impressed by the researches of M. Berthelot on the compound ethers of certain polyatomic alcohols as glycerol[3], he focussed his attention on the action of acetic anhydride on cellulose, starch, sugars, mannite and certain glucosides, and this is the title of his twentieth memoir—presented by his friend Dumas at the September 1865 meeting of the French Academy of Sciences, and published in the Society's journal for that year[4].

Inasmuch as this is the foundation upon which has been developed our knowledge of the diversified technical applications of the cellulose acetates of today, and in order to obtain an insight into the factors underlying the birth

1. Compt. rend. 1858, **46**, 47, 894, 1065, 1234; **47**, 79, 81, 233, 235; abst. Ann. 1858, **108**, 346; J. prakt. Chem. 1858, **74**, 227; Ann. Chim. Phys. 1858, **54**, 56; J. Pharm. Chim. 1859, **35**, 31.

2. Compt. rend. 1862, **54**, 154; Ann. 1862, **123**, 271. Compt. rend. 1862, **54**, 1026.

3. Compt. rend. 1853, **36**, 27; **37**, 398; 1854, **38**, 668; J. prakt. Chem. 1853, **58**, 412; 1854, **62**, 133, 451; J. Pharm. Chim. 1853, **23**, 410; 1854, **25**, 346. Compt. rend. 1853, **37**, 855; Ann. Chim. Phys. 1854, **41**, 432; J. prakt. Chem. 1854, **61**, 156. Ann. Chim. Phys. 1854, **41**, 216; J. prakt. Chem. 1853, **60**, 193; J. Pharm. Chim. 1853, **24**, 259; Paris, Soc. Biol. Mem. 1854, **1**, 191. Compt. rend. 1855, **41**, 452; Ann. Chim. Phys. 1856, **47**, 297; J. prakt. Chem. 1856, **67**, 230, 235; **69**, 450; Nuov. Cimento, 1856, **4**, 59; Paris, Soc. Biol. Mem. 1856, **3**, 203. Compt. rend. 1857, **45**, 175; Ann. Chim. Phys. 1858, **52**, 428; J. prakt. Chem. 1857, **72**, 315; J. Pharm. Chim. 1858, **33**, 347; Inst. 1857, **25**, 266; Nuov. Cimento, 1857, **6**, 142. Compt. rend. Soc. Biol. 1857, **4**, 112; Ann. 1858, **108**, 117. Ann. Chim. Phys. 1862, **66**, 110; 1863, **68**, 364; J. Pharm. Chim. 1863, **43**, 482. Compt. rend. 1863, **56**, 1131, 1168. M. Berthelot and S. de Luca, Compt. rend. 1857, **45**, 178, 244; Ann. Chim. Phys. 1858, **52**, 433; J. prakt. Chem. 1857, **72**, 317; Il Giamb. Vico, 1857, **4**, 127; J. Pharm. Chim. 1858, **34**, 19; Inst. 1857, **25**, 266; Nuov. Cimento, 1857, **6**, 132; **7**, 437. M. Berthelot and L. Pean de St. Gilles, Compt. rend. 1861, **53**, 474; Ann. Chim. Phys. 1862, **65**, 385; **66**, 5; 1863, **68**, 225; J. Pharm. Chim. 1861, **40**, 247. Compt. rend. 1862, **54**, 1263; **55**, 39; Inst. 1862, **30**, 123. Compt. rend. 1862, **55**, 324; Inst. 1862, **30**, 257. Compt. rend. 1863, **56**, 393; J. Pharm. Chim. 1863, **44**, 199. Compt. rend. 1863, **56**, 648.

4. Compt. rend. 1865, **61**, 485, 486; abst. Bull. Soc. Chim. 1866, (2), **5**, 291; Zts. Chem. 1866, **9**, 16; Chem. Centr. 1865, **36**, 1036; J. prakt. Chem. 1866, **97**, 250; J. Pharm. Chim. 1865, (4), **2**, 376; Jahr. Chem. 1865, **18**, 594; Ber. 1869, **2**, 163, 556.

of this important division of human progress, the words of the discoverer of acetated cellulose as contained in the contribution above cited, are reproduced in full.

"The paper which I have the honor to submit to the Academy of Sciences, has for its aim to record the first results of an extended work which will be the subject of a subsequent paper. The remarkable and important researches of Mr. Berthelot have demonstrated that the sugars and their congeners perform the functions of polyatomic alcohols of a high order, and are capable like glycerol, of forming true compound ethers.

"The method by means of which this eminent chemist obtains the etherified derivatives of sugars and of their congeners, consists in heating these substances with an acid hydrate at temperatures varying with the stability of the substances employed. This process has the advantage of being general, but besides the fact that it requires considerable time (40-50 hours), it furnishes in many cases but very small amounts of derived products—too small to admit of analysis, much less to be profoundly studied.

"In the specific case of derived acetic esters of sugars, of cellulose, etc., I obtained results much more advantageous from the viewpoint of yield and rapidity of action, by replacing the crystallizable acetic acid by the anhydride. The organic substance, generally insoluble (in the proper sense of the word) in boiling anhydride, commences to corrode (disintegrate) as soon as the temperature of 138°-140° has been reached. The phenomenon once commenced, continues of itself and is accompanied by an active ebullition without the aid of artificial heat. The only products engendered are: 1, hydrated acetic acid; 2, an acetic derivative soluble in hydrated acetic acid, soluble or insoluble in water according to the nature of the substance employed. In the latter case it suffices to pour the syrup into water, the syrup being thick and remaining until the completion of the reaction, which takes but a few minutes. The precipitate is washed with water. In the first case it is diluted with

water, decolorized if necessary by means of washed animal charcoal, and dried in a vacuum over lime.

"Under these conditions the starch or the fecula has given two colorless and solid acetic compounds; one insoluble in water, but soluble in alcohol and acetic acid; the other soluble in water and alcohol, of a bitter taste. Both readily saponify with potash, and furnish dextrin and an acetate. The soluble derivative contains more acetate than the other.

"Cellulose is not attacked by acetic anhydride until 160°, when it dissolves in it with the formation of a thick syrup and hydrated acetic acid. The *cellulose acetique* is a white, amorphous solid, insoluble in water and alcohol, but soluble in hydrated acetic acid; boiling potash decomposes it rapidly with recovery (regeneration) of cellulose. Cane sugar, glucose, lactose, mannite and dulcite, give water soluble derivatives under these conditions, solid or very viscous, and of bitter taste. They probably differ from the liquid compounds formed by Berthelot by a smaller proportion of combined acid. Analysis and profound study of these products will be given later and will serve as adjuncts to the fine researches of Berthelot.

"Anhydrous acetic acid reacts in the same manner on the natural glucosides such as tannin, salicin, amygdalin, etc., and on many vegetable coloring matters (bresiline, hematine, chrysoramnine, etc.). By means of these acetic esters—the preparation of which in large amounts is easy—I shall probably arrive at obtaining other esters whose synthesis has as yet not been realized.

"Heated with ammonium hydroxide, they readily produce nitrogenous products precipitable by tannin, and which approximate those which P. Thenard and myself obtained by submitting hydrocarbonated substances to the action of ammonia at 140°."

It is evident from the above, that in order to obtain an esterification approaching near the maximum, Schuetzenberger was compelled to use extremely high temperatures in the absence of acetic anhydride and a catalyst, and in

doing so, the cellulose underwent profound degradation, so that large amounts of the acetated cellulosebioses were formed as well as appreciable amounts of water soluble esters (sugars). However, this investigator was the first to show that cellulose could be so treated as to introduce the acetic acid molecule into the cellulosic aggregate, and in doing so there resulted a new product insoluble in water, but soluble in alcohol and acetic acid.

This announcement of Schuetzenberger apparently created but little discussion among men of reflection, for no one apparently sought to verify or amplify these original observations, and it was not until four years later that Schuetzenberger in conjunction with Naudin returned to the subject and contributed the following additional information[1]:

"Acetic anhydride easily reacts with a large number of organic substances playing the part of polyatomic alcohols. Thus in a very short time there is obtained a complete transformation of the substance into acetic derivatives of a degree of substitution which is higher or lower, depending on the amount of anhydride and the temperature. This reaction may be utilized:

"1. To determine the degree of atomicity of an alcohol.

"2. For the formation and study of acetic derivatives difficult to otherwise secure.

"3. To ascertain as to whether a basic substance plays the role of alcohol.

"The use of acetic anhydride offers the advantages over the use of acetyl chloride that the formation of hydrochloric acid is avoided, which in many cases may modify the composition of the substance experimented upon. Furthermore, the reaction is very often obtainable in an open vessel or at any rate requires only a slight pressure as it sets in between 130° and 160°. It is for the purpose of turning such a plain

1. Compt. rend. 1869, **68**, 814; abst. Chem. Centr. 1869, **40**, 681; Zts. Chem. 1869, **12**, 264; Bull. Soc. Chim. 1868, (2), **10**, 178; 1869, **12**, 107, 204; Jahr. Chem. 1869, **22**, 750.

phenomenon to account that these ingestivations have been undertaken.

"Acetic cellulose. The cellulose (cotton or the paper of Berzelius), is heated in a closed vessel to 180° with six or eight times its weight of acetic anhydride, when it dissolves and yields a thick syrup which, when poured into water, precipitates white flakes of triacetic cellulose, $C_6H_7(C_2H_3O)_3O_5$, insoluble in water, alcohol or ether, soluble in concentrated acetic acid, and easily saponified by alkalis with regeneration of cellulose:

	Found		Calculated
Carbon	49.90	49.50	50.00
Hydrogen	5.81	5.85	5.56
Acetyl (by saponification with *N*/1 soda)	44.73	44.22	44.79

"Irrespective of the duration of the heating and excess of anhydride used, no higher figure is obtained. The cellulose then is a triatomic alcohol $C_6H_7O_2H_3O_3$. Using only 2 parts of anhydride and heating only to 150°, the cotton inflates without dissolving, on account of the production of diacetic and monoacetic esters which are formed at the same time, and which I have not separated.

"Starch and dextrin. Starch heated to 140° with an excess of anhydride swells considerably without dissolving. When washed with water, the mass gives a white, amorphorous substance, insoluble in water, alcohol, ether and *acetic acid;* is not turned blue by iodine, and is saponified by caustic alkalis with a regeneration of starch turned blue by iodine. It represents triacetic starch $C_6H_7(C_2H_3O)_3O_5$ in which, with calculated composition as above, there was found C, 50; H, 5.63; and acetyl (by saponification with soda), 45.10.

"If the mixture of starch and acetic acid be heated to 160°, the inflated mass dissolves, yielding an amber colored syrup from which water precipitates a white, amorphous substance, insoluble in water, alcohol or ether, soluble in crystallizable acetic acid, readily saponified by alkalis with formation of dextrin. This new product gives by analysis,

C, 49.54; H, 5.54, acetyl (by saponification with soda), 45.20. Hence it has the same composition as the preceding substance, and represents triacetic dextrin which is directly obtained through the action of acetic acid on dextrin. It is impossible to surpass the degree of substitution of the third order. As for lower degrees, these have not been studied in view of the difficulty of distinguishing them from a mixture of starch and the triacetic derivatice. Starch and dextrin, therefore, act as triatomic alcohols. . . ."

This second contribution aroused apparently considerable interest and stimulated much discussion. The Zeitschrift fuer Chemie published the article in its entirety[1], and R. Fittig commented therein on the work as follows:

"The interesting results of the above experiments agree perfectly with an opinion which I had long ago formed on the constitution of carbohydrates. All these substances are saturated derivatives of the hexyl-hydrocarbons C_6H_{14} and derivatives of a 7-acid alcohol $C_6H_7(OH)_7$. This alcohol is probably incapable of existance as it contains two hydroxyl atoms to one of carbon. In the attempt to produce it by disengagement from its well known acetic ether, the alcohol like the aldehyde [for instance the alcohol $CH_3CH(OH)_2$] will decompose into water and its first anhydride $C_6H_7O(OH)_5$, which is grape sugar. As shown by the transformation of mannite into mannitan $C_6H_8(OH)_6$ to $C_6H_8O(OH)_4$, the polyatomic alcohols easily are transformed into aldehydes. If the grape sugar once more loses water, this may happen in two ways: first by the union of two grape sugar molecules with the formation of water in which we obtain the anhydride $C_6H_7O(OH)_4O\ (OH)_4OC_6H_7$, i.e., milk sugar, cane sugar, etc.; or second, through the elimination of water from a grape sugar molecule. Then the triacid alcohol $C_6H_7OO(OH)_3$ is obtained, i.e., starch, cellulose, etc. The numerous isomerides accompanying these condensations (coalitions) are easily understood, and are caused, it seems,

1. Zts. Chem. 1869, **12**, 264.

largely by the difference in constitution of the hexylhydrocarbon from which they are derived, but chiefly by the uneven grouping of the O and OH atoms. According to this view, another formula $C_{12}H_{14}(C_2H_3O)_8O_{11}$ is much more probable for the saturated compound than Schuetzenberger's second formulae. The grape sugar has been transformed into saturated cane sugar ether, with loss of water —a very interesting reaction."

In 1870 P. Schuetzenberger[1] extended and summarized his investigations on the acetation of carbohydrates in general and on the esterification of cellulose and starch in particular, and published his preferred method of cellulose acetation. He directs that 1 part of cellulose be treated in a closed tube with 6-8 parts of acetic anhydride around the temperature 180° for one to two hours, and until a perfect solution results. This is precipitated by pouring into water, an abundant flocculent or horny mass being obtained, soluble in glacial acetic acid and in concentrated sulfuric acid, insoluble in water, alcohol, ether or benzene; readily saponified with the regeneration of cellulose, and when dried at 120°, gave combustion figures pointing to a triacetate of cellulose. Polariscopically, the product was found to be substantially inactive. By decreasing both the amount of anhydride and the temperature of esterification to 150°, the cotton intumesced but hardly dissolved, forming ether a mono- or diacetyl-cellulose, insoluble in all the above named solvents whether crude or purified. It was, however, extremely soluble in concentrated sulfuric acid which instantly liquefied it.

It will be observed that these three investigations of Schuetzenberger approached the subject from the purely academic side, and nothing appears in the original memoirs indicative of the fact that the products produced by him might have an interesting technical future, although he

1. Ann. Chim. Phys. 1870, (4), **21**, 235; abst. Chem. Centr. 1871, **42**, 568; Ann. 1871, **160**, 74; J. C. S. 1872, **25**, 366; abst. Chem. Centr. 1871, **42**, 740.

was aware of the resemblance of the acetic esters produced by him with the nitrocelluloses which had, at this time, attained considerable commercial importance, both in the peaceful and warlike arts. There is no doubt but that all the acetated celluloses produced by him were profoundly modified and considerably degraded, yet these experiments aroused the interest, laid the foundation, and furnished the generalizations upon which subsequent investigations were constructed, and to Paul Schuetzenberger, therefore, is rightfully to be accorded the honor of initiating the steps which have resulted in the development of this broad art—an art which, notwithstanding the multitude of investigators who have contributed of their time and energy to its development, is still in such a transitory state of progress.

Researches of A. Franchimont. As preliminary to the work of Franchimont, are to be mentioned the publications of A. Girard on hydrocellulose in 1875[1], 1876[2] and 1879[3], and more specifically described under the topic "Hydrocellulose" in E. Worden, "Technology of Cellulose Esters," pages 127-151, in which many principles in connection with subsequent patent litigation were laid down, but especially to the disclosures of C. Liebermann and O. Hoermann made in 1878[4]. Incidentally to their work upon the formulae of

1. Compt. rend. 1875, **81**, 1105; abst. Ber. 1876, **9**, 65; Jahr. Chem. 1875, **28**, 786; Chem. Centr. 1876, **47**, 83; J. C. S. 1876, **29**, 676; Chem. News, 1875, **33**, 10. Amer. J. Sci. 1876, (3), **11**, 483; Schweizerische Wochenschrift f. Farmacie, June 2, 1876, 180; Pharm. J. and Trans. 1876-77, (3), **7**, 26; Year-book Pharm. 1877; Zts. Oesterr. Apoth. Verein, 1876, 557; Chem. Tech. Rep. 1874, **14**, II, 179; Industriebl. 1876, 164; Dingl. Poly. 1876, **219**, 549.

2. Ann. Chim. Phys. 1876, (5), **9**, 116; abst. Chem. Centr. 1877, **48**, 6.

3. Compt. rend. 1879, **88**, 1322; **89**, 170; Ann. Chim. Phys. 1881, (5), **24**, 337; abst. J. C. S. 1879, **36**, 779; 1882, **42**, 378; Mon. Sci. 1879, **21**, 958; Ber. 1879, **12**, 2085, 2158; 1881, **14**, 2834; Chem. Centr. 1879, **50**, 531; Jahr. Chem. 1879, **32**, 835, 1116; 1881, **34**, 985; Wag. Jahr. 1879, **25**, 419, 1099; J. Pharm. 1879, **30**, 348; Year Book of Pharm. 1880, 80; Zts. ges. Brauw. 1879, 413; Proc. U. S. Nav. Inst. 1882, **8**, 309; Bull. d'encour. **81**, 176; Bull. Musee, **82**, 80; Naturforscher, **15**, 26.

4. Ber. 1878, **11**, 1618; abst. J. C. S. 1879, **36**, 271; Bull. Soc. Chim. 1879, **32**, 338; Jahr. Chem. 1878, **31**, 92; Chem. Centr. 1878, **49**, 710.

rhamnetin and xanthorhamnetin, and also of rhamnodulcite[1], they prepared a number of derivatives including the acetyl compounds. An improvement upon the Schuetzenberger method of acetylation was made in that by the use of "dephlegmated" (anhydrous) sodium acetate and acetic anhydride under a reflux condenser at atmospheric pressure, a more complete esterification results, no closed tube is required, less troublesome by-products are formed, the yield of acetylated product is increased and the reaction proceeds with smoothness and is completed in a shorter period of time.

Franchimont in his investigations on plant cellulose, attempted to apply the above method to the acetylation of various carbohydrates[2], but found that ordinary Swedish filter paper does not seem to react with acetic anhydride and fused sodium acetate, the paper refusing to dissolve upon boiling. Realizing that sodium acetate acts as a weak dehydrating agent, he tried a stronger one, and added a few drops of sulfuric acid, thereby probably unwittingly laying the foundation for the commercial manufacture of cellulose acetate. Immediately a violent reaction took place, the paper almost immediately dissolved in the acetic anhydride which boiled vigorously, and the liquid became dark colored. The material was at once poured into water, a white precipitate forming which settled incompletely and with difficulty, and was found to be partially soluble in cold alcohol to a yellow solution. The residue dissolved in boiling alcohol, and upon cooling, white crystals of a triacetylglucose deposited. It is evident that the reaction was allowed to go too far, beyond the state of cellulose acetation into the acetylbioses or even further. He added 4 parts of acetic anhydride to 1 part of cellulose, and to this, a *few drops* of sul-

1. Ber. 1878, **11**, 952; abst. Chem. News, 1878, **38**, 60; J. C. S. 1879, **36**, 39; Bull. Soc. Chim. 1879, **32**, 315; J. Pharm. Chim. 1879, **29**, 118; Jahr. Chem. 1878, **31**, 926; Jahr. reine Chem. 1878, **6**, 482.

2. Ber. 1879, **12**, 1938, 1941; abst. Chem. Centr. 1879, **50**, 771; Jahr. Chem. 1879, **32**, 832; Jahr. Tierchemie, 1879, **9**, 52; Jahr. reine Chemie, 1879, **7**, 503; J. C. S. 1880, **38**, 159.

furic acid meanwhile shaking, when brisk reaction was at once evident even without the application of external heat the cellulose gradually passing into solution from which it is precipible by the addition of an excess of water. The product thus obtained after purification with ethyl alcoho gave upon analysis, numbers corresponding to an elever times acetylated glucose.

In order to mollify the energy of the dehydrating agent[1] the sulfuric acid was substituted by fused zinc chloride as a more efficient and less powerful "drier." He heated 1 part of cellulose, 4 parts acetic anhydride and 0.5 part melted zinc chloride together, when the cellulose dissolved in a few minutes without appreciable discoloration the thick mass being dissolved in acetic acid, filtered, and precipitated by pouring into a large bulk of water. When the precipitate was dried, washed with alcohol and then with ether, elementary analysis gave figures closely approaching a triacetylcellulose.

Whereas with sulfuric acid as the condensing agent Franchimont was able to obtain two analytically distinguishable products as evidenced by their solubility and insolubility in ethyl alcohol, with zinc chloride as the condensing agent, but one product apparently results, this being the derivative soluble in hot alcohol. The colorless solution indicated that the profundity of decomposition of the cellulose had been far less reaching.

While zinc chloride is seldom, if ever, used as the dehydrating agent in the commercial acetation of cellulose at the present time, sulfuric acid in some form is almost universally so employed, usually as the straight oil of vitriol as will subsequently be detailed under the commercia methods of cellulose esterification.

1. Compt. rend. 1879, **89**, 711, 713, 755; Ber. 1879, **12**, 2059 Bull. Soc. Chim. 1880, **34**, 354; Chem. News, 1879, **40**, 264; J. C. S 1880, **38**, 233; Jahr. Chem. 1879, **32**, 832; Jahr. reine Chemie, 1879 **7**, 503. See also Bull. Soc. Ind. Rouen, 1882, **10**, 448; 1883, **11**, 230 Rec. Trav. Chim. Pays-Bas, 1883, **2**, 239; abst. Jahr. Chem. 1883, **36** 1366; Chem. Centr. 1884, **55**, 60.

Franchimont found in endeavoring to determine the amount of sulfuric acid in the acetating mixture[1] that barium salts failed to induce precipitation, and was thus lead to investigate the properties of sulfacetic acid, and the action in general, of sulfuric acid upon acetic acid. His observations, while not in accord with modern ideas of the mechanics of esterification, nevertheless have been widely quoted in questions of priority of conception and novelty in connection with patent litigation.

In 1881[2] appeared his results on the solubility of acetated cellulose in various solvents, in which was determined that the acetated product of melting point of 232° with decomposition, was soluble in boiling nitrobenzene (original gives nitrobenzine), the mass jellifying on cooling even with a large amount of the solvent. Not soluble in amyl alcohol.

As the result of the publication by Z. Skraup[3] of his work on the acetylation of cellulose, Franchimont returned to this subject in 1899[4] and showed that cellulose acetate of melting point 212° is not identical with inosite hexacetate which has the same melting point, and also that the former may be hydrolyzed by aqueous ammonia or an ammoniacal solution of cuprous oxide, the cellulose being recoverable. It was he who pointed out the resemblance to collodion of a cellulose acetate solution in chloroform.

Franchimont to Cross and Bevan. Succeeding the work of Franchimont are the investigations of C. Guignet on

1. Compt. rend. 1881, **92**, 1054; abst. Chem. Centr. 1881, **52**, 422; Jahr. Chem. 1881, **34**, 859; J. C. S. 1881, **39**, 716; Ber. 1881, **14**, 1284.

2. Compt. rend. 1881, **92**, 1053; abst. Chem. Centr. 1881, **52**, 424; Jahr. Chem. 1881, **34**, 985; J. C. S. 1881, **40**, 709; Ber. 1881, **14**, 1290. Les Mondes, 1881, **55**, 58.

3. Ber. 1889, **32**, 2413; abst. J. C. S. 1899, **76**, i, 852; Jahr. Chem. 1899, **52**, 1288; J. S. C. I. 1899, **18**, 941; Chem. Centr. 1899, **70**, II, 752; Bull. Soc. Chim. 1900, (3), **24**, 619. Monats. 1898, **19**, 458; abst. J. C. S. 1899, **76**, i, 112; Bull. Soc. Chim. 1898, (3), **20**, 898; Jahr. Chem. 1898, **51**, 1123; J. S. C. I. 1898, **17**, 895.

4. Rec. Trav. Chim. Pays-Bas, 1899, **18**, 472; abst. J. C. S. 1900, **78**, i, 141; Jahr. Chem. 1899, **52**, 1289; Chem. Centr. 1900, **71**, I, 172. See also Chem. Weekblad, 1919, **16**, 980; abst. C. A. 1919, **13**, 2157.

artificial parchment and the action of sulfuric acid upon cellulose[1], in which considerable data was accumulated on the role played by the sulfuric acid in respect to cellulose, but especially to the series of publications by E. Erwigs and W. Koenigs upon the acetyl derivatives of quinic acid[2], pentacetyl dextrose[3], galactose[4] and levulose[5]. These investigators studied the various acetylation methods which had been brought forward up to that time and especially that proposed by Franchimont in 1879, in which zinc chloride was added to acetic anhydride in place of sulfuric acid or sodium acetate.

They found that when grape sugar (5 gm.) is boiled for 10 minutes with acetic anhydride (20-22 cc.) and a trace of zinc chloride, a good yield of pentacetyldextrose is obtained which can readily be obtained in a pure state by crystallization. It was also observed that whereas the boiling of quinic acid with acetic anhydride and sodium acetate gives as the main product only a triacetyl derivative, when a small quantity of zinc chloride is employed instead of sodium acetate, tetracetylquinic acid is formed in almost theoretical quantities. From this they reasoned that zinc chloride is the superior condensing medium for maximum acetylation. They obtained a crystalline pentacetylglactose, differing from the gummy product of H. Fudakowsky[6], both

1. Compt. rend. 1889, **108**, 1258; abst. Jahr. Chem. 1889, **42**, 2839; Ber. 1889, **22**, 574; Chem. Centr. 1889, **60**, II, 124; J .C. S. 1889, **51**, 847; Chem. News, 1889, **60**, 24.

2. Ber. 1889, **22**, 1457; abst. J. C. S. I. 1889, **8**, 723; Jahr. Chem. 1889, **42**, 1692; J. C. S. 1889, **56**, 991; Chem. Centr. 1889, **60**, 251.

3. Ber. 1889, **22**, 1464; abst. J. S. C. I. 1889, **8**, 718; Jahr. Chem. 1889, **42**, 2041; J. C. S. 1889, **56**, 952; Chem. Centr. 1889, **60**, 250.

4. Ber. 1889, **22**, 2207; abst. J. S. C. I. 1889, **8**, 994; Jahr. Chem. 1889, **42**, 2041; J. C. S. 1889, **56**, 1131; Chem. Centr. 1889, **60**, 748.

5. Ber. 1890, **23**, 672; abst. J. S. C. I. 1890, **9**, 637; Jahr. Chem. 1890, **43**, 2132; J. C. S. 1890, **58**, 732; Chem. Centr. 1890, **61**, 757.

6. Ber. 1878, **11**, 1071; abst. J. C. S. 1878, **34**, 377; Bull. Soc. Chim. 1878, (2), **30**, 433; Chem. Centr. 1878, **49**, 417; Jahr. Chem. 1878, **31**, 921; Jahr. reinen. Chem. 1878, **6**, 476; Jahr. Pharmacog. Tox. 1878, **13**, 376.

by the use of sodium acetate and of zinc chloride. Best yields of pentacetyllevulose were obtained by the use of zinc chloride.

Researches of C. Cross and E. Bevan. In 1889 these investigators approached the problem of cellulose acetylation where it had been discontinued by Franchimont, in attempts to bring the subject to a commercial realization[1], their method being first to heat the anhydride to the boiling point, a fragment of zinc chloride added, and the cellulose (especially purified cotton) added in successive small portions, digestion being continued for two or three days. Preliminary observations on the crude product indicated that the acetic acid obtainable by saponification was considerably in excess of the quantity obtainable from a triacetylcellulose. Their product when purified by solution in glacial acetic acid—a tedious process—was limpid and not gelatinous as described by Franchimont in the case of the acetated cellulose as prepared by him. The product when purified by treatment with permanganate and sulfurous acid gave 51.6% C and 5.8% H—results agreeing closely with a pentacetylcellulose (51.6%) and being too high for a triacetylcellulose (50.0%). Determination of acetic acid by saponification gave from 79%-82%, the percentages calculated for tri-, tetra-, and penta-acetylcellulose being 62, 73 and 81 respectively.

In a later communication[2], the previous ground was carefully reviewed experimentally, the yield of acetated cellulose as prepared by them being 170%-190% of the original cotton fiber. The acetated cellulose dissolved freely in acetic acid, from which it is precipitated by the addition of water in dense, oqaque masses which dry to a granular powder. It melts at a high temperature to a clear liquid

1. Chem. News, 1889, **60**, 163; abst. Chem. Centr. 1889, **60**, II, 790; Jahr. Chem. 1889, **42**, 2066. Compare also Amat. Phot. 1890, **30**, 146.

2. Proc. Chem. Soc. 1889, 133; J. C. S. 1890, **57**, 2; abst. Chem. News, 1889, **60**, 254; Ber. 1890, **23R**, 247; Chem. Centr. 1890, **61**, 21, 390; Jahr. Chem. 1890, **43**, 2152.

without decomposition. Soluble in boiling nitrobenzene, the solution gelatinizing on cooling, a property considered by Franchimont as characteristic of the "ethereal salts" of cellulose, in contradistinction to those of allied carbohydrates of lower molecular weight. Although sulfuric acid dissolves it and at the same time decomposes it, from its solution in a nitrating mixture of equal volumes of nitric and sulfuric acids, it is precipitated apparently unchanged, the precipitate when examined for nitrogen by the method of J. Eder[1] yielding no nitric acid, nor any sulfuric acid upon fusion with KOH and KNO_3. The product as produced by Cross and Bevan was soluble in nitric acid from which it is re-precipitated from water without change. It also resists prolonged boiling with dilute mineral acid. When hydrolyzed with sodium hydroxide, it yields a residue of cellulose of 32%.

This art was materially advanced as the result of patent application dated May 17, 1894, to C. Cross and E. Bevan[2] for a method of cellulose acetate manufacture, in which is described in detail a commercial process for the acetylation of cellulose, starting with an intermediate product consisting of cellulose and zinc acetate, or a hydrated cellulose as obtained by precipitation from a zinc chloride or cuprammonium solution, or from caustic soda and carbon bisulfide. These investigators at this time were engaged in the development of the cellulose sulfocarbonates

1. Ber. 1880, **13**, 169; abst. J. C. S. 1880, **38**, 372; Zts. Chem. Grossgew. 1880, **5**, 42; Jahr. reinen. Chem. 1880, **8**, 492; Bull. Soc. Chim. 1881, **35**, 79; Phot. News, 1881, **25**, 149; Wien. Akad. Ber. 1879, **79**, II, 537; Phot. Corr. 1879, **16**, 67, 117, 216; Phot. Mitth. 1879, **16**, 97; Zts. anal. Chem. 1881, **20**, 135.

2. U. S. P. 530826, 1894. E. P. 9676, 1894; abst. J. S. C. I. 1895, **14**, 496, 987; Mon. Sci. 1913, **78**, 389; Chem. Centr. 1895, **66**, I, 405; II, 268. F. P. 243546, 1894; abst. Mon. Sci. 1895, **46**, 220; 1913, **78**, 389, 551. D. R. P. 85329, 1894; abst. Mon. Sci. 1896, **47**, 72; 1908, **69**, 465, 471; 1913, **78**, 389; Ber. 1896, **29**, 312, 461; Chem. Centr. 1896, **67**, 1119, II, 567; Chem. Ind. 1897, **20**, 548; Chem. Tech. Rep. 1896, **35**, 175; Chem. Ztg. 1895, **19**, 1853; 1896, **20**, 221; Chem. Zts. 1903, **2**, 610; Jahr. Chem. 1896, **49**, 1030; Wag. Jahr. 1896, **42**, 684. Aust. P. Feb. 9, 1895; abst. Chem. Ztg. 1895, **19**, 512. Belg. P. 113156, 1894; abst. Chem. Ztg. 1895, **19**, 560; Mon. Sci. 1913, **78**, 389.

(viscose) and undoubtedly realized the facility of reaction of the modified celluloses as compared with such a natural cellulose as cotton. The cellulose hydrate as obtained by one of the above mentioned processes is thoroughly mixed with a concentrated zinc acetate solution in the proportion of from one to two equivalents of zinc acetate to one equivalent of cellulose, the mixture after thorough incorporation being dried and then carefully dehydrated. After finely powdering, acetyl chloride is carefully mixed in small portions and with vigorous stirring, maintaining the temperature below 30°, and until two equivalents of acetyl chloride to one of zinc acetate have been used.

The reaction is continued with stirring and until a sample is found to be soluble in chloroform, the temperature meanwhile being kept below 30°, when the esterified cellulose is precipitated by means of water, washed until zinc salts and acid have been completely eliminated and then dried at a low temperature. The chloroformic solution deposited transparent pellicles, applicable as a substitute for collodion in surgical work as an artificial skin, and as a varnish in those applications where collodion finds use.

The patentees in the disclosure of this process made a distinct advancement over their predecessors in that by the modification of the cellulose before acetation, and by the employment of acetyl chloride instead of anhydride and a catalyst, esterification could be conducted at much lower temperature with a corresponding increase in ease of control, the result being the preparation of an ester less profoundly modified than those previously described as having been formed at relatively high temperatures, and also the process was under control of the manipulator. The reaction of the acetyl chloride may be inhibited by dilution with chloroform or anhydrous ethyl acetate free from alcohol, as pointed out by the patentees. No mention is made as to whether the portion insoluble in chloroform was free from acetyl groups—an important point. The process was

shortly afterwards modified by the substitution of magnesium acetate for zinc acetate[1].

The two foregoing mentioned communications of Cross and Bevan constitute the published groundwork upon which their first patent application was predicated, this being the first patent protection sought for the acetation of a water-insoluble carbohydrate, and from this initial patent, the art has expanded and ramified until its various activities are now protected by upwards of five thousand separate patent specifications detailed in this Chapter.

Working along lines analogous to those of the patentees above, C. Weber produced an acetylated cellulose by means of acetyl chloride and magnesium acetate, described as insoluble in methyl or ethyl alcohols, ethyl acetate, amyl acetate, acetone and ether, but soluble in ethyl benzoate, chloroform, acetic anhydride and acetic acid, and in nitrobenzene and epichlorhydrin. On account of the relatively low inflammability, resistance to moisture and high temperature, and a high insulating capacity, Weber predicted that the acetylcelluloses would eventually become powerful rivals of celluloid—a prediction that at the present time appears not so far from general realization.

In 1895[2] Cross and Bevan in a contribution to the general chemistry of cellulose, summarized their work in this field up to that date as follows:

"In examining the modification of cellulose as obtained from its solutions as xanthate, we were early impressed with its greater chemical activity as manifested, for instance, by its reacting with acetic anhydride at the boiling point of the latter. The resulting solution of acetate has, however, such extraordinary viscosity that the action is considerably impeded when the proportions of liquid to

1. D. R. P. 86368, 1894; abst. Ber. 1896, **29**, 461; Chem. Centr. 1896, **67**, I, 1119; II, 567; Chem. Ztg. 1896, **20**, 411; Wag. Jahr. 1896, **42**, 684; Mon. Sci. 1900, **55**, 134; 1908, **68**, 471; 1913, **78**, 389.

2. C. Cross, E. Bevan and C. Beadle, Proc. Chem. Soc. 1895, 31; J. C. S. 1895, **67**, 433; abst. Chem. News, 1895, **71**, 121; Ber. 1895, **28**, 645; Chem. Centr. 1895, **6**, I, 742; Jahr. Chem. 1895, **48**, 1348; Wag. Jahr. 1895, **41**, 1028.

cellulose are less than 20 to 1 by weight. Even at this dilution the action is difficult to control: prolonged boiling is necessary, and there are evidences of secondary changes which invalidate the conclusions to be drawn from the composition of the product. We found, however, that the acetylation could be reduced to a reaction of great simplicity as follows:

The regenerated cellulose (xanthate reaction) is thoroughly purified in the finely divided condition and mixed with zinc acetate in concentrated aqueous solution. The proportion of the latter to cellulose is that of the molecular ratio $C_6H_{10}O_5$: 2 $ZnAc_2$. The mixture is evaporated down on the water-bath with continual stirring, and when dry it is reduced to a fine powder; this is finally dehydrated by heating at 105-110° and is then gradually mixed in the cold with the equivalent of acetyl chloride; reaction ensues, the temperature being kept below 35° by suitable means. The product is drenched with glacial acetic acid after being warmed to promote solution of the acetate and the bye-products, the viscous solution is poured into water, and the gelatinous precipitate washed till free from zinc salts. It is then dried, the cellulose acetate dissolved in chloroform and the solution freed, by filtration or prolonged standing, from any unattacked cellulose; the product is finally isolated by evaporating the solvent. When this is carried out on a glass plate upon which an even layer of the solution is spread, the product is obtained as a brilliant colorless film of considerable tenacity.

When the precautions mentioned have been duly observed, the product has all the characteristics of a simple acetate of an unresolved cellulose; thus, on saponification, the cellulose is obtained as a "continuous" film, and on boiling with aqueous alkali (NaOH) and adding Fehling's solution, there is no reduction of CuO, either in the solution or on the film.

In certain cases, however, the acetylising action is attended by local or general rise of temperature. The prod-

uct in such cases has very different characteristics. It gives comparatively brittle films which become disintegrated on saponification; yellow soluble products are obtained which reduce cupric oxide freely, and the regenerated "cellulose" has the properties of a hydro- or oxy-cellulose also reducing cupric oxide. This differentiation of the products is confirmed by the results of analysis: the brittle product gives numbers corresponding with an acetate higher than the tetracetate, $C_6H_6O(OAc)_4$; the normal product gives number, both for saponification and yield of cellulose, in general concordance with the above formula.

Before citing the analytical results, it is necessary to say to few words as to the methods employed. The most rapid and satisfactory process of saponification is that of boiling with normal sodium hydroxide diluted with its own volume of alcohol. The acidimetric estimations were in some cases confirmed by distilling off the acetic acid and estimating it in the distillate. The residual cellulose is digested with dilute acid, well washed, dried and weighed. The following results are typical:

		Acetic Acid		
		Acidimetric estimation	Saponification and distillation	Cellulose
Products in coherent films	(1)	72.4	.....	43.6
Cellulose regenerated	(2)	73.1	69.2	43.2
of normal characteristics.	(3)	73.3		44.0
	(4)	68.0		50.0
Products giving brittle films				
Cellulose in part hydrolysed on saponification; products reducing CuO	(1)	81.2	. .	
	(2)	80.3-81.7	. . . .	32.0
	(3)	82.8		22.4

The quantities calculated are for the formula—

	Acetic Acid	Cellulose
$C_6H_6O(OAc)_4$	72.7	49.1

It is, of course, impossible to formulate a more highly substituted cellulose derivative, and it is unnecessary to speculate as to the relationship of the higher acetates to the lower, or to the original cellulose. On the main question, the evidence is distinct. The further resolution of the problem will be undertaken with very much larger supplies of the products, which will soon be available, as the industrial preparation of products is in course of arrangement.

By way of further elucidating the reaction of acetylation, and confirming the hypothesis on which the method was devised, other experiments were made. The most striking result was obtained with a mixture of the regenerated cellulose and urea. The mixture was prepared as in the case of the zinc salt: 6 grams of the cellulose (calc. dry) were stirred into a concentrated aqueous solution of 4 grams of urea, dried at 100°, and then dehydrated at 105-110°. This mixture reacted with the acetyl chloride similarly to the zinc acetate mixture, and satisfactory yields of the purified product were obtained, namely, from 10 grams of the mixture (a) 4 grams, and (b) 5 grams of the products. These were analysed, with the following results:

	Acetic Acid	(saponification)		Cellulose
(a)	67.4	67.3	68.0	47.0%
(b)		70.0		

The function of the urea in determining the action, we regard as similar to that of the zinc oxide, that is combining with the acid groups of the cellulose molecule sufficiently to bring the alcohol OH- groups into freer play, and afterwards combining with the hydrogen chloride in the reaction.

Other bases, such as ammonia and hydroxylamine, give similar, but inferior, results, the action being much more limited than in the case of urea."

C. Cross and C. Weber combined their activities in the patent field, assigned their interests to I. Frankenburg, and patents were taken out in nearly all the countries which

at that time had protective patent laws[1]. The rights for Germany were sold[2] and patents taken out there by the purchaser. This carries the activities of Cross and his associates up to 1900.

In 1895[3] C. Townsend contributed an article on cellulose acetate as a substitute for collodion containing little that was new.

1. C. Cross and C. Weber, Dan. P. 2558, 2636, 1899; abst. Chem. Ztg. 1899, **23**, 1001; Mon. Sci. 1913, **78**, 389. C. Weber and C. Cross, Luxom. P. 3302, 3361, 7610, 1898. Russ. P. Aug. 14, Oct. 14, 1898; 3264, 3378, 1900; abst. Chem. Ztg. 1899, **23**, 182; Mon. Sci. 1913, **78**, 389. Swed. P. 10976. Port. P. 2899, 2930, 1899; abst. Chem. Ztg. 1899, **23**, 954; Mon. Sci. 1913, **78**, 389. Nor. P. 7610, 1898. C. Weber and C. Cross assignor to I. Frankenburg, U. S. P. 627031, 632605, 1899; abst. Chem. Ztg. 1899, **23**, 572, 805. E. P. 18283, 1898; abst. J. S. C. I. 1898, **17**, 896; 1899, **18**, 728, 756. E. P. 22029, 1898; abst. J. S. C. I. 1898, **17**, 1090; 1899, **18**, 732, 756; Mon. Sci. 1913, **78**, 389. Russ. P. 3378, 1899; abst. Chem. Ztg. 1899, **23**, 182, 342. I. Frankenburg, Can. P. 62188, 63101, 1899; abst. Chem. Ztg. 1899, **23**, 321; Mon. Sci. 1913, **78**, 389. C. Weber, Zts. ang. Chem. 1899, **12**, 5; abst. Proc. Amer. Pharm. Assoc. 1900, **48**, 786; Chem. News, 1899, **80**, 247; Chem. Centr. 1899, **70**, I, 337; Jahr. Chem. 1899, **52**, 1289; Wag. Jahr. 1899, **45**, 1065. They produce cellulose butyrate or acetobutyrate by the action of the magnesium salt in conjunction with butyryl chloride upon cellulose, preferably that obtained from cellulose sulfocarbonate, the ester formed being dissolvable in the usual cellulose acetate solvents.

2. G. Henckel-Donnersmarck, D. R. P. Anm. D-9221, 1898; D-9431, 1898; abst. Chem. Ztg. 1899, **23**, 341; 1900, **24**, 232. D. R. P. 105347, 1898; abst. Mon. Sci. 1900, **56**, 134; 1910, **72**, 156; Chem. Centr. 1900, **71**, I, 272; Chem. Ztg. 1899, **23**, 998; Chem. Zts. 1903, **2**, 610; Jahr. Chem. 1899, **52**, 1290; 1900, **53**, 843; Wag. Jahr. 1899, **45**, 1064; Zts. ang. Chem. 1899, **12**, 1067. D. R. P. 112817, 1900; abst. Mon. Sci. 1913, **58**, 389; Chem. Centr. 1900, **71**, II, 510; Chem. Ztg. 1900, **24**, 654; Jahr. Chem. 1900, **53**, 843; Wag. Jahr. 1900, **46**, II, 450; Zts. ang. Chem. 1900, **13**, 773. Aust. P. Jan. 1, 1899; Feb. 4, 1899; abst. Chem. Ztg. 1899, **23**, 154, 279. Aust. P. Appl. June 25, 1901; abst. Chem. Ztg. 1902, **26**, 142. Aust. P. 8165, 1902; abst. Chem. Ztg. 1902, **1**, 611. Luxom. P. 3361; abst. Chem. Ztg. 1898, **22**, 1001. Belg. P. 137577, 138462, 1898; abst. Chem. Ztg. 1898, **22**, 966, 1074. C. Cross and E. Bevan, D. R. P. 85329, 1894; abst. Mon. Sci. 1896, **48**, 72; 1908, **68**, 465, 471; 1913, **78**, 389; Ber. 1896, **29**, 312; Chem. Centr. 1896, **67**, I, 1119; II, 567; Chem. Ind. 1897, **20**, 548; Chem. Ztg. 1896, **20**, 221; 1898, **22**, 783; Chem. Zts. 1903, **2**, 610; Jahr. Chem. 1896, **49**, 1030; Wag. Jahr. 1896, **42**, 684. D. R. P. 86368, 1895; abst. Mon. Sci. 1908, **68**, 471; 1913, **78**, 389; Ber. 1896, **29**, 461; Chem. Centr. 1896, **67**, II, 567; Chem. Ztg. 1898, **22**, 783; Chem. Zts. 1903, **2**, 610; Wag. Jahr. 1896, **42**, 685. F. P. 280848, 1898; abst. Mon. Sci. 1899, **54**, 133.

3. Photogram, (London) 1895, **2**, 177. See also C. Cross and E. Bevan, Brit. J. Phot. 1899, **46**, 471. J. Frank. Inst. 1900, **150**, 237.

Less than a month after the filing date of the first Cross and Bevan application, A. Little was given patent protection by application[1], for a carbon filament for electric lamps in which cellulose acetate—on accounts of its large percentage of carbon—is specified. In carrying out his invention, Little treats cellulose with 6 to 8 times its weight of acetic anhydride, heating the mixture in a closed tube to 180° (Schuetzenberger method), thus producing a solution of acetated cellulose, the material being projected in a fine stream into water as the coagulant. The strips or filaments after formation are carbonized, it being claimed such filaments are homogeneous and with on inequality in resistance. The essence of the Little patent is the *application* of a cellulose acetate already formed, in contradistinction to the Cross and Bevan patent, which was for the *manufacture* of cellulose acetate.

In 1895 E. Hermet[2] received patent protection in England for a composition called "liegine," being an artificial leather and substitute for natural cork in which collodion or "acetic cellulose" is combined with the powdered material, with or without the addition of linseed or other oil and acetic acid. "Acetic cellulose, a novel chemical agent, is produced by heating guncotton, or if preferred, filtering-paper or tissue paper or indeed any similar body capable of producing the same results, together with anhydrous acetic acid at about 190°." It is surmised that liegine was not a commercial success, if produced according to the patented description.

Three years after the issuance of the E. Hermet patent, appeared the process of A. Luck, in which cellulose ace-

1. A. Little, U. S. P. 532468, 1895. E. P. 21913, 1913. A. Little, W. Walker and H. Mork, U. S. P. 709922, 1902; abst. J. A. C. S. 1903, **25R**, 207; J. S. C. I. 1902, **21**, 1345; J. Soc. Dyers Col. 1905, **21**, 105; Mon. Sci. 1903, **59**, 165; 1905, **63**, 327; 1908, **69**, 462; Chem. Ztg. 1902, **26**, 1019. E. P. 20660, 1902; abst. J. S. C. I. 1903, **22**, 1011; J. Soc. Dyers Col. 1903, **19**, 281. F. P. 324862, 1902; abst. J. S. C. I. 1903, **22**, 646; Mon. Sci. 1904, **61**, 43; 1905, **63**, 327; Chem. Zts. 1903, **2**, 347.

2. E. P. 6473, 1895; abst. J. S. C. I. 1895, **14**, 1061.

tate, butyrate or benzoate was set forth as a desirable addition to cellulose nitrate explosives in order "to produce more stable compounds and also to give restraining effects in explosives required for certain purposes."[1] In checking up and amplifying the work on oxyhydroquinone triacetate by E. Sarauw[2] and by K. Buschka[3], chlorhydroquinone diacetate of H. Schulz[4], and dioxydiphenylsulfone of O. Hinsberg[5], J. Thiele[6] acetated quinone and dibenzoylstyrene with 1 part of sulfuric acid to 40-45 parts of acetic anhydride, and obtained as a crystalline product, over 80% of the theoretical yield.

Z. Skraup in 1899[7] studied the action of sulfuric acid as an aid in acetylation, and in successive experiments he was able to attenuate the amount of sulfuric acid to cellulose to 0.01% of the weight of acetic anhydride in the case of mucic acid, and still produce tetracetylmucic acid equivalent to 79% of the amount theoretically possible. Only amorphous products were obtained when acetic anhydride

1. U. S. P. 649852, 1900; abst. Chem. Ztg. 1900, **24**, 490. E. P. 24662, 1898; abst. Arms Expl. 1900, **8**, 70; J. S. C. I. 1900, **19**, 375; J. Soc. Dyers Col. 1898, **17**, 1214.

2. Ann. 1881, **209**, 129; abst. J. C. S. 1881, **40**, 1135; Bull. Soc. Chim. 1882, (2), **37**, 415; Ber. 1881, **14**, 2584; Jahr. reinen Chem. 1881, **9**, 279; Jahr. Chem. 1881, **34**, 633. Compare E. Sarauw, Ber. 1879, **12**, 680; 1880, **13**, 209; abst. J. C. S. 1879, **36**, 718; 1880, **38**, 385; Jahr. reinen Chem. 1879, **7**, 325; 1880, **8**, 298.

3. Ber. 1881, **14**, 1327.

4. Ber. 1882, **15**, 652; abst. Jahr. Chem. 1882, **35**, 778. Compare Jahr. Chem. 1879, **32**, 584; 1881, **34**, 632, 633.

5. Ber. 1894, **27**, 3259; abst. Jahr. Chem. 1894, **47**, 1302.

6. Ber. 1898, **31**, 1247; abst. J. C. S. 1899, **74**, i, 469; Chem. Centr. 1898, **69**, II, 31; Jahr. Chem. 1898, **51**, 2010; Bull. Soc. Chim. 1898, (3), **20**, 596.

7. Monats. 1898, **19**, 458; abst. J. C. S. 1899, **76**, i, 112; Bull. Soc. Chim. 1898, (3), **20**, 898; Jahr. Chem. 1898, **51**, 1123; J. S. C. I. 1898, **17**, 895. Ber. 1899, **32**, 2413; abst. J. C. S. 1899, **76**, i, 852; J. S. C. I. 1899, **18**, 941; Chem. Centr. 1899, **70**, II, 2140; Jahr. Chem. 1899, **52**, 1288; Bull. Soc. Chim. 1900, (3), **24**, 619. Annuario Soc. Chim. 1899, 27. Ber. 1901, **34**, 1115; abst. Bull. Soc. Chim. 1902, (3), **28**, 317; Jahr. Chem. 1901, **54**, 878; Chem. Centr. 1901, **72**, I, 1197; J. C. S. 1901, **80**, i, 370. Skraup and J. Koenig saponified the crystalline acetate obtained by the method of Franchimont by the action of acetic anhydride on cellulose in the presence of sulfuric acid, the acetate being saponified by alcoholic potash, and yielding ordinary glucose upon inversion.

and anhydrous sodium acetate were employed. When traces of sulfuric acid only were used (0.0001%) the reaction proceeds, but probably is incomplete. It was Skraup who first made clear that when relatively small amounts of sulfuric acid are employed and the acetylation carried on at lower temperatures, compounds of a more complicated nature are more often obtained than when the quantity of sulfuric acid is increased and the temperature raised. We now know that increased amounts of mineral acid and elevation of temperature diminish the size of the cellulose aggregate, diminish the viscosity and tensile strength, and result in the formation of esters of decreased technical importance in that their tensile strength, resiliency and pliability when dissolved and cast into films or projected into filaments is much lower.

Skraup demonstrated that starch gives, under weak acetylation, an acetyl derivative which when saponified with alkali, leaves a compound possessing the important properties of soluble starch; e.g., blue color with iodine, nonreduction of copper solution; while under energetic acetylation a substance which reduces copper solution is formed, and is no longer colored by iodine. By vigorous acetylation a splitting takes place similar to hydrolysis, and this results upon the addition of acetic anhydride. He maintains that in the energetic acylation of cellulose, a product is obtained which can only be formed from cellulose by the addition of anhydride, and that by very careful acetation of cellulose and starch, compounds arise which contain more acetyl groups than can be accounted for by the ordinary gross formulae.

In 1899 appeared the patent of C. Henry[1], for the impregnation of silk and wool fabrics with a solution of 1 part acetate of cellulose in 100 parts nitrobenzene, or celluloid in ether, amyl acetate, acetone or methyl alcohol. Any impregnating effect would necessarily be very weak

1. E. P. 20092, 1899; abst. J. S. C. I. 1899, **18**, 964; 1900, **19**, 950, 1104; J. Soc. Dyers Col. 1900, **16**, 274.

by the employment of but a 1% solution of cellulose acetate. The first of the L. Lederer patents appeared in this year[1], disclosing a method of cellulose acetation in which hydrocellulose as prepared by the method of A. Girard[2], is brought into reaction with sulfuric acid at a temperature of 60°-70° until the hydrocellulose passes into solution, the ester being then precipitated out and washed to neutrality. Lederer observes that if the hydrocellulose be first digested with acetic anhydride, no sulfuric acid is required. The product formed according to the patent specification is soluble in chloroform and in nitrobenzene.

A. Wohl[3] observed, in endeavoring to commercialize the manufacture of cellulose acetate, that when esterifying large quantities there was great difficulty in controlling the action so as to produce a uniform product. He realized the destructive effect of the cataylsts employed, and sought to modify this by the introduction into the acetating bath of such basic materials as pyridine and quinoline, further controlling the action by means of diluents as acetone, nitrobenzene or naphthalene.

Cellulose Acetate Development 1900-1904. In the year 1900 appeared the first of the L. Lederer patents in this art[4], in which his process for acetylcellulose manufacture

1. U. S. P. 654988, 1900; abst. Mon. Sci. 1901, **57**, 98. E. P. 11749, 1900; abst. J. S. C. I. 1901, **20**, 741; J. Soc. Dyers Col. 1901, **17**, 238. F. P. 301749, 1900; abst. Mon. Sci. 1901, **57**, 63. D. R. P. 118538, 1899; abst. Mon. Sci. 1901, **57**, 213; 1903, **59**, 284; 1905, **63**, 327; 1908, **68**, 465; Chem. Centr. 1901, **72**, 712; Chem. Ztg. 1901, **25**, 271; Jahr. Chem. 1901, **54**, 891; Wag. Jahr. 1901, **47**, II, 611; Zts. ang. Chem. 1901, **14**, 345. D. R. P. 120713, 1900; Addn. to D. R. P. 118538, 1899; abst. Mon. Sci. 1901, **57**, 283; 1908, **68**, 465; Chem. Centr. 1901, **72**, I, 1219; Chem. Ztg. 1901, **25**, 491; Jahr. Chem. 1901, **54**, 891; Wag. Jahr. 1901, **47**, II, 612; Zts. ang. Chem. 1901, **14**, 574.

2. Ann. Chim. Phys. 1881, (5), **24**, 360.

3. D. R. P. Anm. W. 15730, 1899; abst. Chem. Ztg. 1901, **24**, 812. D. R. P. 139669, 1899; abst. Mon. Sci. 1905, **63**, 327; Chem. Centr. 1903, **74**, I, 744; Chem. Ztg. 1903, **27**, 285; Chem. Zts. 1902-3, **2**, 610, 673; Jahr. Chem. 1903, **56**, 1014; Wag. Jahr. 1903, **49**, II, 418; Zts. ang. Chem. 1903, **16**, 285. Compare Phot. Mitth. 1899, **36**, 301. Pap. Ztg. 1899, **24**, 155.

4. U. S. P. 654988, 1900; abst. Mon. Sci. 1901, **57**, 98; Chem. Ztg. 1900, **24**, 720. E. P. 11749, 1900; abst. J. S. C. I. 1901, **20**, 741; J. Soc. Dyers Col. 1901, **17**, 238. F. P. 301749, 1900; abst. Mon. Sci.

consisted in using hydrocellulose as obtained by the process of A. Girard[1], with four fold quantity of acetic anhydride, the reaction taking place in a short time with the evolution of heat. The gravelly powder of acetylcellulose thus obtained is soluble in chloroform and in nitrobenzene. Observe in this process that no acetic acid is specified. This year also brought forth the first of the R. Sthamer methods of hydrocellulose manufacture on a commercial scale[2], by treating cellulose with glacial acetic acid containing free chlorine, the material being especially applicable for the preparation of cellulose acetate[3] when treated with glacial

1901, **57**, 63. D. R. P. 118538, 1899; abst. Wag. Jahr. 1901, **47**, II, 611; Chem. Centr. 1901, **72**, I, 712; Chem. Ztg. 1901, **25**, 271; Zts. ang. Chem. 1901, **14**, 345; Jahr. Chem. 1901, **54**, 891; Mon. Sci. 1901, **57**, 213. D. R. P. 120713, 1900, (Addn. to D. R. P. 118538); abst. Wag. Jahr. 1901, **47**, II, 612; Chem. Centr. 1901, **72**, I, 1219; Chem. Ztg. 1901, **25**, 491; Jahr. Chem. 1901, **54**, 891; Mon. Sci. 1901, **57**, 283; Zts. ang. Chem. 1901, **14**, 574; J. Soc. Dyers Col. 1905, **21**, 105, which differs from the principal patent in specifying that the temperature of the acetating mixture shall be kept at 30° or lower. G. Donnersmarck, Aust. P. 8165, 1902; abst. Chem. Ztg. 1902, **26**, 614.

1. See E. Worden, "Technology of Cellulose Esters," 1921, **1**, 36, 40, 59, 60, 117, 119, 122, 130, 131, 132, 133, 134, 135, 137, 138, 140, 143, 145, 146, 147, 162, 163, 413, 460, 1618, 1711, 1848, 1849, 1901, 2957, 2987.

2. M. Althausse, assignor to Fabrik Chemischer Praeperate R. Sthamer, U. S. P. 679204; abst. Mon. Sci. 1901, **57**, 284. E. P. 19039, 1900; abst. J. S. C. I. 1901, **20**, 926. F. P. 304723, 1900; abst. J. S. C. I. 1901, **20**, 469; Chem. Ztg. 1901, **25**, 270; Mon. Sci. 1900, **55**, 20. F. P. 308506, 1901; abst. J. S. C. I. 1902, **21**, 64, 362; Mon. Sci. 1902, **58**, 159; J. Soc. Dyers Col. 1901, **17**, 246. F. P. 309759; abst. J. S. C. I. 1902, **21**, 65; Mon. Sci. 1902, **58**, 170. D. R. P. 123121, 123122, 1900; abst. Zts. ang. Chem. 1901, **14**, 905; J. S. C. I. 1901, **20**, 1133; Jahr. Chem. 1901, **54**, 892; Chem. Centr. 1901, **72**, II, 567; Mon. Sci. 1902, **58**, 9; Wag. Jahr. 1901, **47**, II, 612, 613; Chem. Ztg. 1901, **25**, 707; Chem. Zts. 1902, **1**, 142. Aust. P. 8172, 1902. D. R. P. Anm. F-12687, F-12688, 1900; abst. Chem. Ztg. 1901, **24**, 340. See also R. Hoemberg, D. R. P. Anm. H-53315; abst. Kunst. 1912, **2**, 260. For details of these processes, see "Technology of Cellulose Esters," 1921, **1**, 132, 141, 150, 660, 1901.

3. M. Althausse, assignor to Fabrik Chemischer Praeperate R. Sthamer, U. S. P. 679203, 1901; abst. Mon. Sci. 1901, **57**, 284; Chem. Ztg. 1901, **25**, 687; J. A. C. S. 1902, **24**, 141. U. S. P. 692497, 1902; abst. J. S. C. I. 1902, **21**, 362; Mon. Sci. 1902, **58**, 161; J. A. C. S. 1902, **24**, 403. U. S. P. 692775, 1902; abst. J. S. C. I. 1902, **21**, 356; Mon. Sci. 1902, **58**, 161; J. A. C. S. 1902, **24**, 405; Chem. Zts. 1902, **2**, 92. D. R. P. 137206, 1901; abst. Jahr. Chem. 1903, **56**, 1014; Mon. Sci. 1904, **61**, 37; Wag. Jahr. 1902, **48**, II, 595; Chem. Centr. 1903, **74**, I, 107; Zts. ang. Chem. 1902, **15**, 1301; Chem. Zts. 1903, **2**, 373.

acetic acid and acetyl chloride in the proportion of about 350 parts of each reagent to 199 of hydrocellulose, this latter process issuing in 1901.

The researches of L. Vignon and F. Gerin on acetylized derivatives of cellulose and oxycellulose issued in 1900[1] and in 1901[2], although primarily of an academic character, nevertheless established several important quantitative points. They acetylated cellulose (from cotton)[3] and oxycellulose with acetic anhydride and zinc chloride, the former also with glacial acetic acid and zinc chloride, using the proportions of anhydride 100, cotton dried at 110°, 10, and fused $ZnCl_2$, 2; or glacial acid 150, cotton 15, and $ZnCl_2$ 3. The product obtained was insoluble in water or ether, noncrystallizable, infusible, but little soluble in alcohol, and readily soluble in acetic acid, acetone, ethyl acetate and chloroform. The yield amounted to but 25%-26% in case of the cellulose, and 40% where oxycellulose was used—thus indicating the formation of large amounts of subsidiary products. Analytical figures indicated a percentage composition agreeing with a tetracetate formula of cellulose, the results being based upon the following figures:

	Percentage of Cellulose	Hydrogen	Acetic Acid
Cellulose, $C_6H_{10}O_5$	44.44	6.17	
Cellulose monoacetate, $C_6H_6O(OH)_3(CO_2CH_3)$	47.05	5.88	
Cellulose diacetate, $C_6H_6O(OH)_2(CO_2CH_3)_2$	47.88	5.69	
Cellulose triacetate, $C_6H_6O(OH)(CO_2CH_3)_3$	50.	5.55	62.5

1. Compt. rend. 1900, **131**, 588; abst. Chem. News, 1900, **82**, 219; J. C. S. 1900, **78**, i, 629; J. S. C. I. 1900, **19**, 1103; Mon .Sci. 1900, **55**, 833; Rev. Phys. Chem. 1901, **5**, 36; Chem. Centr. 1900, **71**, II, 1069; Chem. Ztg. 1900, **24**, 932; Jahr. Chem. 1900, **53**, 843.

2. Bull. Soc. Chim. 1901, **25**, 139; abst. Rep. Chim. 1901, **1**, 103, 130; Chem. Centr. 1901, **72**, I, 440; Jahr. Chem. 1901, **54**, 891; Meyer Jahr. Chem. 1901, **11**, 447.

3. See "Technology of Cellulose Esters," 1921, **1**, 169, 1667, 1848, 1866, 2988. "Nitrocellulose Industry," 1911, **2**, 1003.

Cellulose tetracetate,			
$C_6H_6O(CO_2CH_3)_4$	50.9	5.45	72.5
Cellulose pentacetate,			
$C_6H_3(CO_3CH_3)_5$	51.6	5.37	80.6

The acetyl derivatives only apparently reduced Fehling's solution, a green precipitate of copper acetate being formed, while the acetyl derivatives of oxycellulose retained the reducing property of oxycellulose.

In their second communication undertaken to determine the alcoholic character of cellulose, acetic anhydride and zinc chloride were previously heated together on a paraffin bath to boiling, the cotton added thereto gradually in small amounts, heating being continued under a reflux condenser for sixteen hours. As in the earlier experiments of P. Schuetzenberger, the solution became brown, the cotton being dissolved after 25 minutes. A final black liquid mixed with tar was eventually obtained, from which the acetated product was precipitated by water, purified by several times solution in acetic acid, filtration through animal charcoal and reprecipitation, the end product being white. Irrespective of the state of the cellulose and the method of manipulation, the products obtained by them were almost identical.

In 1901 appeared the first of the many patents in this field of the Farbenfabriken vorm. F. Bayer & Co.[1] "Hard spirits" or "solidified alcohol" is prepared by the solution of 100 gm. cellulose acetate in 500 gm. glacial acetic acid, to which is added 2 liters of ethyl alcohol. Their method of manufacture of an alcohol-soluble acetate[2] was by means of "larger" amounts of sulfuric acid at room temperature,

1. D. R. P. 134721, 1901; abst. Wag. Jahr. 1902, **48**, II, 456; Chem. Centr. 1902, **73**, II, 1022; Chem. Ztg. 1902, **26**, 970; Jahr. Chem. 1902, **55**, 774; Chem. Zts. 1903, **2**, 733, 736.

2. D. R. P. Anm. F-15279, 1901; abst. Chem. Ztg. 1902, **26**, 222. D. R. P. 153350, 1901; abst. J. C. S. 1904, **86**, i, 853; Wag. Jahr. 1904, **50**, II, 394; Zts. ang. Chem. 1904, **17**, 1697; Chem. Zentr. 1904, **75**, II, 625; Jahr. Chem. 1904, **57**, 1168; Chem. Ind. 1904, **27**, 538. Aust. P. 21213, 1904; abst. Chem. Ztg. 1905, **29**, 797. D. R. P. 169364, 1902; abst. Wag. Jahr. 1906, **52**, II, 485; Chem. Centr. 1906, **77**, II, 187;

the product obtained being soluble in five volumes of hot alcohol from which it gelatinizes in the cold. In an improvement on this method, issued later in the same year[1], a "triacetylized" derivative of cellulose was obtained by treating cellulose with a mixture of acetic anhydride and sulfuric acid, with or without the addition of a solvent as glacial acid. The body obtained is soluble in chloroform, epichlorhydrin, nitrobenzene, glacial acetic acid, acetone and pyridine, but insoluble in alcohol, ether, ethyl acetate, amyl acetate and glycerol. By substituting hydrocellulose for cellulose in the above described process, the acetylized derivative is readily soluble in ethyl alcohol. It was subsequently found[2] that the reaction takes place in two stages, the first being the formation of an acetyl derivative soluble in alcohol, and secondly the formation of an alcohol insoluble derivative by the further action of acetic anhydride on the

Mon. Sci. 1907, **67**, 150. Aust. P. 32636, 1907. E. P. 21628, 1901 (similar to D. R. P. 153350 and 159524); abst. J. S. C. I. 1902, **21**, 1293; J. Soc. Dyers Col. 1902, **18**, 24, 275, 282. F. P. 317007, 1901; and addn. 1425 thereto; abst. Mon. Sci. 1903, **59**, 54; J. S. C. I. 1902, **21**, 870; Chem. Ztg. 1902, **26**, 586; Chem. Zts. 1903, **2**, 649. Cf. F. P. 317008, 1901; abst. J. S. C. I. 1902, **21**, 873. F. P. 326468, 1902; abst. J. S. C. I. 1903, **22**, 820. A. Eichengruen and T. Becker (assignors); U. S. P. 734123, 1903; abst. J. S. C. I. 1903, **22**, 961; Mon. Sci. 1903, **59**, 173; J. A. C. S. 1904, **26R**, 83. U. S. P. 790565, 1905; abst. J. S. C. I. 1905, **24**, 686; Chem. Zts. 1905, **4**, 331; J. A. C. S. 1906, **28R**, 51; Mon. Sci. 1905, **63**, 143. U. S. P. 809935, 1906; abst. J. S. C. I. 1906, **25**, 195; Mon. Sci. 1906, **65**, 120; Chem. Zts. 1906, **5**, 135; J. A. C. S. 1906, **28R**, 417. The French Patents were issued to the Soc. anon. Prod. F. Bayer & Co.

1. E. P. 7346, 1903; abst. J. S. C. I. 1904, **23**, 337; J. Soc. Dyers Col. 1904, **20**, 140. Cf. Addn. 1425 to F. P. 307007; abst. J. S. C. I. 1903, **22**, 1015. D. R. P. 159524, 1901; abst. Chem. Centr. 1905, **76**, II, 527; Wag. Jahr. 1905, **51**, II, 190; Jahr. Chem. 1905-8, II, 984; Chem. Ztg. 1905, **29**, 826; Zts. ang. Chem. 1905, **18**, 1636. D. R. P. Anm. F-16871 (addn. to D. R. P. 159524); abst. Chem. Ztg. 1906, **30**, 117. Aust. P. 31391, 1906; abst. Chem. Ztg. 1907, **31**, 1234. Ital. P. 62042, 1901.

2. U. S. P. 809935, 1906; abst. J. S. C. I. 1906, **25**, 195; Mon. Sci. 1906, **61**, 120; Chem. Zts. 1906, **5**, 135; J. A. C. S. 1906, **28R**, 417. E. P. 7346, 1903; abst. J. S. C. I. 1904, **23**, 337; J. Soc. Dyers Col. 1904, **20**, 140. See Addn. 1425, 1903, to F. P. 317007; abst. J. S. C. I. 1903, **22**, 1015. D. R. P. 185837 (addn. to D. R. P. 159524); abst. Chem. Ind. 1907, **30**, 313; Chem. Ztg. Rep. 1907, **31**, 302; Zts. ang. Chem. 1908, **21**, 269; Chem. Zentr. 1907, **78**, II, 654; Jahr. Chem. 1905-8, II, 984; Wag. Jahr. 1907, **53**, 403. Aust. P. 32637 (addn. to Aust. 31391).

first product. Realizing the destructive action of sulfuric acid on the cellulose and the difficulty of its control in the acetylizing bath, phosphoric acid, or phenol- or naphthol-sulfonic acids were proposed to replace a portion of the H_2SO_4[1]. The first cellulose acetate plastic composition to be protected is probably that of A. Eichengruen and T. Becker as assignors to Bayer, who combined either camphor, *p*-toluenesulfamide, methyl-*p*-toluenesulfonate, naphthalene, or methyl oxalate or phthalate with acetated cellulose, chloroform being used as the mutual solvent[2].

In the acetylation method of L. Lederer[3], as an alleged improvement of his process of the preceding year, the hydrolysis and acetylation occur simultaneously according to the statement of the patentee, but the examples cited in the patent whereby the cellulose is first treated with glacial

1. The history of this series of patents is as follows: E. P. 21628, 1901; F. P. 317007, 1901; Aust. P. 31391; Ital. P. 62042, 1901, cover the acetylation of cellulose and hydrocellulose by means of glacial acetic acid, acetic anhydride and H_2SO_4, while U. S. P. 734123, 1903; D. R. P. 153350, 1901, covers the acetylation of hydrocellulose only, and U. S. P. 790565, 1905; D. R. P. 159524, 1901, covers the acetylation of cellulose only, in the manner above described. Next, U. S. P. 809935, 1906, is in reality an addition to U. S. P .790565, as also is D. R. P. 185837, because D. R. P. 185837 and U. S. P. 809935 are additions to D. R. P. 159524 and U. S. P. 790565, which are the corresponding portions of a general patent, and both relate to acetylation of unmodified cellulose only. Furthermore E. P. 7346, 1903, is an addition to E. P. 21628, 1901, or rather it is an addition to a portion of it. U. S. P. 734123 and D. R. P. 153350 cover the acetylation of hydrocellulose. U. S. P. 790565 and D. R. P. 159524 cover acetylation of cellulose. E. P. 21628, 1901; F. P. 317007, 1901; Aust. P. 31391; Ital. P. 62042, 1901, cover acetylation of hydrocellulose and cellulose, in all processes glacial acetic acid, acetic anhydride and H_2SO_4 being used. Therefore the U. S. P. and D. R. P. were divided as regards the other countries.

2. U. S. P. 738533, 1903; abst. J. S. C. I. 1903, **22**, 1100; Mon. Sci. 1904, **61**, 9; J. A. C. S. 1904, **26R**, 193. F. P. 317008, 1901; abst. J. S. C. I. 1902, **21**, 870, 873; Mon. Sci. 1903, **59**, 54; Chem. Ztg. 1902, **26**, 586. E. P. 26075, 1901; abst. J. S. C. I. 1902, **21**, 1469.

3. D. R. P. 163316, 1901; abst. Zts. Elektrochem. 1905, **11**, 561; Chem. Centr. 1905, **76**, II, 1301; Wag. Jahr. 1905, **51**, II, 191; Jahr. Chem. 1905-8, II, 984; Zts. ang. Chem. 1906, **19**, 204; Mon. Sci. 1906, **65**, 159; Chem. Ztg. 1905, **29**, 1109. D. R. P. Anm. L-21855, 1905; (addn. to D. R. P. 163316); abst. Chem. Ztg. 1907, **31**, 304. D. R. P. 200916, 1905; (addn. to D. R. P. 163316); abst. Zts. ang. Chem. 1908, **21**, 2047; Chem. Zentr. 1908, **79**, II, 738; Chem. Ind. 1908, **31**, 559; Wag. Jahr. 1908, **54**, 364; Jahr. Chem. 1805-8, II, 984;

acetic acid containing sulfuric acid, and then further treated with acetic anhydride or acetyl chloride, indicates that hydrolysis precedes acetation.

A. Wagner weaves colorless or colored acetylcellulose filaments into a fabric with ordinary cotton and then dyes the piece[1], the ester remaining unchanged in the dye bath, or[2], uses ordinary fibers coated with cellulose acetate to produce differential dyeing effects. In the manufacture of acetate films, C. Waite[3] uses lactic acid to impart softness and suppleness. L. Blumer[4] in elaborating upon the previous work of L. Schultze[5] and of I. Frankhausen[6] on the action of dilute acids on starch, treated starch at about 115° for 4-6 hours with 1%-10% solutions of formic and acetic acids, but it is a question as to what proportion (if any) of the starch is esterified by this treatment. L. Landsberg partially or wholly replaced sulfuric acid in the ester-

Zts. Schiess Spreng. 1908, **3**, 374. F. P. 319848, 1902; abst. J. S. C. I. 1902, **21**, 1550; Mon. Sci. 1903, **59**, 123. Aust. P .33508, 1908; abst. Chem. Ztg. 1908, **32**, 588. Belg. P. 163251, 1902; abst. Chem. Ztg. 1902, **26**, 638. Hung. P. May 20, 1902; abst. Chem. Ztg. 1902, **26**, 696. See also Addn. 811, 1902, to F. P. 319724, 1902; abst. J. S. C. I. 1902, **21**, 1550; 1904, **23**, 1159; Mon. Sci. 1903, **59**, 123. U. S. P. 774677, 1904; abst. J. S. C. I. 1904, **23**, 1159. E. P. 7088, 1902; abst. J. S. C. I. 1903, **22**, 563. See also W. Walker, U. S. P. 774713, 1904; abst. Mon. Sci. 1905, **63**, 50; Chem. Ztg. 1904, **28**, 1157; J. A. C. S. 1905, **27R**, 434.

1. D. R. P. 152432, 1901; abst. Wag. Jahr. 1904, **50**, II, 417; Chem. Ztg. 1904, **28**, 628; Zts. ang. Chem. 1904, **17**, 1252; Chem. Zts. 1904, **3**, 809; Mon. Sci. 1905, **63**, 328.

2. D. R. P. 158217, 1901, (addn. to D. R. P. 152432); abst. Wag. Jahr. 1905, **51**, II, 432; Chem. Ztg. 1905, **29**, 202; Zts. ang. Chem. 1905, **18**, 1397; Mon. Sci. 1906, **65**, 79.

3. U. S. P. 690211, 1901; abst. J. A. C. S. 1902, **24**, 339; J. S. C. I. 1902, **21**, 272.

4. E. P. 10872, 1902; abst. J. S. C. I. 1903, **22**, 642. F. P. 322206, 1902; abst. J. S. C. I. 1903, **22**, 310; Mon. Sci. 1903, **59**, 126; Chem. Zts. 1903, **2**, 121; J. Soc. Dyers Col. 1903, **19**, 138. D. R. P. 137330, 1901; abst. Wag. Jahr. 1904, **50**, II, 224; Chem. Centr. 1903, **74**, I, 306; Zts. ang. Chem. 1903, **16**, 90; Jahr. Chem. 1903, **56**, 1005; Mon. Sci. 1904, **61**, 37.

5. J. prakt. Chem. 1883, **136**, 324; abst. Chem. News, 1884, **49**, 79; J. C. S. 1884, **46**, 284; Bull. Soc. Chim. 1884, **42**, 292; Ber. 1883, **16**, 3064; Chem. Tech. Rep. 1883, **22**, II, 133; Chem. Ztg. 1883, **7**, 1552; Jahr. Chem. 1883, **36**, 1366; Wag. Jahr. 1883, **29**, 671; Zts. deut. Spiritusfabr. 1883, 1022.

6. Zts. Spiritus Ind. 1887, **8**, 49; abst. Dingl. Poly. 1887, **266**, 603; Jahr. Chem. 1887, **40**, 2642.

izing bath by means of meta-, ortho- or pyro-phosphoric acids or phosphorous pentoxide (phosphoric anhydride)[1].

In May, 1901, there was filed the first G. Miles patent[2], in which is disclosed that in the acetation of cellulose "the addition of sufficiently minute quantities of sulfuric acid to the anhyride of a monobasic fatty acid not only enables one to form the corresponding cellulose ester directly from cellulose in its highly aggregated and fibrous form by treatment of the cellulose (cotton)" the reaction taking place at temperatures not exceeding 70°. All commercial processes up to this time had involved the preliminary treatment of the cellulose before immersion in the esterizing bath. The disclosures of E. Valenta[3] were for the applications of the cellulose acetates as a substitute for nitrocellulose in connection with photography.

In the field of non-inflammable celluloid substitutes, L. Lederer in 1902 described combinations of cellulose acetate with various plasticizing agents as phenol, alone[4] or in conjunction with acetone[5], compound phenols[6], chloral[7], and

1. E. P. 4886, 1902; abst. J. S. C. I. 1903, **22**, 315. F. P. 316500, 1901; abst. J. S. C. I. 1902, **21**, 719; Mon. Sci. 1903, **59**, 53; Chem. Ztg. 1902, **26**, 442. Aust. P. 17456; Hung. P. Appl. Feb. 27, 1902; D. R. P. Anm. L-15737; abst. Winther, Pat. organ. Chem. **1**, 134. Belg. P. 160378, 1901; abst. Chem. Ztg. 1902, **26**, 212.

2. U. S. P. 733729, 1903; abst. J. S. C. I. 1903, **22**, 961; J. Soc. Dyers Col. 1905, **21**, 105; Mon. Sci. 1903, **59**, 173; Chem. Zts. 1903, **2**, 743; J. A. C. S. 1904, **26**-R, 82. Can. P. 90848, 1905; Chem. Ztg. 1905, **29**, 797.

3. Phot. Corr. 1901, **38**, 305; abst. Jahr. Chem. 1901, **54**, 801; Chem. Centr. 1901, **72**, II, 40; Meyer Jahr. Chem. 1901, **11**, 477.

4. E. P. 7988, 1902; abst. J. S. C. I. 1903, **22**, 563. F. P. 319724, 1902; abst. J. S. C. I. 1902, **21**, 1550; Mon. Sci. 1903, **59**, 123.

5. D. R. P. 151918, (addn. to D. R. P. 145106); abst. Wag. Jahr. 1904, **50**, I, 512; Chem. Centr. 1904, **75**, II, 1180; Chem. Ztg. 1904, **28**, 934; Zts. ang. Chem. 1905, **18**, 353; Jahr. Chem. 1904, **57**, 1168; J. Soc. Dyers Col. 1905, **21**, 106; Mon. Sci. 1913, **78**, 392. Aust. P. 19604, 1904, (addn. to Aust. P. 16377).

6. D. R. P. 145106, 1902; abst. Jahr. Chem. 1904, **57**, 1168; Mon. Sci. 1904, **61**, 93; Zts. ang. Chem. 1903, **16**, 1090; Chem. Centr. 1903, **74**, II, 1155; Wag. Jahr. 1904, **50**, II, 512.

7. D. R. P. 152111, 1902; abst. Zts. ang. Chem. 1904, **17**, 1250; Chem. Centr. 1904, **75**, II, 382; Jahr. Chem. 1904, **57**, 1168; Chem. Ztg. 1904, **28**, 579; Wag. Jahr. 1904, **50**, II, 572. F. P. 319724, 1902, and Addn. 811 thereto; abst. J. S. C. I. 1902, **21**, 1550; 1903, **22**, 563.

similar bodies[1] for the formation of horn-like products. There was granted to him patent protection in England[2] for a process of cellulose acetylation similar to that of Miles (example 1 in the patent), coupled with a method of superficial acetylation of cellulose fabrics (example 2 of the patent). France in 1902[3], and the United States in 1910[4] allowed protection only to the process comprised in the second example. The alcohol-soluble cellulose acetate has been claimed as a photographic emulsifying agent[5]. J. Schmerber and L. Morane[6] advocated as an "incombustible celluloid" combinations of nitrocellulose and cellulose acetate with camphor, mixed by means of the mutual solvent acetone, this differing from the previously cited product of the Bayer firm in that acetated cellulose alone was combined with camphor. The Zuehl & Eisemann process is

1. U. S. P. 774677, 1904; abst. J. S. C. I. 1904, **23**, 1159; J. A. C. S. 1905, **27**-R, 434; Mon. Sci. 1913, **78**, 392. The relation of these patents may be seen from the materials specified therein as being suitable for combination with acetylcellulose to produce horny solid bodies. U. S. P. 774677: phenol, chloral hydrate, aniline, acetophenone. E. P. 7088, 1902: phenol, chloralhydrate, acetone, aniline, acetophenone, acetamide. F. P. 319724: phenol, chloralhydrate, aniline, acetophenone, acetamide. Addn. 811 to F. P. 319724: phenol, phenol and acetone, chloralhydrate. D. R. P. 145106: phenols or their substituted derivatives (resorcinol, pyrogallol, naphthol, aminophenol, saligenin, nitrophenol, salicylic acid ester), phenol. D. R. P. 151918: phenol in acetone, with or without metallic salts and oxides such as lead oxide. D. R. P. 152111: chloralhydrate. Therefore U. S. P. 774677 is same as Addn. 811 to F. P. 319724.

2. E. P. 11164, 1902; abst. J. S. C. I. 1903, **22**, 646.

3. F. P. 320885, 1902; abst. Mon. Sci. 1905, **62**, 328; J. S. C. I. 1903, **22**, 160.

4. U. S. P. 954310, 1910; abst. J. S. C. I. 1910, **29**, 557; C. A. 1910, **4**, 1671; Chem. Ztg. Rep. 1910, **34**, 209; Mon. Sci. 1910, **73**, 135.

5. A. Eichengruen and A. Braun, (assignors to Farbenfabr. vorm. F. Bayer & Co.,) U. S. P. 752388, 1904; abst. J. A. C. S. 1904, **26**-R, 406; J. S. C. I. 1905, **24**, 337; Mon. Sci. 1905, **63**, 64. E. P. 25821, 1902, abst. J. S. C. I. 1903, **22**, 1256; Chem. Ztg. 1904, **28**, 365. D. R. P. 169364, 1902; abst. Chem. Centr .1906, **77**, II, 187; Wag. Jahr. 1905, **51**, II, 485; Mon. Sci. 1907, **67**, 150. Aust. P. 32636, 1907; F. P. 326468, 1902; abst. J. S. C. I. 1903, **22**, 820; Mon. Sci. 1905, **63**, 88; Chem. Zts. 1903, **2**, 442. See also Eder's Jahr. Phot. 1902, 582.

6. E. P. 4863, 1903; abst. J. S. C. I. 1904, **23**, 382; Chem. Ztg. 1904, **28**, 668. F. P. 324121, 1902; abst. J. S. C. I. 1904, **23**, 569; Chem. Zts. 1903, **2**, 347.

similar[1]. The first of the C. Cross and J. Traquair processes for the formation of soluble starch by esterification was published in 1902[2], in which dried starch is subjected to the action of concentrated acetic or formic acids in the liquid or gaseous form.

This same year the B. Boesch process of acetylcellulose formation was disclosed[3], consisting in treating 25 parts of dry viscose with 16 parts acetyl chloride and 20 parts acetic anhydride.

It was in 1902 that E. Thomson and J. Callan[4] were allowed patent protection for covering conducting wires first with a film of rubber and then with acetated cellulose, and three years later when the latter brought out his process for the manufacture of bushings of this material[5], and for coating metallic conductors first with nitrocellulose and then with the acetic ester[6]. The process of cellulose acetation of H. Mork, A. Little and W. Walker[7] sought to

1. D. R. P. 162239, 1902; abst. Jahr. Chem. 1905-8, II, 993; Chem. Centr. 1905, **76**, II, 1000; Zts. ang. Chem. 1906, **19**, 498; Wag. Jahr. 1905, **51**, II, 571; Chem. Ztg. 1905, **29**, 887.

2. (Assignors to W. Wotherspoon); U. S. P. 778173, 1904; abst. J. S. C. I. 1905, **24** ,98; Mon. Sci. 1905, **63**, 174; J. A. C. S. 1905, **27**-R, 502. E. P. 9868, 1902; abst. J. S. C. I. 1903, **22**, 1008; Mon. Sci. 1904, **61**, 37; Chem. Ztg. 1903, **27**, 862; J. Soc. Dyers Col. 1903, **19**, 275. W. Wotherspoon, F. P. 334154, 1904; abst. Mon. Sci. 1904, **61**, 73; Chem. Zts. 1904, **3**, 179; J. S. C. I. 1904, **23**, 29. D. R. P. 182558, 1903; abst. Zts. ang. Chem. 1907, **20**, 1781; Wag. Jahr. 1907, **53**, II, 214; Chem. Zentr. 1907, **78**, I, 1295; Chem. Ztg. Rep. 1907, **31**, 177; Jahr. Chem. 1905-8, II, 3724; Mon. Sci. 1909, **71**, 77. Belg. P. 171743, 1903.

3. U. S. P. 708456 (preparing cellulose acetate from viscose), U. S. P. 708457 (purifying the acetate thus prepared), 1902; abst. J. S. C. I. 1902, **21**, 1243; Mon. Sci. 1903, **59**, 165; J. Soc. Dyers Col. 1905, **21**, 105; J. A. C. S. 1903, **25**-R, 200.

4. U. S. P. 695127, Re-11997, 1902, (assigned to General Electric Co.); abst. J. A. C. S. 1902, **24**, 431. E. P. 2264, 1902, (assigned to The British Thomson-Houston Co.); abst. J. S. C. I. 1903, **22**, 303.

5. J. Callan, U. S. P. 805260, 1905; abst. J. A. C. S. 1906, **28**-R, 346. (assigned to General Electric Co.)

6. J. Callan (assigned to General Electric Co.), U. S. P. 792001, 1905. E. P. 19565, 1902. See also E. P. 11997, 1902.

7. (Assigned to Chemical Products Co.), U. S. P. 709922, 1902; abst. Mon. Sci. 1903, **59**, 165; Chem. Ztg. 1902, **26**, 1019; J. A. C .S. 1903, **25**-R, 207; J. Soc. Dyers Col. 1905, **21**, 105; J. S. C. I. 1902, **21**, 1345. E. P. 20660, 1902; abst. J. S. C. I. 1903, **22**, 1011; J. Soc. Dyers Col. 1903, **19**, 281. F. P. 324862, 1902; abst. J. S. C. I. 1903, **22**, 646; Mon. Sci. 1904, **61**, 43; Chem. Zts. 1903, **2**, 347.

obviate the harmful effect of sulfuric acid as a catalyst by the employment of phenol- or naphthol-sulfonic acids or their sodium salts, the product being of especial value in the manufacture of artificial silk[1], especially in connection with phenol, cresol and a softening body as oleic acid or castor oil[2].

The next year (1903) appeared the L. Lilienfeld patents for the production of glossy silk-like effects on fabrics by means of cellulose acetate, either alone[3], or[4] mixed with mica or pigments and subsequently goffering or embossing. To assist in the production of these special effects, various high boilers and plasticizers new to the art were described, such as methyl and ethyl sebacates[5], normal ethyl phthalate alone or with butyl or amyl acetates[6], ethyl palmitate[7], and certain sulfur compounds of hydrocarbons as thioglycerol, mono-, di-, and tri-thiopyroglycides[8], and including aniline and *o*-toluidine[9].

In improvements in electrodes for accumulators, the

1. U. S. P. 712200, 1902; abst. J. S. C. I. 1903, **22**, 24; J. Soc. Dyers Col. 1905, **21**, 106; Mon. Sci. 1903, **59**, 165; Chem. Zts. 1903, **2**, 540; J. A. C. S. 1903, **25**-R, 246.

2. U. S. P. 792149, 1905, abst. J. S. C. I. 1905, **24**, 799; J. A. C. S. 1906, **28**-R, 75; Mon. Sci. 1906, **65**, 22.

3. U. S. P.847379, 1907. E. P. 14483, 1903; abst. J. S. C. I. 1903, **22**, 1345; J. Soc. Dyers Col. 1904, **20**, 30. D. R. P. 175664, 1903; abst. Wag. Jahr. 1906, **52**, II, 444; Zts. ang. Chem. 1907, **20**, 461; Mon. Sci. 1910, **73**, 158; Chem. Ztg. Rep. 1906, **30**, 354.

4. E. P. 4597, 1906; abst. J. S .C. I. 1907, **26**, 146; J. Soc. Dyers Col. 1906, **22**, 179; 1907, **23**, 32; C. A. 1907, **1**, 927. D. R. P. 182773, 1904; abst. Mon. Sci. 1909, **71**, 166; Chem. Ztg. Rep. 1907, **31**, 187; Wag. Jahr. 1907, **53**, II, 463.

5. D. R. P. 169782, 1904; abst. Chem. Ind. 1906, **29**, 233.

6. E. P. 592, 1907; abst. J. S. C. I. 1908, **27**, 73; J. Soc. Dyers Col. 1907, **23**, 62, 90; 1908, **24**, 86; Mon. Sci. 1912, **77**, 55. U. S. P. 888516, 1908; abst. J. S. C. I. 1908, **27**, 683; Chem. Ztg. Rep. 1908, **32**, 455; C. A. 1908, **2**, 2866.

7. U. S. P. 904269, 1908; abst. J. S. C. I. 1908, **27**, 1202; Mon. Sci. 1909, **71**, 142; C. A. 1909, **3**, 721. E. P. 4597, 1906; abst. J. S. C. I. 1907, **26**, 146; J. Soc. Dyers Col. 1906, **22**, 179; 1907, **23**, 32; C. A. 1907, **1**, 927.

8. E. P. 26928, 1910; abst. J. S. C. I. 1912, **31**, 122; J. Soc. Dyers Col. 1912, **28**, 75. F. P. 438448, 1911; abst. J. S. C. I. 1912, **31**, 584; Mon. Sci. 1914, **81**, 13.

9. E. P. 636, 1910; abst. Kunst. 1912, **2**, 255.

process of A. Meygret[1] involves the use of cellulose acetate lacquer for the independent lead plates or wires. The phonograph record coating of A. and L. Lumiere[2] depends upon the use of cellulose acetate or nitrate. In the method for cellulose acetylation as elaborated by R. Balston and J. Briggs[3], a small quantity of an anhydrochloride of a mineral acid as phosphorous pentachloride or oxychloride is added to the acetylizing bath, the mixture being kept at 55° for 7-8 hours, and until the desired solubility is obtained. Researches on the velocity of acetylation from a theoretical viewpoint were contributed by K. Panoff[4] and by A. and L. Lumiere and H. Barbier[5].

L. Lederer made a distinct contribution to the art in 1904 by describing the value of acetylene tetrachloride (tetrachlorethane) as a cellulose acetate solvent and incipient plasticizer[6], and although the toxicity of this liquid

1. U. S. P. 756176, 1904; abst. J. S. C. I. 1904, **23**, 445. U. S. P. 776192, 1904; abst. J. A. C. S. 1905, **27**-R, 441; Centr. Akk. Techn. 1905, **4**, 199. U. S. P. 776480, 1904; abst. J. A. C. S. 1905, **27**-R, 442; J. S. C. I. 1904, **23**, 1223. U. S. P. 779553, 1905; 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, 1901; abst. Zts. ang. Chem. 1904, **17**, 1215; Jahr. Chem. 1904, **57**, 239.

2. F. P. 338849, and addns. 2694, 2707, 1903; abst. Mon. Sci. 1905, **63**, 180; J. S. C. I. 1904, **23**, 1041. E. P. 15490, 1903.

3. E. P. 10243, 1903; abst. J. S. C. I. 1904, **23**, 557; Chem. Ztg. 1904, **28**, 872; J. Soc. Dyers Col. 1904, **20**, 141; 1905, **21**, 105; Mon. Sci. 1905, **63**, 327.

4. J. Russ. Phys. Chem. Soc. 1903, **35**, 93; abst. J. C. S. 1903, **84**, ii, 357; Bull. Soc. Chim. 1904, **32**, 37; Rep. Chim. 1903, **3**, 410; Chem. Centr. 1903, **74**, I, 1128; Jahr. Chem. 1903, **56**, 229; Meyer Jahr. Chem. 1903, **13**, 170.

5. Bull. Soc. Chim. 1905, **33**, 783; abst. J .C. S. 1905, **88**, i, 652.

6. U. S. P. 804960, 1905; abst. J. S. C. I. 1905, **24**, 1314; Mon. Sci. 1907, **67**, 57; J. A. C. S. 1906, **28**-R, 344. E. P. 6751, 1905; abst. J. S. C. I. 1906, **25**, 326; Mon. Sci. 1913, **78**, 392. F. P. 352896, 1905; abst. Mon. Sci. 1906, **65**, 104; C. A. 1907, **1**, 360, 381. F. P. 352897, 1905; abst. J. S. C. I. 1905, **24**, 978; Mon. Sci. 1907, **67**, 331; C. A. 1907, **1**, 1476, 1497. D. R. P. 175379, 1904; abst. Chem. Ztg. 1906, **30**, 758; Chem. Centr. 1906, **77**, II, 1544; Wag. Jahr. 1906, **52**, II, 512; Jahr. Chem. 1905-8, II, 985; Chem. Ind. 1906, **29**, 559; Zts. ang. Chem. 1907, **20**, 2045; Mon. Sci. 1908, **69**, 43; C. A. 1907, **1**, 1064. D. R. P. 188542, 1905; abst. Jahr. Chem. 1905-8, II, 984; Chem. Ztg. 1907, **31**, 707; Wag. Jahr. 1907, **53**, II, 404; Chem. Zts. 1907, **6**, No. 258; Chem. Zentr. 1907, **78**, II, 1815; Chem. Ind. 1907, **30**, 334; Mon. Sci. 1910, **73**, 77; C. A. 1908, **2**, 733. Aust. P. 29219, 1907; abst. Chem. Ztg. 1907, **31**, 671. Belg. P. 195838, 195840, 1906. Hung. P. June 23, 1904.

was early recognized, interest was materially stimulated. Just as in the earlier and better known cellulose nitrate art, advances of a permanent nature came at those periods when someone discovered new solvents or improved methods of utilizing those then known. Advancement in the *Technology of Cellulose Esters* is an enumeration of progress due to the application of solvents in contradistinction to the development of ester manufacture, and the underlying thought as brought out by a careful study of the chronological steps which have led to the manifold uses of the uninflammable cellulose esters at the present time, is that new ways of ester manufacture resulted in a commercial value only when such products were found soluble in cheaper or more widely obtained solvents. The above disclosures of Lederer, therefore, are to be regarded as a distinct stepping stone in progress. Threads, ribbons, films and tubes[1] and other variously shaped industrial objects were therefore possible, and their production made a reality.

The Farbenfabriken vorm. F. Bayer & Co.[2] combines boric acid with acetylcellulose to increase the consistency so that printing colors for textiles are producable which are thick masses with excellent adhesion. This product under the name of Sericose L. has been extensively employed with satisfactory effect for the simulation of damask

1. E. P. 7341, 1903; abst. J. S. C. I. 1904, **23**, 501. F. P. 330714, 1903; abst. J. S. C. I. 1903, **22**, 1100; Mon. Sci. 1904, **61**, 67. D. R. P. 200916, 1905 (addn. to D. R. P. 163316, 1901); abst. Wag. Jahr. 1908, **54**, II, 364; Chem. Zentr. 1908, **79**, II, 738; Zts. ang. Chem. 1908, **21**, 2047; Jahr. Chem. 1905-8, II, 984; Zts. Schiess Spreng. 1908, **3**, 374. Aust. P. 42440, 1909; abst. Chem. Ztg. 1910, **34**, 518. See also Aust. P. 36843, 1908.

2. F. P. 341007, 1904; abst. J. S. C. I. 1904, **23**, 864; Mon. Sci. 1906, **65**, 33; J. Soc. Dyers Col. 1904, **20**, 223; Chem. Ztg. 1904, **28**, 852; Chem. Zts. 1904, **3**, 621. D. R. P. 292589, 1915; abst. C. A. 1917, **11**, 2410; Chem. Ztg. Rep. 1916, **40**, 296; Zts. ang. Chem. 1916, **29**, II, 328; Wag. Jahr. 1916, **62**, II, 225. D. R. P. 291802, 1915; abst. C. A. 1917, **11**, 1310; Wag. Jahr. 1916, **62**, II, 224; Chem. Zentr. 1916, **85**, I, 1048; Chem. Ztg. Rep. 1916, **40**, 224; Zts. ang. Chem. 1916, **29**, II, 328.

effects. For sizing and dressing threads[1] a lacquer of acetated cellulose in alcohol, acetone, ethyl acetate or acetylene tetrachloride is advocated.

The Badische Anilin & Soda Fabrik[2] recommend that the acetation be conducted upon cellulose in a moistened state, as by a preliminary treatment of the cellulose with dilute sulfuric acid (hydrocellulose formation), or that the acetation be effected in presence of benzene, toluene or ether as a non-solvent, the acetylated cellulose being thereby obtained in a fibrous state.

The A. Corti[3] cellulose acetate manufacturing process replaced sulfuric acid by dimethyl sulfate; and I. Hoffsuem-

1. E. P. 28773, 1904; abst. J. S. C. I. 1905, **24**, 1299. F. P. 350442, 1904; abst. J. S. C. I. 1906, **25**, 262; Mon. Sci. 1906, **65**, 169; 1908, **69**, 19; J. Soc. Dyers Col. 1906, **22**, 112, 201; Chem. Ztg. 1906, **30**, 225; C. A. 1907, **1**, 1073. D. R. P. 240188, 1909; abst. Wag. Jahr. 1911, **57**, II, 468; C. A. 1912, **6**, 2178; Chem. Zentr .1911, **82**, II, 1563; Chem. Ztg. Rep. 1911, **35**, 576; Zts. ang. Chem. 1911, **24**, 2336; Chem. Zts. 1911, **10**, No. 2590. Belg. P. 181504, 1904.

2. E. P. 24083, 1904; abst. J. S. C. I. 1905, **24**, 1081; J. Soc. Dyers Col. 1905, **21**, 304. F. P. 347906, 1904; abst. J. S. C. I. 1905, **24**, 454; 1906; **25**, 232; Chem. Zts. 1905, **4**, 112; Mat. Color. 1905, **9**, 147; Mon. Sci. 1906, **65**, 15; 1913, **79**, 551; Chem. Ztg. 1905, **29**, 494; J. Soc. Dyers Col. 1905, **21**, 106, 124. D. R. P. 184145, 1904; abst. Chem. Ind. 1907, **30**, 238; Wag. Jahr. 1907, **53**, II, 401; Chem. Zentr. 1907, **78**, II, 365; Jahr. Chem. 1905-8, II, 983; Zts. Schiess Spreng. 1907, **2**, 195; Mon. Sci. 1909, **71**, 77; C. A. 1907, **1**, 2523. D. R. P. 184201, 1904; abst. Chem. Zentr. 1907, **78**, II, 365; Wag. Jahr. 1907, **53**, II, 207; Jahr. Chem. 1905-8, II, 984; Zts. ang. Chem. 1908, **21**, 268; Zts. Schiess Spreng. 1907, **2**, 195; Mon. Sci. 1909, **71**, 77; C. A. 1907, **1**, 2524. Aust. P. 35015, (addn. to Aust. P. 8165 and 31391); abst. Chem. Ztg. 1908, **32**, 1036. Belg. P. 182216, 1905; abst. Chem. Ztg. 1905, **29**, 294. Norw. P. 15082. Russ. P. 11492, 1907. Swed. P. 20249, 1905; abst. Chem. Ztg. 1906, **30**, 281. R. Strehlenert, D. R. P. Anm. St.-9000, 1904; abst. Chem. Ztg. 1905, **29**, 847. R. Strehlenert and F. Reubold, (assignors to Badische Anilin- u. Sodafabrik); U. S. P. 812098, 1906; abst. J. S. C. I. 1906, **25**, 232; Mon. Sci. 1906, **65**, 120; 1908, **68**, 464; Chem. Zts. 1906, **5**, 159; J. A. C. S. 1906, **28**-R, 461.

3. U. S. P. 826229, 1906; abst. J. S. C. I. 1906, **25**, 825; Mon. Sci. 1907, **67**, 35; Chem. Ztg. Rep. 1906, **30**, 292; Chem. Zts. 1906, **5**, 495; C. A. 1907, **1**, 104, 118. Fabrique de Produits Chimiques Flora, F. P. 345764, 1904; abst. J. S. C. I. 1905, **24**, 40, 855; Mon. Sci. 1906, **65**, 12; J. Soc. Dyers Col. 1905, **21**, 105. E. P. 9998, 1905; abst. J. S. C. I. 1905, **24**, 855; Chem. Ztg. 1906, **30**, 346; J. Soc. Dyers Col. 1905, **21**, 274. D. R. P. Anm. C-12963, 1903. Belg. P. 183877, 1905; abst. Chem. Ztg. 1905, **29**, 538. Ital. P. Apr. 17, 1905; abst. Chem. Ztg. 1905, **29**, 755.

mer replaced nitrocellulose in an earlier patent[1] by acetates of cellulose as a basis for sensitized plates and for printing paper[2]. The W. Walker substitute for celluloid and horn consists of cellulose acetate combined by heat with thymol and chloroform[3], or to still more diminish the volatility of the thymol, castor oil may replace the chloroform[4].

In taking a retrospective glance over the (sixty-three) distinct contributions touched upon herein in this quinquinnial period 1900-1904, one perceives advancement taking place first in endeavors to control the esterizing process, either by a modification of the original cellulose before acetation; by a minimization of the powerful effect of the sulfuric acid used as condensing agent, either by replacement with other materials or (perhaps from a patent circumlocution viewpoint) employing substituted sulfuric acids and sulfonic derivatives, most of which, if not all, eliminate sulfuric acid as such at some stage of acetylization. Another distinct trend of development is in attempts to replace the expensive, narcotic chloroform by less costly and innocuous solvents and solvent combinations. Finally, the patents issued and researches published unmistakably show the interest attached to the search for a body which, when added to acetate cellulose, will impart the properties of thermoplasticity and moldability which camphor induces in the formation of celluloid—a search which has been unremitting up to the present day, but which has, as yet, not been entirely successful.

1. E. P. 25390, 1903; abst. J. S. C. I. 1904, **23**, 337.

2. E. P. 3855, 1904; abst. J. S. C. I. 1904, **23**, 622. F. P. 357473, 1905; abst. Mon. Sci. 1907, **67**, 43; C. A. 1907, **1**, 1516, 1646.

3. U. S. P. 774713, 1904; abst. Bayr. Ind. u. Gewerbebl. 1906, **38**, 193; J. S. C. I. 1904, **23**, 1159; Mon. Sci. 1905, **63**, 50; Chem. Ztg. 1904, **28**, 1157; J. A. C. S. 1905, **27**-R, 434.

4. U. S. P. 774714, 1904; abst. Bayr. Ind. u. Gewerbebl. 1906, **38**, 193; J. S. C. I. 1904, **23**, 1159; Mon. Sci. 1905, **63**, 50; Chem. Ztg. 1904, **28**, 1157; J. A. C. S. 1905, **27**-R, 434. F. P. 417319, 1910; abst. Chem. Ztg. 1910, **34**, 1026; J. S. C. I. 1911, **30**, 19; Mon. Sci. 1913, **78**, 392; **79**, 30. Compare L. Lederer, Addn. 811, to F. P. 319724; abst. J. S. C. I. 1903, **22**, 563. See also Elbee, Cosmos, 1904, **50**, 789.

Advancement of the Art, 1905-1909. The most important contribution to the art in 1905 undoubtedly was the partial hydration disclosures of G. Miles. Up to this time all acetated cellulose had been used dissolved in either unduly expensive or toxic solvents as chloroform and tetrachlorethane, and the art in its commercial applications, if not practically at a standstill, was nevertheless limited in its advancement by too few and too costly solvents and solvent combinations. In Miles' United States application 24575 dated July 23, 1900 (allowed Dec. 18, 1900, abandoned, and included in his application dated May 27, 1901) was first disclosed a practical method of preparing chloroform-soluble cellulose acetate directly from fibrous natural cellulose (cotton or tissue paper) and without the necessity of a preliminary treatment of the cellulose for hydrocellulose formation. At this time the most satisfactory acetated celluloses for commercial film formation were those soluble in chloroform.

It was Miles, also, who made the next important step, that of partial hydration of the acetated cellulose after formation into the compound of maximum elasticity, strength and flexibility, which he found resulted when the partial hydration was carried to the point of incipient plasticity in cold chloroform, ready plasticity in warm chloroform, and complete solubility in substantially anhydrous acetone, these three solubility results being given at the same time to the product of maximum strength. This partial hydration of acetated cellulose by the successive withdrawal of acetyl from the ester opened up new and much broader fields, in that it permitted of the use of solvents of less cost, lower boiling point, greater speed of evaporation, and solvents which were readily obtainable in unlimited quantities[1].

1. The credit for the discovery of the commercially valuable cellulose acetates, and those of maximum strength, pliability and elasticity as suitable for film formation, has been erroneously ascribed to A. Eichengruen and the Farbenfabriken vorm. F. Bayer & Co., to whom many of his patents have been assigned. In the interests of

In the first Miles patent (see page 347) the acetated derivative was formed "directly from cellulose." In the second patented process, Miles clearly sets forth the principles of partial hydration or successive withdrawal of acetic acid from the formed cellulose acetate. The primary requisite of this process is not the formation as some stage of production of a cellulose hydrate or hydrocellulose, but by an anhydrous method, in which no water, practically speaking, is allowed to enter into the reaction or combination. The final product is characterized as a partly hydrated cellulose acetate rather than an acetated cellulose hydrate—a differentiation which has withstood the test of succeeding patent litigation. He found "that by employing various degrees of partial or incomplete hydration—in other words by varying the quantitative proportions of water employed to effect the partial hydration—a variety of products may be formed which differ in their characteristics, especially in their behavior with the solvents which serve as effective vehicles." With 100 gm. cellulose, 240

historical accuracy, the following facts—all public documents available for inspection—are recorded. G. W. Miles was the first to acetate natural cellulose as cotton to a commercially utilizable product, as shown by U. S. Application No. 24575, filed June 23, 1900, and the File Wrapper of which the application forms a part. This eliminated the previous tedious processes of first preparing the cotton for acetylation by a distinct series of operations. Miles was the first to recognize and establish priority of conception by patent application for the process of partial hydration whereby less expensive solvents could be used and the maximum of strength for film formation still be obtained. His German Application, embodying the partial hydration of acetated cellulose, made Sept. 30, 1905, as Application No. M-28289, was, after seven years of continuous litigation, passed by the German Patent Office for issuance, and was then purchased by the litigants and issued by them as D. R. P. 252706 to F. Bayer & Co. This firm had an application covering substantially the same idea, which was applied for on November 29, 1905, as F-20963, and elected by them as an Addition to Miles Application M-28289, which later issued as D. R. P. 252706. The Bayer Co. did not purchase the Miles F. P. 358079, 1905, covering partial hydration in France. It is true that Bayer & Co. was granted a patent in England (see E. P. 21628, 1901; 24067, 1906) for the partial hydration of acetated cellulose by precipitating the acetated cellulose, washing to neutrality, drying, and then hydrating. But anyone who has attempted to hydrate dry, normal cellulose acetate will at once appreciate the futility and commercial impossibility of such a method.

gm. commercial acetic anhydride, 400 gm. glacial acetic acid and 20 gm. of 95% sulfuric acid, 40-45 gm. water is required for the hydration treatment from the acetated cellulose obtained as above[1].

L. Lederer endeavored to reduce the inflammability of the nitrocelluloses by the partial replacement of acetyl radicles for nitro[2], and this is made possible by acting upon collodion at temperatures below 60° with acetyl chloride with or without the addition of a condensing agent. The

1. U. S. P. 733729, 1903; abst. J. A. C. S. 1904, **26**-R, 82; J. I. E. C. 1906, **25**, 195; J. S. C. I. 1903, **22**, 961; J. Soc. Dyers Col. 1905, **21**, 105; Mon. Sci. 1903, **60**, 173; 1905, **63**, 327; Chem. Zts. 1903, **2**, 743. U. S. P. 838350, 1906; abst. C. A. 1907, **1**, 640, 653; J. S. C. I. 1907, **26**, 165, 634; Mon. Sci. 1907, **67**, 116, 116, 159; 1908, **69**, 19; 1913, **78**, 393; Chem. Ztg. 1907, **31**, 119; Chem. Ztg. Rep. 1907, **31**, 77. U. S. P. Re-12637, 1907; to U. S. P. 838350, 1906; abst. J. S. C. I. 1907, **26**, 634. E. P. 19330, 1905; abst. J. S. C. I. 1906, **25**, 865; Mon. Sci. 1913, **78**, 393. F. P. 358079, 1905; abst. C. A. 1907, **1**, 1059, 1081; J. S. C. I. 1906, **25**, 195; Mon. Sci. 1906, **64**, 169; 1908, **69**, 19; 1913, **78**, 393, 551; Chem. Zts. 1906, **5**, 38. D. R. P. Anm. M-28289, 1905; abst. Chem. Ztg. 1907, **31**, 161. Aust. P. Anm. 5187, 1905; abst. Chem. Ztg. 1909, **33**, 914. Aust. P. 41461, 1905; abst. Mon. Sci. 1913, **78**, 393; Chem. Ztg. 1911, **35**, 214. Belg. P. 187308, 1905; abst. Mon. Sci. 1913, **78**, 393; Chem. Ztg. 1905, **29**, 1165. Can. P. 90848, 1905; 103045, 1906; abst. Mon. Sci. 1913, **7**, 393; Chem. Ztg. 1907, **31**, 874. Hung. P. 35866, 1905. Ital. P. No. 97, Vol. 215, 1905. Farbenfabriken vorm. F. Bayer & Co., D. R. P. 252706, 1905; abst. C. A. 1913, **7**, 550; Chem. Zentr. 1912, **83**, II, 1755; Chem. Ind. 1912, **35**, 770; Chem. Ztg. Rep. 1912, **36**, 732; Kunst. 1912, **2**, 399; 1913, **3**, 35; Wag. Jahr. 1912, **58**, I, 503; Zts. ang. Chem. 1912, **25**, 2621. D. R. P. Anm. E-20963, 1905; abst. Chem. Ztg. 1913, **37**, 215; Kunst. 1913, **3**, 100.

2. E. P. 19107, 1906; abst. C. A. 1907, **1**, 1342; J. S. C. I. 1907, **26**, 220; Mon. Sci. 1913, **78**, 389. F. P. 368766, 1906; abst. J. S. C. I. 1907, **26**, 30, 273; Mon. Sci. 1908, **69**, 19; 1913, **78**, 389, 551. D. R. P. Anm. L-21238, 1905; abst. Chem. Ztg. 1906, **30**, 885. D. R. P. 179947, 1905; abst. C. A. 1907, **1**, 1468, 1507; J. S. C. I. 1907, **26**, 889; Mon. Sci. 1909, **71**, 68; 1913, **78**, 389; Chem. Zentr. 1907, **78**, I, 433; Chem. Ztg. 1906, **30**, 1198; Chem. Ztg. Rep. 1907, **31**, 37; Jahr. Chem. 1905-08, II, 986; Wag. Jahr. 1907, **53**, I, 419; Zts. ang. Chem. 1907, **20**, 1194; Zts. Schiess Spreng. 1907, **2**, 75. D. R. P. 200149, 1905; Addn. to D. R. P. 179947, 1905; abst. Mon. Sci. 1911, **75**, 63; 1913, **78**, 389; Chem. Zentr. 1908, **79**, II, 551; Jahr. Chem. 1905-08, II, 986; Wag. Jahr. 1908, **54**, II, 365; Zts. ang. Chem. 1908, **21**, 2047; Zts. Schiess Spreng. 1908, **3**, 334. D. R. P. 210778, 1906; abst. Mon. Sci. 1913, **78**, 389; Chem. Zentr. 1909, **80**, II, 247; Chem. Ztg. Rep. 1909, **33**, 341; Chem. Zts. 1909, **8**, 1474; Jahr. Chem .1909, **62**, 389; Wag. Jahr. 1909, **55**, II, 390; Zts. ang. Chem. 1909, **22**, 1620. Aust. P. 34272, 1908; abst. Chem. Ztg. 1908, **32**, 774. Hung. P. Feb. 6, 1907; abst. Chem. Ztg. 1907, **31**, 426. Compare C. Cross, E. Bevan and J. Briggs, Ber. 1905, **38**, 1251.

next year (1906) appeared modifications of the original process in which other condensing agents were recommended, as phosphoric acid, benzenesulfonic acid, benzenesulfinic acid, and dimethyl sulfate[1]. In an improvement of his processes of cellulose acetylation of 1900 and of 1901 L. Lederer conducts the esterification in the presence of a non-solvent of acetated cellulose, carbon tetrachloride being specified as the diluent[2], the amount added being sufficient so the acetylated derivative does not pass into solution during the esterizing, a fibrous cellulose acetate being thereby produced. The acetic anhydride may also be recovered by the use of a non-aqueous precipitant after acetation, carbon tetrachloride also being recommended for this purpose[3].

Knoll & Co. described the advantages of using the sulfinic acids as condensing agents[4] in cellulose acetation, and

1. L. Lederer, D. R. P. 200149, 1906; Addn. to D. R. P. 179947, 1905; abst. Mon. Sci. 1911, **75**, 63; 1913, **78**, 389; Chem. Zentr. 1908, **79**, II, 551; Jahr. Chem. 1905-08, II, 986; Wag. Jahr. 1908, **54**, II, 365; Zts. ang. Chem. 1908, **21**, 2047; Zts. Schiess Spreng. 1908, **3**, 334. Farbenfabriken vorm. F. Bayer & Co. had described the use of phosphoric acid in 1901 (see p. 337, n. 1); also L. Landsberg (p. 339, n. 1). The use of dimethylsulfate had previously been proposed by A. Corti in 1904 (see p. 345, n. 3).

2. L. Lederer, D. R. P. 200916, 1905; Addn. to D. R. P. 163316, 1901; abst. Mon. Sci. 1911, **75**, 82; Chem. Zentr. 1908, **79**, II, 738; Chem. Ztg. 1908, **32**, 737; Jahr. Chem. 1905-08, II, 984; Wag. Jahr. 1908, **54**, II, 364; Zts. ang. Chem. 1908, **21**, 2047; Zts. Schiess Spreng. 1908, **3**, 374. F. P. 374370, 1907; abst. C. A. 1908, **2**, 2620; J. S. C. I. 1907, **26**, 776, 889; Mon. Sci. 1908, **69**, 84; 1910, **73**, 452; 1913, **78**, 389, 551; Chem. Ztg. 1907, **31**, 339; Chem. Zts. 1907, **6**, 139. Aust. P. 41811, 1908; abst. Chem. Ztg. 1911, **35**, 242.

3. U. S. P. 902093, 1906; abst. C. A. 1909, **3**, 713; J. S. C. I. 1908, **27**, 1130; Chem. Ztg. 1908, **32**, 1155. E. P. 2650, 1906; abst. C. A. 1907, **1**, 1797; J. S. C. I. 1907, **26**, 430; Chem. Ztg. 1907, **31**, 288. F. P. 371356, 1906; abst. C. A. 1908, **2**, 2453; J. S. C. I. 1907, **26**, 340; Mon. Sci. 1908, **68**, 79; 1910, **72**, 452; Chem. Ztg. 1907, **31**, 162; Chem. Ztg. Rep. 1907, **31**, 130. D. R. P. 185151, 1905; abst. C. A. 1907, **1**, 2656; Chem. Ind. 1907, **30**, 282; Chem. Zentr. 1907, **78**, II, 498; Chem. Ztg. 1907, **31**, 426; Jahr. Chem. 1905-08, II, 985; Wag. Jahr. 1907, **53**, II, 403; Zts. ang. Chem. 1907, **20**, 1541; 1908, **21**, 269.

4. E. P. 2026, 1907; abst. C. A. 1908, **2**, 2620, 2729; J. S. C. I. 1908, **27**, 353; Mon. Sci. 1913, **78**, 389. F. P. 369123, 1906; abst. C. A. 1908, **2**, 1363; J. S. C. I. 1907, **26**, 91, 112; 1908, **27**, 353; Mon. Sci. 1908, **68**, 28; 1910, **73**, 453; Chem. Ztg. 1906, **30**, 1186. D. R. P. 180666, 1905; abst. C. A. 1907, **1**, 1622, 1655; Mon. Sci. 1909, **70**, 77; Chem. Zentr. 1907, **78**, I, 773; Chem. Ztg. Rep. 1907, **31**, 91; Jahr. Chem. 1905-08, II, 982; Wag. Jahr. 1907, **53**, II, 404; Zts. ang. Chem.

subsequently found[1] that as small amounts as 0.1 part benzolsulfinic acid gave dependable results. It was early found that very erratic results occur in attempting to dye acetated cellulose by the methods and materials found suitable for the coloring of other cellulose esters, and this question at the present day appears to be far from being satisfactorily solved, especially in endeavoring to produce *uniform* dyeings. The Actiengesellschaft fuer Anilin Fabrikation[2] obtained best results by means of a dye bath composed of ethyl alcohol and water, the former appearing to aid in the penetration of the dyestuff so that full or dark shades are obtainable with the usual basic colors. In attempts to minimize the harmful effect of the catalyst, mon-, di-, and tri-chloracetic acids are advocated for acetating cellulose,

1907, **20**, 1541, 1786; Zts. Schiess Spreng. 1907, **2**, 75. Belg. P. 199492, 1907; abst. Chem. Ztg. 1907, **31**, 612. Aust. P. 33452, 33508, 1908; abst. Chem. Ztg. 1908, **32**, 588. Hung. P. Appl. K-3414, 1908; abst. Chem. Ztg. 1909, **33**, 946. For the Knoll method of dyeing cellulose acetate see E. P. 7743, 1909; abst. C. A. 1911, **5**, 206; J. S. C. I. 1910, **29**, 269; J. Soc. Dyers Col. 1909, **25**, 153; 1910, **26**, 90, 95. D. R. P. 199559, 1907; abst. Chem. Zentr. 1908, **79**, II, 271; Wag. Jahr. 1908, **54**, II, 410; Zts. ang. Chem. 1908, **21**, 1810; D. R. P. 234028, 1908; abst. C. A. 1911, **5**, 2948; Chem. Zentr. 1911, **82**, II, 1471; Chem. Ztg. Rep. 1911, **35**, 250; Chem. Zts. 1911, **10**, 2574; Kunst. 1911, **1**, 215; Wag. Jahr. 1911, **57**, II, 422; Zts. ang. Chem. 1911, **24**, 1151. E. Knoevenagel, U. S. P. 981574, 1911; abst. C. A. 1911, **5**, 1192; J. S. C. I. 1911, **30**, 126; J. Soc. Dyers Col. 1911, **27**, 74; Mon. Sci. 1912, **77**, 29; Kunst. 1911, **1**, 174.

1. D. R. P. 180667, 1905; Addn. to D. R. P. 180666, 1905 (this patent 180667 is the same as 180666 but they use a small (0.1) part of sulfinic acid).; abst. C. A. 1907, **1**, 1622, 1655; Mon .Sci. 1909, **70**, 77; Chem. Zentr. 1907, **78**, I, 773; Chem. Ind. 1907, **30**, 110; Chem. Ztg. Rep. 1907, **31**, 91; Jahr. Chem. 1905-08, II, 982; Wag. Jahr. 1907, **53**, 404; Zts. ang. Chem. 1907, **20**, 1541, 1786; Zts. Schiess Spreng. 1907, **2**, 75.

2. E. P. 1939, 1906; abst. C. A. 1907, **1**, 911, 924; J. S. C. I. 1906, **25**, 1216; J. Soc. Dyers Col. 1906, **22**, 147; Chem. Ztg. 1906, **30**, 1211. F. P. 362721, 1906; abst. C. A. 1907, **1**, 2427; J. S. C. I. 1906, **25**, 692, 1216; J. Soc. Dyers Col. 1906, **22**, 246; Mon. Sci. 1907, **67**, 102; Chem. Ztg. 1906, **30**, 443; Chem. Ztg. Rep. 1906, **30**, 283; Chem. Zts. 1906, **5**, 278. D. R. P. 193135, 1905; abst. C. A. 1908, **2**, 1216; Chem. Zentr. 1908, **79**, I, 183; Chem. Zts. 1908, **7**, 630; Wag. Jahr. 1907, **53**, II, 433; Zts. ang. Chem. 1908, **21**, 1266.

the product formed being soluble in chloroform, acetylene tetrachloride and epichlorhydrin[1].

H. Cathelineau and A. Fleury described plastics formed from casein and a cellulose ester, either nitrocellulose or cellulose acetate, by the incorporation of various phenols, especially phenol, thymol and naphthol[2], to which camphor[3] may be added. The P. Leemans plastic[4] involves the use of dry cellulose acetate and dry casein which are impregnated by means of the mutual solvent glacial acetic acid, then rolled and masticated in the usual manner.

1. Actien Gesellschaft Fur Anilin Fabrikation, E. P. 14255, 1906; abst. C. A. 1907, **1**, 1341; J. S. C. I. 1907, **26**, 220; J. Soc. Dyers Col. 1907, **23**, 87; Mon. Sci. 1913, **78**, 389, 392; Chem. Ztg. 1907, **31**, 161. F. P. 368738, 1906; abst. C. A. 1908, **2**, 2456; J. S. C. I. 1907, **26**, 30, 220; Mon. Sci. 1908, **69**, 76; 1910, **73**, 452; 1913, **78**, 389; Chem. Ztg. 1906, **30**, 1133; Chem. Zts. 1907, **6**, 266. D. R. P. Anm. A-12478, 1905; abst. Chem. Ztg. 1906, **30**, 927. D. R. P. 198482, 1905; abst. Chem. Zentr. 1908, **79**, II, 118; Chem. Ztg. 1908, **32**, 478; Jahr. Chem. 1905-08, II, 982; Wag. Jahr. 1908, **54**, II, 362; Zts. ang. Chem. 1908, **21**, 1760. D. R. P. 203642, 1906; abst. Mon. Sci. 1912, **77**, 96; Chem. Zentr. 1908, **79**, II, 1705; Chem. Ztg. Rep. 1908, **32**, 651; Chem. Zts. 1909, **8**, 1218; Jahr. Chem. 1905-08, II, 983; Wag. Jahr. 1908, **54**, II, 367; Zts. ang. Chem. 1908, **21**, 2426.

2. E. P. 12277, 1905; abst. J. S. C. I. 1906, **25**, 327; Mon. Sci. 1913, **78**, 392. F. P. 354942, 1905; abst. C. A. 1907, **1**, 1059, 1077; J. S. C. I. 1905, **24**, 1226; Mon. Sci. 1906, **65**, 167; 1913, **78**, 392; Chem. Ztg. 1906, **30**, 133. D. R. P. 185240, 1906; abst. C. A. 1908, **2**, 349; Mon. Sci. 1910, **73**, 80; 1913, **78**, 392; Chem. Zentr. 1907, **78**, II, 1037; Chem. Ztg. Rep. 1907, **31**, 361; Wag. Jahr. 1907, **53**, 563; Zts. ang. Chem. 1907, **20**, 2177.

3. E. P. 12278, 1905; abst. J. S. C. I. 1906, **25**, 327; Mon. Sci. 1913, **78**, 392. F. P. 4898, 1905; Addn. to F. P. 354942, 1905; abst. J. S. C. I. 1905, **24**, 1226. D. R. P. 185241, 1906; Addn. to D. R. P. 185240, 1906; abst. C. A. 1908, **2**, 728; Mon. Sci. 1910, **73**, 76; 1913, **78**, 392; Chem. Zentr. 1907, **78**, II, 1819; Chem. Ztg. Rep. 1907, **31**, 396; Wag. Jahr. 1907, **53**, II, 563; Zts. ang. Chem. 1908, **21**, 211.

4. Belg. P. 182050, 1905, is for the manufacture of a plastic from dry casein and cellulose acetate in powdered form. The ingredients are mixed and impregnated with glacial acetic acid, pressed, rolled and masticated and the solvent is evaporated off. Belg. P. 182051, 1905, (abst. Chem. Ztg. 1905, **29**, 278) is for the treatment of hydrocellulose with acetic anhydride in the presence of aromatic sulfuric acid. Belg. P. 182052, 1905, is for the manufacture of objects from cellulose acetate. In Belg. P. 181194, 1905, he treats cellulose with appropriate acid in presence of small quantities, aromatic sulfonic acid, then adds fatty anhydride to manufacture cellulose acetate or higher esters. In Belg. P. 201017, 1907, cellulose and cellulose esters, such as cellulose acetate, formate and butyrate are treated with borneol and isoborneol.

The continuous horse hair-like fibers of the Vereinigte Kunstseidefabriken[1], is made from the waste from twisted artificial thread which is first untwisted and then bound together by saturation with cellulose acetate, collodion, viscose, cuprammonium cellulose or cellulose in zinc chloride. Whereas L. Lederer acetated nitrocellulose, C. Haeussermann[2] nitrated acetated cellulose, his method being to dissolve acetylhydrocellulose in fuming nitric acid, and after 14 days the mixed ester was obtained as a fine white powder, soluble in acetone, ethyl acetate and amyl acetate. The substance was explosive and contained 11.5% of nitrogen, forming the corresponding hydrocellulose by denitration with sodium hydrosulfide, and this product was found to be entirely soluble in cold 10% caustic soda and capable of reducing Fehling's solution. The M. Henzman plastic[3] is composed of blood, aluminum hydroxide, cellulose acetate or nitrocellulose, the mass being further stabilized by the addition of hexamethyltetramine. Ulzer[4] and F. Marsden[5] contributed data of comparatively minor importance.

In the next year (1906), Knoll & Co. described their process for the manufacture of cellulose esters in the presence of halogen-substituted fatty acids as condensers, specifically mono-, di-, and tri-chloracetic acids[6], a method disclosed the previous year. Hydrochloric acid and nitric

1. D. R. P. 181784, 1905; abst. C. A. 1907, **1**, 2440; Mon. Sci. 1909, **71**, 166; Chem. Zentr. 1907, **78**, II, 110; Chem. Ztg. Rep. 1907, **31**, 149; Wag. Jahr. 1907, **53**, II, 392.

2. Chem. Ztg. 1905, **29**, 667; Lehne's Faerb. Ztg. 1905, **16**, 248; abst. J. C. S. 1905, **88**, 574; J. S. C. I. 1905, **24**, 748; Chem. Centr. 1905, **76**, II, 760; Jahr. Chem. 1905-8, II, 983; Wag. Jahr. 1905, **51**, II, 192; Zts. ang. Chem. 1905, **18**, 1989.

3. Aust. P. 29281 and Addn. thereto 29831, 1905.

4. Mitt Gew. Mus. 1905, **15**, 241.

5. J. Soc. Dyers Col. 1905, **21**, 103. Compare Muster Ztg. 1905, **54**, 81; Faerb. Ztg. 1906, **42**, 172.

6. Knoll & Co., D. R. P. 203642, 1908; abst. Mon. Sci. 1912, **77**, 96; Chem. Zentr. 1908, **79**, II, 1705; Chem. Ind. 1908, **31**, 74; Chem. Ztg. Rep. 1908, **32**, 651; Chem. Zts. 1909, **8**, 1218; Jahr. Chem. 1905-08, II, 983; Wag. Jahr. 1908, **54**, II, 367; Zts. ang. Chem. 1908, **21**, 2334, 2426. In this connection see Zts. ang. Chem. 1908, **21**, 1760.

acid, either alone or together[1], was also specified by this firm as suitable contact agents for assisting esterification, and including certain neutral salts[2], as ferrous sulfate, ferric chloride, ferric sulfate, zinc sulfate, zinc chloride, cupric sulfate, tin or antimony chlorides, dimethylamine chloride or sulfate, ammonium sulfate or magnesium or calcium chlorides. Especially was methylamine sulfate claimed as advantageous for this purpose[3]. In the foregoing mentioned processes, the contact substances named were specified as taking the place of the sulfuric acid usually employed for this purpose, but several years afterwards when the process of partial hydration or "ripening" was more fully understood and its commercial value appreciated, this firm protected by patent application, the use of many of these bodies for the purposes of transforming the chloroform-soluble and acetone-insoluble cellulose acetates, into the chloroform-insoluble, acetone-soluble modifications. Methylamine bisulfate, methylamine sulfate or sodium ethyl

1. Knoll & Co., F. P. 373994, 1907; abst. J. S. C. I. 1907, **26**, 776; 1908, **27**, 252, 765; Mon. Sci. 1908, **68**, 83; 1910, **72**, 452; Chem. Ztg. Rep. 1907, **31**, 302; Chem. Zts. 1907, **6**, 232. D. R. P. 201233, 1906; abst. Zts. Chem. Ind. Koll. 1908, **3**, 190; Mon. Sci. 1911, **75**, 124; 1913, **78**, 389; Chem. Zentr. 1908, **79**, II, 994; Chem. Ind. 1908, **31**, 587; Chem. Zts. 1908, **7**, 993; Jahr. Chem. 1905-08, II, 982; Wag. Jahr. 1908, **54**, II, 366; Zts. ang. Chem. 1908, **21**, 2233; Zts. Schiess. Spreng. 1908, **3**, 374. Belg. P. 197484, 1907; abst. Chem. Ztg. 1907, **31**, 316. E. Knoevenagel and H. Lebach, U. S. P. 891218 ,1908; abst. C. A. 1908, **2**, 2999; J. S. C. I. 1908, **27**, 765; Mon. Sci. 1909, **70**, 116; 1913, **78**, 389. For collodion artificial threads see E. Breuer, D. R. P. 55293; abst. Wag. Jahr. 1891, **37**, 1113.

2. Knoll & Co., E. P. 2026-A, 1907; abst. J. S. C. I. 1908, **27**, 353; Chem. Ztg. 1908, **32**, 260. D. R. P. 203178, 1906; abst. Zts. Chem. Ind. Koll. 1909, **4**, 156; Mon. Sci. 1912, **77**, 96; 1913, **78**, 389; Chem. Zentr. 1908, **79**, II, 1549; Chem. Ind. 1908, **31**, 741; Chem. Ztg. 1908, **32**, 651; Chem. Zts. 1909, **8**, 1053; Jahr. Chem. 1905-08, II, 984; Wag. Jahr. 1908, **54**, II, 366; Zts. ang. Chem. 1908, **21**, 2426; Zts. Schiess Spreng. 1908, **3**, 433. Aust. P. 41831; abst. Mon. Sci. 1913, **78**, 389.

3. Knoll & Co., D. R. P. 206950, 1907; Addn. to D. R. P. 203178, 1906; abst. Mon. Sci. 1912, **77**, 96; Chem. Zentr. 1909, **80**, I, 961; Chem. Ind. 1909, **32**, 153; Chem. Ztg. Rep. 1909, **33**, 164; Chem. Zts. 1909, **8**, 1183; Wag. Jahr. 1909, **55**, II, 397; Zts. ang. Chem. 1909, **22**, 656. E. Knoevenagel and H. Lebach, E. P. 2026-B, 1907; abst. C. A. 1908, **2**, 2620; J. S. C. I. 1908, **27**, 353; Chem. Ztg. 1908, **32**, 260.

sulfate[1]; or aniline[2] were recommended for modifying the solubility of acetated cellulose.

The Farbenfabriken vorm. F. Bayer & Co.[3] hydrates the *dry* acetylcellulose in a mixture of 5 parts HCl (of about 25° Be.) and 25 of water until a whitish granular powder soluble in acetone is obtained. Instead of hydrochloric acid, oxalic, citric, lactic, tartaric, monochloracetic, dilute nitric, and phosphoric acids are specified.

A series of acetate plastic combinations was brought forth by L. Lederer in 1906, in which camphor is replaced by chloral alcoholate[4], or chloral hydrate[5]. An unsuccessful endeavor was made[6] to use cellulose acetate in solution

1. E. P. 16905, 1913; abst. J. S. C. I. 1915, **34**, 793; Chem. Ztg. 1913, **37**, 1038; 1915, **39**, 532. F. P. 453825, 1913; abst. C. A. 1914, **8**, 248; J. S. C. I. 1913, **32**, 785; Mon. Sci. 1914, **81**, 9; Chem. Ztg. Rep. 1913, **37**, 557. In this connection see Knoll & Co., E. P. 2491, 4353, 1913; abst. C. A. 1914, **8**, 2482, 2804.

2. Chemische Fabrik auf Aktien vorm. E. Schering and A. Loose, F. P. 452374, 1912; Addn. 17104, 1913; abst. C. A. 1913, **7**, 3663; J. S. C. I. 1913, **32**, 652, 784; Mon. Sci. 1914, **81**, 8; Chem. Ztg. Rep. 1913, **37**, 523; Kunst. 1913, **3**, 274.

3. E. P. 24067, 1906; abst. C. A. 1908, **2**, 482; J. S. C. I. 1907, **26**, 1213. F. P. 371447, 1906; abst. C. A. 1908, **2**, 2455; J. S. C. I. 1907, **26**, 340, 1213; Mon. Sci. 1908, **68**, 79; 1910, **73**, 451; 1913, **78**, 551; Chem. Ztg. 1907, **31**, 162; Chem. Ztg. Rep. 1907, **31**, 149; Chem. Zts. 1907, **6**, 279.

4. E. P. 9537, 1907; abst. C. A. 1908, **2**, 3283; J. S. C. I. 1908, **27**, 589; J. Soc. Dyers Col. 1909, **25**, 21; Mon. Sci. 1913, **78**, 392. F. P. 377010, 1907; abst. C. A. 1909, **3**, 253; J. S. C. I. 1907, **26**, 1027; J. Soc. Dyers Col. 1908, **27**, 589; Mon. Sci. 1908, **6**, 144; 1913, **7**, 392. D. R. P. 189703, 1906; Addn. to D. R. P. 152111, 1902; abst. C. A. 1908, **2**, 735; Mon. Sci. 1910, **73**, 159; 1913, **78**, 392; Chem. Zentr. 1907, **78**, II, 1822; Chem. Ind. 1907, **30**, 623; Chem. Ztg. Rep. 1907, **51**, 570; Chem. Zts. 1907, **6**, No. 387; Wag. Jahr. 1907, **53**, II, 562. U. S. P. 1195040, 1916 (includes both chloral hydrate and chloral alcoholate); abst. C. A. 1916, **10**, 2637; J. S. C. I. 1916, **35**, 961; Mon. Sci. 1917, **84**, 28; Chem. Ztg. 1916, **40**, 1004; Kunst. 1917, **7**, 27, 52.

5. D. R. P. 220228, 1907; abst. Zts. Chem. Ind. Koll. 1910, **7**, 237; Mon. Sci. 1913, **7**, 392; Chem. Zentr. 1910, **81**, II, 1310; Chem. Ind. 1910, **33**, 271; Chem. Ztg. Rep. 1910, **34**, 180; Chem. Zts. 1910, **9**, 1934; Jahr. Chem. 1910, **63**, II, 429; Wag. Jahr. 1910, **56**, II, 589. Aust. P. 34908, 1908; abst. Zts. ang. Chem. 1909, **22**, 505.

6. E. P. 26502, 1906; abst. C. A. 1907, **1**, 2180, 2199; J. S. C. I. 1907, **26**, 634; Chem. Ztg. 1907, **31**, 504. F. P. 371357, 1906; abst. C. A. 1908, **2**, 2453; J. S. C. I. 1907, **26**, 340, 634; Mon. Sci. 1908, **68**, 79; 1910, **73**, 453; Chem. Ztg. 1907, **31**, 162; Chem. Ztg. Rep. 1907, **31**. 130.

in the reacting mixture for commercial purposes without going to the trouble of precipitating out, washing to neutrality, drying and again dissolving, by overcoming the injurious effect of the condensing medium by the addition of such basic substances as methylamine, guanidine, aniline, amidophenols, as well as salts of formic and acetic acid, such as potassium acetate. It is a fact that the addition of alkaline acetates— especially sodium acetate—is of value in some instances, in inhibiting or minimizing the action of the condensing agent, and thereby bringing the acetating process under greater control. The L. Lederer photo-emulsion[1] combined cellulose acetate with alkaline earth chlorides, silver nitrate and citric acid; the artificial filament mixtures being a denitrated acetylated nitrocellulose (cellulose acetonitrate)[2].

1. E. P. 26503, 1906; abst. C. A. 1908, **2**, 1504; J. S. C. I. 1907, **26**, 1295. F. P. 371358, 1906; abst. C. A. 1909, **3**, 152; J. S. C. I. 1907, **26**, 344, 1295; Mon. Sci. 1908, **69**, 150. D. R. P. 191326, 1906; abst. C. A. 1908, **2**, 1634; Chem. Zentr. 1908, **79**, I, 695; Chem. Ztg. 1907, **31**, 1007; 1912, **36**, 175; Chem. Ztg. Rep. 1907, **31**, 644; Wag. Jahr. 1907, **53**, II, 507. Belg. P. 195837, 195838, 195839, 1906; abst. Chem. Ztg. 1907, **31**, 62.

2. U. S. P. 1028748, 1912; abst. C. A. 1912, **6**, 2528; J. S. C. I. 1912, **31**, 637; Mon. Sci. 1912, **77**, 164; 1913, **78**, 389. E. P. 19107, 1906; abst. C. A. 1907, **1**, 1342; J. S. C. I. 1907, **26**, 220; Mon. Sci. 1913, **78**, 389. E. P. 11625, 1909; abst. C. A. 1910, **4**, 669; J. S. C. I. 1909, **28**, 1030, 1221; Mon. Sci. 1914, **81**, 112; Chem. Ztg. Rep. 1910, **34**, 267. F. P. 368766, 1906; abst. J. S. C. I. 1907, **26**, 17, 30, 220, 273; Mon. Sci. 1908, **69**, 19; 1913, **78**, 389, 551; Chem. Ztg. Rep. 1907, **31**, 14. F. P. 402072, 1909; abst. J. S. C. I. 1909, **28**, 1221; Mon. Sci. 1911, **74**, 153. D. R. P. Anm. L. 23161, 1906; Addn. to D. R. P. 179947, 1906; abst. Chem. Ztg. 1908, **32**, 322. D. R. P. 200149, 1905; Addn. to D. R. P. 179947; abst. Mon. Sci. 1911, **75**, 63; 1913, **78**, 389; Chem. Zentr. 1908, **79**, II, 551; Jahr. Chem. 1905-08, II, 986; Wag. Jahr. 1908, **54**, II, 365; Zts. ang. Chem. 1908, **21**, 2047; Zts. Schiess Spreng. 1908, **3**, 334. D. R. P. 210778, 1909; abst. Mon. Sci. 1913, **78**, 389; Chem. Zentr. 1909, **80**, II, 247; Chem. Ind. 1909, **32**, 383; Chem. Ztg. Rep. 1909, **33**, 341; Chem. Zts. 1909, **8**, 1474; Jahr. Chem. 1909, **62**, 389; Wag. Jahr. 1909, **55**, II, 390; Zts. ang. Chem. 1909, **22**, 1620. D. R. P. 240751, 1908; abst. C. A. 1912, **6**, 2179; Chem. Zentr. 1911, **82**, II, 1843; Chem. Ind. 1911, **34**, 798; Chem. Ztg. 1911, **35**, 624; Kunst. 1912, **2**, 15; Wag. Jahr. 1911, **57**, II, 421; Zts. ang. Chem. 1912, **25**, 47, 1884. D. R. P. 248559, 1909; Addn. to D. R. P. 240751, 1908; abst. C. A. 1912, **6**, 2849; Chem. Zentr. 1912, **83**, 305; Chem. Ztg. Rep. 1912, **36**, 437; Kunst. 1912, **2**, 296; Wag. Jahr. 1912, **58**, II, 445; Zts. ang. Chem. 1912, **25**, 1884.

In this year (1906) appeared an important resume of the state of the art up to that time by H. Ost[1], in which were independently investigated the processes of cellulose acetation of Cross and Bevan (see p. 328, n. 1) by the action of acetyl chloride and zinc acetate; L. Lederer's process (see p. 332, n. 4) by the action of acetic anhydride and sulfuric acid upon hydrocellulose; and the Bayer process (see p. 335, n. 2) by the action of the same reagents on normal cellulose, all yielding the same product, a triacetylcellulose.

Although realizing that his results obtained were somewhat uncertain in view of the inadequacy of the methods of chemical examination employed, certain fundamentals were formulated of general acceptance at the present time. He doubted (and quite rightly) the existence of a strictly normal cellulose triacetate, regarding the esters which had been prepared up to this time as the triacetates of a series of hydrocelluloses of varying degrees of degradation, the position of any member in the series being determined by the relative viscosity of its solution, and the elasticity of its

1. Zts. ang. Chem. 1906, **19**, 993; abst. J. S. C. I. 1906, **25**, 606; Bull. Soc. Chim. 1906, (3), **36**, 1058; Mon. Sci. 1908, **68**, 465; Chem. Zentr. 1906, **77**, II, 672; Jahr. Chem. 1905-08, II, 983; Wag. Jahr. 1906, **52**, II, 484. In this connection see O. Voigt, Acetylizing cellulose, Dissertation, Hannover, 1906. H. Ost, Studies on cellulose acetate, Zts. ang. Chem. 1906, **19**, 993. W. Schliemann, Cellubiose and acetolysis of cellulose. Ann. 1911, **378**, 366; abst. J. C. S. 1911, **100**, i, 179. F. Westhoff, On viscose. Dissertation, Hannover, 1911. H. Ost, F. Westhoff and L. Gessner, Cellulose viscose and starch viscose, Ann. 1911, **382**, 340. H. Ost, Historical notes on cellulose acetate, Zts. ang. Chem. 1911, **24**, 304. H. Ost and F. Katayama, Comparative acetation of cellulose, hydrocellulose and alkalized cellulose, Zts. ang. Chem. 1912, **25**, 1467. F. Klein, The Benzoylation of cellulose, Dissertation, Hannover, 1912. H. Ost, Acetoylsis of cellulose to dextrose acetate, Chem. Ztg. 1912, **36**, 1099. H. Ost and F. Klein, Benzoyl esters of cellulose, Zts. ang. Chem. 1913, **26**, 437. H. Ost, Hydrolysis and acetolysis of cellulose, Ann. 1913, **398**, 313. Muehlmeister, Hydrolysis and sulfolysis of cellulose, Dissertation, Hannover, 1913. H. Ost, Filament formation in spinning artificial silk, Zts. ang. Chem. 1918, **31**, 141. H. Ost, Chloroform and acetone-soluble cellulose acetates, Zts. ang. Chem. 1919, **32**, 66, 76, 82. H. Ost and R. Prosiegel, A Cello-biose, Zts. ang. Chem. 1920, **33**, 100. R. Prosiegel, Acetolytic decomposition products of cellulose, Dissertation, Hannover, 1920.

films. The estimated relation of such a hydrocellulose to a normal cellulose may be expressed by the fixation by hydrolysis, of one molecule of water to six molecules of cellulose. The incipient hydrolysis of the cellulose which appears to be a condition necessary for the esterification, may be effected simultaneously as in the Bayer process, or in a separate preliminary treatment as in the Lederer method. The contention of H. Ost that the ester produced by Cross and Bevan is not a tetracetate but rather a triacetate, has since received general acceptance, and he attributed the error of the latter author's work to the fact that the saponification of these esters by boiling aqueous-alcoholic potash is accompanied by the production of acids at the expense of the cellulose residue, thus making the results appear too high. Ost maintained that the production of triacetates is preceded by the formation of diacetates which can be isolated by stopping the reaction while still incomplete. However, we now know that the preparation and separation of a distinct and definitely characterized cellulose acetate has not been accomplished, for acetation as with nitration is a continuous and progressive process whereby a series of analytically indistinguishable esters are formed at one and the same time (see E. Worden, "Technology of Cellulose Esters," 1921, Vol. I, p. 1682-1684).

The wood coating and preservation composition of M. Zelensky was brought forth in 1906[1], in which wood intended to be used for posts is steeped in cellulose acetate, being afterwards spirally wound with canvas coated with viscose. The W. Balser fabric impenetrable to Roentgen rays[2] is formed of heavy metal oxides or salts finely divided, mixed to a liquid or plastic mass with cellite or collodion, and drawn to fibers which are then woven. Z.

1. E. P. 2156, 1906.

2. D. R. P. 202267, 1906; abst. C. A. 1909, **3**, 492; Chem. Zentr. 1908, **79**, II, 1399.

Skraup, E. Knaffl-Lenz, F. Menter and H. Sirk[1] reported upon the action of acetic anhydride saturated with hydrogen chloride on cellulose; P. Minck[2] described a method for preparing cellulose suitable for acetation from cotton-seed hulls and other waste products (see E. Worden, "Technology of Cellulose Esters," Vol. I, p. 571, 579, 1878, 2927); and R. Marzahn contributed a general summary of advancement[3], which closed the contributions for the year 1906.

Knoll & Co. patented the use of sodium acetate[4], and nitrates as ammonium nitrate[5] to temper the destructive action of sulfuric acid and other contact substances in the acetating bath, potassium acetate having been patented for this purpose the year previous. In another process[6], ammonium sulfate is specified as a desirable catalyst in

1. Monats. 1905, **26**, 1415; abst. J. C. S. 1906, **90**, i, 67; J. S. C. I. 1906, **25**, 43; Bull. Soc. Chim. 1906, **36**, 591; Chem. Centr. 1906, **77**, II, 655; Jahr. Chem. 1905-08, II, 929.

2. P. Minck and Bremer Baumwollwerke Ges., E. P. 12718, 1906.

3. Materialien Kunde Fur den Koutschuk Techniker, 1906, 89.

4. U. S. P. 981574, 1911; abst. C. A. 1911, **5**, 1192; J. S. C. I. 1911, **30**, 126; J. Soc. Dyers Col. 1911, **27**, 74; Mon. Sci. 1912, **77**, 29; Chem. Ztg. 1911, **35**, 202; Kunst. 1911, **1**, 174. F. P. 376578, 1907; abst. C. A. 1908, **2**, 2620; J. S. C. I. 1907, **26**, 988, 1213; Mon. Sci. 1910, **72**, 452; Chem. Ztg. Rep. 1907, **31**, 449. F. P. 9194 ,1908; Addn. to F. P. 376578, 1907; abst. J. S. C. I. 1908, **27**, 996; Mon. Sci. 1910, **72**, 452. D. R. P. 201910, 1907; abst. Mon. Sci. 1912, **77**, 57; Chem. Zentr. 1908, **79**, II, 1310; Chem. Ztg. Rep. 1908, **32**, 526; Chem. Zts. 1909, **8**, 1052; Wag. Jahr. 1908, **54**, II, 365; Zts. ang. Chem. 1908, **21**, 2333.

5. D. R. P. 196730, 1906; abst. C. A. 1908, **2**, 2301; Mon. Sci. 1911, **74**, 92; Chem. Centr. 1908, **79**, I, 1349; Chem. Ind. 1908, **31**, 422; Chem. Ztg. 1908, **32**, 275; Chem. Zts. 1908, **7**, 806; Jahr. Chem. 1905-08, II, 989; Wag. Jahr. 1908, **54**, II, 365; Zts. ang. Chem. 1908, **21**, 1194. E. P. 8369, 1907; abst. C. A. 1908, **2**, 487; 1909, **3**, 1214; J. S. C. I. 1907, **26**, 1213; abst. Chem. Ztg. 1909, **31**, 440. E. P. 8727, 1906; abst. C. A. 1909, **3**, 1214; J. S. C. I. 1908, **27**, 996; J. Soc. Dyers Col. 1909, **25**, 16. Aust. P. 36126. Belg. P. 199492, 1907.

6. Knoll & Co., D. R. P. 206950, 1907; Addn. to D. R. P. 203178, 1906; abst. Chem. Zentr. 1909, **80**, I, 961; Chem. Ztg. 1909, **33**, 106; Chem. Ztg. Rep. 1909, **33**, 164; Chem. Zts. 1909, **8**, 1183; Jahr. Chem. 1909, **62**, II, 397; Wag. Jahr. 1909, **55**, II, 397; Zts. ang. Chem. 1909, **22**, 656.

cellulose propionate manufacture, and methylamine sulfate in cellulose butyrate formation. A series of patents were issued to E. Knoevenagel and assigned by him to this firm, for dyeing and increasing the elasticity of cellulose acetate and filaments made therefrom, the pertinent points being first swelling the filaments to increase their receptiveness to dyestuff[1]; impregnation of the cellulose ester with *b*-naphthol, *p*-aminophenol[2]; *p*-nitranilin, aminoazobenzene, *b*-naphthylamine, benzidin, dianisidin, *m*-phenylenediamine, and naphthoic acid[3]. After diazotization and development, the permanent shades are produced.

1. E. Knoevenagel, U. S. P. 961241, 1910; abst. C. A. 1910, **4**, 2575; J. S. C. I. 1910, **29**, 876; J. Soc. Dyers Col. 1910, **26**, 207; Mon. Sci. 1910, **73**, 135. U. S. P. 981574, 1911; abst. C. A. 1911, **5**, 1192; J. S. C. I. 1911, **30**, 126; J. Soc. Dyers Col. 1911, **27**, 74; Mon. Sci. 1912, **77**, 29; Chem. Ztg. 1911, **35**, 202; Kunst. 1911, **1**, 174. U. S. P. 1002408, 1911; abst. C. A. 1911, **5**, 3917; J. S. C. I. 1911, **30**, 126, 1157; J. Soc. Dyers Col. 1911, **27**, 242; Mon. Sci. 1912, **77**, 165; Chem. Ztg. 1911, **35**, 1070; Chem. Ztg. 1911, **35**, 599; Kunst. 1912, **2**, 75. U. S. P. 1090074, 1914; abst. C. A. 1914, **8**, 1667; J. S. C. I. 1914, **33**, 349; Kunst. 1914, **4**, 332. Knoll & Co., E. P. 24284, 1907; abst. C. A. 1909, **3**, 1593; 1911, **5**, 206; J. S. C. I. 1908, **27**, 1150; J. Soc. Dyers Col. 1909, **25**, 33; Mon. Sci. 1911, **74**, 92; Chem. Ztg. Rep. 1908, **32**, 664. F. P. 383636, 1907; abst. C. A. 1909, **3**, 1094; J. S. C. I. 1908, **27**, 332; Mon. Sci. 1908, **69**, 168; Chem. Ztg. 1908, **32**, 117. D. R .P. 198008, 1907; abst. Bull. Soc. Chim. 1909, (4), **6**, 557; Mon. Sci. 1911, **75**, 60; Chem. Zentr. 1908, **79**, I, 1809; Chem. Ztg. 1908, **32**, 556; Chem. Ztg. Rep. 1908, **32**, 379; Chem. Zts. 1908, **7**, 865; Jahr. Chem. 1905-08, II, 3179; Wag. Jahr. 1908, **54**, II, 409; Zts. ang. Chem. 1908, **21**, 1471. Ital. P. 268/234; Nov. 4, 1907; abst. Chem. Ztg. 1908, **32**, 823.

2. E. Knoevenagel, U. S. P. 979966, 1910; abst. C. A. 1911, **5**, 996; J. S. C. I. 1911, **30**, 206; J. Soc. Dyers Col. 1911, **27**, 41; Mon. Sci. 1912, **77**, 30; Chem. Ztg. 1911, **35**, 148; Chem. Ztg. Rep. 1911, **35**, 156. Knoll & Co., F. P. 10738, 1909; Addn. to F. P. 383636, 1907; abst. J. S. C. I. 1909, **28**, 1194; Mon. Sci. 1910, **73**, 451; Chem. Ztg. 1909, **33**, 946. D. R. P. 199559, 1907; abst. Bull. Soc. Chim. 1909, (4), **6**, 557; Chem. Zentr. 1908, **79**, 271; Wag. Jahr. 1908, **54**, 410; Zts. ang. Chem. 1908, **21**, 1810.

3. Knoll & Co., E. P. 7743, 1909; abst. C. A. 1911, **5**, 206; J. S. C. I. 1910, **29**, 269; J. Soc. Dyers Col. 1909, **25**, 153; 1910, **26**, 90, 95. D. R. P. 234028, 1908; abst. C. A. 1911, **5**, 2948; Chem. Zentr. 1911, **82**, I, 1471; Chem. Ztg. Rep. 1911, **35**, 250; Chem. Zts. 1911, **10**, 2574; Kunst. 1911, **1**, 215; Wag. Jahr. 1911, **57**, II, 422; Zts. ang. Chem. 1911, **24**, 1151.

In another method for increasing the receptivity of cellulose acetate for dyes[1], the water-repellent nature of the fatty acid esters is partially overcome by the addition of acetin or other esters of glycerol or glycol, the depth of shade producible being governed by the amount of acetin used.

In extending the possible list of solvents applicable to cellulose acetate, formic acid was proposed in 1907 as being especially useful for artificial filament formation[2]. In the manufacture of cellulose formate according to the methods as disclosed by the Nitritfabrik Aktienges., either cellulose is dissolved in 55° vitriol, precipitated and then redissolved

1. Fuerst Guido Donnersmarck'Sche Kunstseiden und Acetatwerke, D. R. P. 228867, 1907; abst .C. A. 1911, **5**, 2187; J. S. C. I. 1911, **30**, 21; Chem. Zentr. 1911, **82**, I, 48; Chem. Ztg. Rep. 1910, **34**, 638; Chem. Zts. 1910, **9**, 2138; Kunst. 1911, **1**, 16; Wag. Jahr. 1910, **56**, II, 487; Zts. ang. Chem. 1910, **23**, 2389. Ital. P. 85229, 1907; abst. Chem. Zts. 1907, **31**, 401. Aust. P. Appl. 577, 1909; abst. Chem. Ztg. 1911, **35**, 78. See also D. R. P. Anm. D-18204, 1907; abst. Chem. Ztg. 1909, **33**, 1169. D. R. P. Anm. D-18317, 1907; abst. Chem. Ztg. 1908, **32**, 574. D. R. P. Anm. D-19112, D-19113; abst. Chem. Ztg. 1909, **33**, 682; 1910, **34**, 1102. D. R. P. Anm. D-19374, 1907; abst. Chem. Ztg. 1909, **33**, 1153; abst. Chem. Ztg. 1909, **33**, 1153. D. R. P. Anm. D-23640, 1910; abst. Chem. Ztg. 1911, **35**, 587. Aust. P. Appl. 1905, 1909.

2. A. Schloss (Assignor to Fuerst Guido Donnersmarack'sche Kunst. und Acetatewerke), U. S. P. 922340, 1909; abst. C. A. 1909, **3**, 2056; J. S. C. I. 1909, **28**, 671; Chem. Ztg. 1909, **33**, 706. E. P. 6554, 1909; abst. C. A. 1910, **4**, 2570; J. S. C. I. 1910, **29**, 18; J. Soc. Dyers Col. 1910, **26**, 33. Fuerst Guido Donnersmarck'sche Kunst. u Acetatewerke, E. P. 23683, 1906, (patent not granted). F. P. 370741, 1907; abst. J. S. C. I. 1907, **26**, 253; Mon. Sci. 1910, **72**, 453. F. P. 400652, 1909; abst. C. A. 1911, **5**, 992; J. S. C. I. 1909, **28**, 1061; Mon. Sci. 1910, **73**, 165; Chem. Ztg. 1909, **33**, 764. D. R. P. 237599, 1907; abst. C. A. 1912, **6**, 1679; Chem. Zentr. 1911, **82**, 814; Chem. Ztg. 1911, **35**, 857; Chem. Ztg. Rep. 1911, **35**, 481; Kunst. 1911, **1**, 354; Wag. Jahr. 1911, **55**, II, 419; Zts. ang. Chem. 1911, **23**, 1838. D. R. P. 237718, 1907; abst. C. A. 1912, **6**, 1672; J. S. C. I. 1911, **30**, 1040; Chem. Zentr. 1911, **82**, II, 922; Chem. Ind. 1911, **34**, 573; Chem. Ztg. 1911, **35**, 857; Chem. Ztg. Rep. 1911, **35**, 481; Kunst. 1911, **1**, 378; Wag. Jahr. 1911, **55**, II, 419; Zts. ang. Chem. 1911, **24**, 1988. D. R. P. 239701, 1910; abst. C. A. 1912, **6**, 1502, 2169; Mon. Sci. 1913, **78**, 393; Chem. Zentr. 1911, **82**, II, 1502; Chem. Ztg. Rep. 1911, **35**, 556; Kunst. 1911, **1**, 437; Wag. Jahr. 1911, **57**, II, 552. Belg. P. 214671, 1909; abst. Chem. Ztg. 1909, **33**, 449. Swiss P. 46329; abst. Chem. Ztg. 1911, **35**, 117. Aust. P. 1905, 1909; abst. Chem. Ztg. 1910, **34**, 501. Ital. P. 89594, 1907; 101262, 1909; abst. Chem. Ztg. 1908, **32**, 48; 1910, **34**, 671.

in formic acid[1], or the cellulose is directly dissolved in formic acid in the presence of zinc chloride[2]. This firm has also received protection for the manufacture of formins by heating glycerol directly with formic acid, mono-, di-, and tri-formins resulting[3].

In connection with endeavors to develop the cellulose formates—primarily with the idea of eliminating the counterpart (acetic anhydride) of the most expensive constituent in the acetating bath,—the J. P. Bemberg Aktienges[4] directly adds cotton to a mixture of sulfuric and formic acids, the colorless, syrupy solution of formylated cellulose thus produced being precipitated and washed to neutrality in the usual manner.

L. Lederer has been granted protection for a method of manufacturing fibrous cellulose acetate in which the physical appearance of the cotton fiber suffers no visible

1. U. S. P. 953677, 1910; abst. C. A. 1910, **4**, 1544; J. S. C. I. 1910, **25**, 557; Mon. Sci. 1910, **73**, 90; 1913, **78**, 389. E. P. 17036, 1909; abst. J. S. C. I. 1910, **29**, 1005; Mon. Sci. 1913, **78**, 389. F. P. 405293, 1909; abst. C. A. 1911, **5**, 1661; J. S. C. I. 1910, **29**, 417, 557; Mon. Sci. 1910, **73**, 171, 457; 1913, **78**, 389; Chem. Ztg. Rep. 1910, **34**, 75. D. R. P. 219162, 1907; abst. Mon. Sci. 1913, **78**, 389; 1914, **81**, 80; Chem. Zentr. 1910, **81**, I, 972; Chem. Ind. 1910, **33**, 186; Chem. Ztg. Rep. 1910, **34**, 171; Chem. Zts. 1910, **9**, 1988; Jahr. Chem. 1910, **63**, II, 426; Wag. Jahr. 1910, **56**, II, 433; Zts. ang. Chem. 1910, **23**, 768. Belg. P. 198984, 198985, 1907; 217837, 1909.

2. S. von Kapff, U. S. P. 955082, 1910; abst. C. A. 1910, **4**, 1672; J. S. C. I. 1910, **29**, 557; Mon. Sci. 1910, **73**, 131; 1913, **78**, 390; Chem. Ztg. 1910, **34**, 489. Nitritfabrik Akt. Ges., D. R. P. 219163, 1907; abst. Mon. Sci. 1913, **78**, 389; 1914, **81**, 80; Chem. Zentr. 1910, **81**, I, 973; Chem. Ztg. Rep. 1910, **34**, 171; Chem. Zts. 1910, **9**, 1986; Jahr. Chem. 1910, **63**, II, 426; Wag. Jahr. 1910, **56**, II, 433; Zts. ang. Chem. 1910, **23**, 768. Hung. P. Anm. N-952, July 21, 1909. Aust. P. 45765, 1909; abst. Mon. Sci. 1913, **78**, 393.

3. E. P. 28723, 1907; abst. J. S. C. I. 1908, **27**, 356; Mon. Sci. 1910, **73**, 36; Chem. Ztg. Rep. 1908, **32**, 254.

4. E. P. 2511, 1907; abst. C. A. 1907, **1**, 2180, 2191; J. S. C. I. 1907, **26**, 634; J. Soc. Dyers Col. 1907, **23**, 215; Mon. Sci. 1910, **73**, 157; 1913, **78**, 390. F. P. 376262, 1907; abst. C. A. 1908, **2**, 2620; J. S. C. I. 1907, **26**, 988; Mon. Sci. 1908, **68**, 87; 1913, **78**, 390; Chem. Ztg. Rep. 1907, **31**, 449. D. R. P. 189836, 189837, 1906; abst. C. A. 1908, **2**, 1508; J. C. S. 1908, **94**, i, 321; Mon. Sci. 1913, **78**, 390; Chem. Zentr. 1908, **79**, I, 320; Chem. Ind. 1907, **30**, 617; Jahr. Chem. 1905-08, II, 983, 2983; Wag. Jahr. 1907, **53**, II, 400, 401; Zts. ang. Chem. 1908, **21**, 268. Belg. P. 198985, 1907.

change[1], the esterification being conducted in the presence of carbon tetrachloride. This was a modification of his process of the previous year (see p.350, n. 2), the difference being that this method was confined to the acetation of yarns and spun threads and textiles. H. Mork[2] also disclosed a method of formation of fibrous acetate, in which normal cellulose is first converted into hydrocellulose by a previous treatment, and then acetated in a bath containing sufficient benzene so the acetated ester does not pass into solution. The benzene also dilutes the esterizing bath and restrains or moderates the velocity of reaction, thus insuring more complete control of the several steps of esterification.

The "soluble starch" of the Farbenfabriken vorm. F. Bayer & Co.[3] which dissolves completely in hot water to a limpid liquid, is obtained by treating a cold suspension of starch in acetic acid, with small quantities of a mineral acid as nitric, hydrochloric or sulfuric.

In this year also (1907) was brought out by the Act. Ges. f. Anilin-Fabrikation[4] a new class of cellulose esters—cellulose sulfonates—obtained by the action of zinc chloride and HCl in the presence of toluene-*p*-sulfonyl chloride upon alkali-soluble cellulose, sodium hydroxide being used in the reaction. The cellulose toluene-*p*-sulfonate separates after

1. U. S. P. 999236, 1911; abst. J. S. C. I. 1911, **30**, 1050; Chem. Ztg. 1911, **35**, 965. E. P. 3103, 1907; abst. J. S. C. I. 1907, **26**, 899; Chem. Ztg. 1907, **31**, 718. F. P. 374370, 1907; abst. J. S. C .I. 1907, **26**, 776; Mon. Sci. 1908, **68**, 84; Chem. Zts. 1907, **6**, 139. In this connection see D. R. P. 185151, 1907; F. P. 371356, 1907; U. S. P. 902092, 1908; Aust. P. 31203.

2. U. S. P. 854374, 1907; abst. C. A. 1907, **1**, 2316; J. S. C. I. 1907, **26**, 713; Mon. Sci. 1907, **66**, 159; Chem. Ztg. 1907, **31**, 598.

3. E. P. 25274, 1907; abst. J. S. C. I. 1908, **27**, 761. F. P. 383902, 1907; abst. J. S. C. I. 1908, **27**, 415; Mon. Sci. 1908, **69**, 164; Chem. Ztg. Rep. 1908, **32**, 300; C. A. 1909, **3**, 1105. D. R. P. 200145, 1907; abst. Jahr. Chem. 1905-08, II, 941; Chem. Zentr. 1908, **79**, II, 560; Wag. Jahr. 1908, **54**, II, 190; Chem. Ztg. Rep. 1908, **32**, 454; Zts. ang. Chem. 1908, **21**, 2285; Mon. Sci. 1911, **75**, 95. Aust. P. 37386, 1909. Swiss P. 39840, 1907.

4. D. R. P. 200334, 1907; abst. J. C. S. 1908, **94**, i, 955; Chem. Ind. 1908, **32**, 499; Mon. Sci. 1911, **75**, 63; J. S. C. I. 1908, **27**, 1130; Jahr. Chem. 1905-08, II, 987; Chem. Zts. 1908, **7**, 909; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, **79**, 655.

a number of hours as a white, amorphous powder, dissolving in hot glacial acetic acid, epichlorhydrin, chloroform and ethyl acetate. It, as yet, has assumed little industrial importance.

E. Fischer[1] gave details of the use of nitromethane as a common solvent of the cellulose acetates and nitrates, and J. Aylsworth published his formula for a phonograph sound record composed of cellulose acetate and chlorinated stearic acid[2], A. & L. Lumiere having *coated* phonograph records with cellulose acetate in 1903 (see p. 343, n. 2).

The solid alcohol of V. Perelzveich and G. Rosenbusch[3] composed of cellulose tetranitrate and sodium sebacate, differs from that described by Bayer (see p. 335, n. 1) who employed acetated cellulose, thus diminishing the inflammability. This latter ester also forms the essence of the invention of the Societe D'Exploitation des Brevets Dolter[4], who prepare a metallic insulating composition therefrom. In the method of fabrication of acetylated cellulose as put forward by the Societe Anonyme D'Explosifs et de Produits Chimiques, cotton or hydrocellulose is either esterified in the presence of zinc chloride[5], or sulfacetic acid[6]. In the preparation of dip lacquers possessing good covering power,

1. D. R. P. 201907, 1907; abst. Chem. Ztg. 1908, **32**, 855; Jahr. Chem. 1905-08, II, 987; J. S. C. I. 1908, **27**, 1174; Wag. Jahr. 1908, **54**, II, 364; C. A. 1909, **3**, 491; Chem. Ztg. Rep. 1908, **32**, 534; Chem. Zts. 1909, **8**, No. 1040; Zts. ang. Chem. 1908, **21**, 2427; Chem. Zentr. 1908, **79**, II, 1398; Bull. Soc. Chim. 1911, (4), **9**, 557; Mon. Sci. 1913, **78**, 392.

2. U. S. P. 855556, 1907; abst. Mon. Sci. 1913, **78**, 393; C. A. 1907, **1**, 2500. See also U. S. P. 962877, 1910; abst. C. A. 1910, **4**, 2577; Kunst. 1911, **1**, 235; Mon. Sci. 1911, **75**, 11; 1913, **78**, 393.

3. U. S. P. 919759, 1909; abst. J. S. C. I. 1912, **31**, 514; C. A. 1909, **3**, 1802; Mon. Sci. 1911, **75**, 112; Chem. Ztg. Rep. 1909, **33**, 331. E. P. 26915, 1907; abst. J. S. C. I. 1908, **27**, 826; C. A. 1909, **3**, 580. F. P. 392092, 1908; abst. J. S. C. I. 1909, **28**, 693; C. A. 1910, **4**, 3121. Aust. P. 44799, 1910; abst. Chem. Ztg. 1910, **34**, 1123.

4. F. P. 375092, 1907; abst. J. S. C. I. 1907, **26**, 877; Mon. Sci. 1913. **78**, 389.

5. F. P. 385179, 385180, 1907; abst. J. S. C. I. 1908, **27**, 589; Mon. Sci. 1909, **71**, 105, 106; Bull. Soc. Chim. 1909, **6**, 557; C. A. 1909, **3**, 2383; Chem. Ztg. Rep. 1908, **32**, 292; Chem. Ztg. 1908, **32**, 322.

6. F. P. 385180, 1907; abst. J. S. C. I. 1908, **27**, 589; Mon. Sci. 1909, **71**, 106; Chem. Ztg. Rep. 1908, **32**, 292; C. A. 1909, **3**, 2383.

H. Zwick dissolved either nitrocellulose[1] or acetocellulose[2] with resins and castor oil in appropriate solvent combinations. B. Szelinski[3] prepares celluloid-like masses by working up acetylcellulose with the products of reaction of certain organo-magnesium compounds on unsaturated hydroaromatic bodies such as benzyldihydrocarvone, α-naphthyldihydrocarvone, benzyldihydropulegone, and similar bodies as camphor substitutes.

The J. Smith and W. Merckens method of monochrome or polychrome photography[4] involves the use of cellulose nitrate or acetate in the photo support. The F. Bume acetylcellulose plastic[5] combines camphor with the ester, then precipitates the mass together, and kneads into permanent plastic form. In the treatment of yarn according to the C. Cross and J. Briggs method[6], the fiber is modified so as to resist the action of direct cotton dyestuffs and of mercerizing agents by conversion into lower acetylated derivatives without appreciably altering its appearance.

1. D. R. P. 211520, 1907; abst. Wag. Jahr. 1909, **55**, II, 541; J. S. C. I. 1909, **28**, 843; Chem. Zentr. 1909, **80**, II, 398; Chem. Ztg. Rep. 1909, **33**, 459; Zts. ang. Chem. 1909, **22**, 1558.

2. D. R. P. 211573, 1907, (Addn. to D. R. P. 211520); abst. J. S. C. I. 1909, **28**, 993; Zts. ang. Chem. 1909, **22**, 1558; Chem. Zentr. 1909, **80**, II, 399; Chem. Ztg. Rep. 1909, **33**, 459; Wag. Jahr. 1909, **55**, II, 541.

3. D. R. P. 202720, 1907; abst. Zts. ang. Chem. 1908, **21**, 2428; Chem. Zentr. 1908, **79**, II, 1837; Chem. Ztg. Rep. 1908, **32**, 594; Wag. Jahr. 1908, **54**, II, 540; Mon. Sci. 1912, **77**, 57; Jahr. Chem. 1905-08, II, 993. See also J. McClelland, U. S. P. 366231, 1887; abst. J. A. C. S. 1887, **9**, 158.

4. E. P. 2461, 1907; abst. J. S. C. I. 1907, **26**, 1109; Brit. J. Phot. 1907, **54**, 771. Belg. P. 198836, 1907. D. R. P. Anm. S-22257, 1906.

5. D. R. P. 210519, 1907; abst. Mon. Sci. 1913, **79**, 38; Zts. ang. Chem. 1909, **22**, 1620; Chem. Ztg. Rep. 1909, **33**, 341; Wag. Jahr. 1909, **55**, II, 555; J. S. C. I. 1909, **28**, 812.

6. U. S. P. 920828, 1909; abst. Chem. Ztg. Rep. 1909, **33**, 577; C. A. 1909, **3**, 2051; J. S. C. I. 1909, **28**, 623. E. P. 5016, 1907; abst. J. S. C. I. 1908, **27**, 336; Bull. Soc. Chim. 1909, (4), **6**, 557; Mon. Sci. 1911, **75**, 92; Farb. Ztg. **19**, 142. F. P. 383064, 1907; abst. J. S. C. I. 1908, **27**, 330; Mon. Sci. 1910, **73**, 451. D. R. P. 224330, 1907; abst. Chem. Zts. 1910, **9**, No. 2105; Zts. ang. Chem. 1910, **23**, 2056; Chem. Zentr. 1910, **81**, II, 515; Chem. Ztg. Rep. 1910, **34**, 448; Wag. Jahr. 1910, **56**, II, 434; Jahr. Chem. 1910, **63**, II, 426; Mon. Sci. 1916, **83**, 47; C. A. 1910, **4**, 3298.

In a study of the acetylation of oxycelluloses made in 1907 by E. Hardt-Stremayr[1], various oxycelluloses prepared by the action of oxidizing agents on wood, cotton and paper, were treated with acetic anhydride and sulfuric acid according to the method of Z. Skraup and J. Koenig[2], the author obtaining the same cellobiose octoacetate (m. pt. 228°) as is produced by the acetylation of cellulose. The yields of the acetyl compounds from various oxycelluloses, however, were found to vary greatly. Whereas pure cellulose yields about 25% of acetyl compound[3], hydralcellulose gives about the same. The oxycelluloses prepared by the action of nitric acid, potassium chlorate and hydrochloric acid respectively on cellulose[4], yielded 16% and 10% of acetyl compound, while acid cellulose gave only 7%, from which the author concludes that oxycelluloses contain cellobiose groups, but in less quantity than ordinary cellulose.

1. Wien. Akad. Ber. 1907, **116**, II-B, 13; Monats. 1907, **28**, 63, 73; abst. C. A. 1907, **1**, 180; J. C. S. 1907, **92**, i, 389; Bull. Soc. Chim. 1908, (4), **4**, 5; J. S. C. I. 1907, **26**, 482, 483; Rep. Chim. 1907, **7**, 272, 273; Chem. Zentr. 1907, **78**, I, 1571; Jahr. Chem. 1905-08, II, 923; Biochem. Centr. 1907, **6**, 263; Zts. ang. Chem. 1908, **21**, 1186; Chem. Ztg. 1907, **31**, 127.

2. Ber. 1901, **34**, 1115; Monats. 1901, **22**, 1011; abst. J. C. S. 1901, **80**, i, 370; J. S. C. I. 1901, **20**, 740; 1902, **21**, 144; J. Soc. Dyers Col. 1901, **17**, 85, 203; Bull. Soc. Chim. 1902, **28**, 317, 927; Rep. Chim. 1902, **2**, 9, 46; Chem. Centr. 1901, **72**, I, 1197; 1902, **73**, I, 183; Jahr. Chem. 1901, **54**, 878; Meyer Jahr. Chem. 1901, **11**, 106.

3. See G. Bumcke and R. Wolffenstein, Ber. 1899, **32**, 2493; abst. J. C. S. 1899, **76**, i, 852; J. S. C. I. 1899, **18**, 940; Bull. Soc. Chim. 1900, **24**, 620; Chem. Centr. 1899, **70**, II, 752; Jahr. Chem. 1899, **52**, 1290; Meyer Jahr. Chem. 1899, **9**, 300. See also Z. Skraup, Ber. 1899, **32**, 2413; abst. J. C. S. 1899, **76**, i, 852; J. S. C. I. 1899, **18**, 941; Bull. Soc. Chim. 1900, **24**, 619; Chem. Centr. 1899, **70**, II, 752; Jahr. Chem. 1899, **52**, 1288.

4. See O. V. Faber and B. Tollens, Ber. 1899, **32**, 2589; abst. J. C. S. 1899, **76**, i, 854; J. S. C. I. 1899, **18**, 1014; Bull. Soc. Chim. 1900, **24**, 621; Chem. Centr. 1899, **70**, II, 901; Chem. Tech. Rep. 1899, **38**, 550; Chem. Ztg. Rep. 1899, **23**, 321; Jahr. Chem. 1899, **52**, 1292. J. Murumow, J. Sack and B. Tollens, Ber. 1901, **34**, 1427; abst. J. C. S. 1901, **80**, i, 453; J. S. C. I. 1901, **20**, 739; J. Soc. Dyers Col. 1901, **17**, 238; Bull. Soc. Chim. 1902, **28**, 269; Chem. Centr. 1901, **72**, II, 38; Jahr. Chem. 1901, **54**, 896.

This same year E. Berl and W. Smith[1] published their researches on the mixed nitric-acetic cellulose esters, in which they found that nitrated cellulose saturated with glacial acetic acid, when treated with acetic anhydride and concentrated sulfuric acid gave a white, powdery product which contains more acetic acid and less nitrogen the greater the time occupied in its preparation. A product free from nitrogen, however, is only obtained under conditions in which the cellulose undergoes extensive degradation. It was observed that reaction does not take place when the acetic anhydride is replaced by anhydrous formic acid. The latter, however, reacts with hydrocellulose in the presence of concentrated sulfuric acid to form a white powder which is hydrolyzed by sodium hydroxide. Behal's formic-acetic anhydride converts hydrocellulose in the presence of H_2SO_4 into yellowish-brown formyl compounds of degraded cellulose.

F. Meyer[2] devised a method for protecting the tips of cigars by coating the same with cellulose acetate solution, and also the use of cellulose acetate[3] or nitrocellulose[4] in the manufacture of plastics with the aid of camphor or camphor substitutes, an especial feature being to roll on the surface of a textile fabric a pasty plastic mass, so adjusted that it does not adhere to the masticating rollers.

A. Eichengruen[5] published a review of cellulose ace-

1. Ber. 1907, **40**, 903; abst. C. A. 1907, **1**, 2179; J. C. S. 1907, **92**, i, 289; J. S. C. I. 1907, **26**, 273; Rep. Chim. 1908, **8**, 371, 431; Chem. Zentr. 1907, **78**, I, 1108; Chem. Ztg. Rep. 1907, **31**, 257; Jahr. Chem. 1905-08, II, 977; Meyer Jahr. Chem. 1908, **18**, 311; Zts. ang. Chem. 1908, **21**, 1185.

2. U. S. P. 931629, 1909. D. R. P. 193210, 1906; abst. Mon. Sci. 1911, **75**, 92. Can. P. 107996, 1907.

3. D. R. P. 210519, 1907; abst. Wag. Jahr. 1909, **55**, II, 555; Chem. Ztg. Rep. 1909, **33**, 341; Zts. ang. Chem. 1909, **22**, 1620; Mon. Sci. 1913, **79**, 38; J. S. C. I. 1909, **28**, 812.

4. D. R. P. 223793, 1907, (Addn. to D. R. P. 210519); abst. Wag. Jahr. 1910, **56**, II, 483; Kunst. 1911, **1**, 15.

5. See Zts. ang. Chem. 1907, **20**, 922. Oest. Chem. Ztg. 1907, **10**, 182.

tate plastics, and L. Grognot[1], W. Massot[2] and W. Doht[3] compilations of the patent and literature state of the art up to that time.

The year 1908 was especially prolific in disclosures looking to increasing the applications of the uninflammable cellulose esters. F. Meyer[4] brought forward his combinations of nitrocellulose and acetylcellulose to be used for imitation oil-cloth, India rubber and patent leather, camphor being the plasticizing agent, while the Internationale Celluloseester Ges.[5] specified cellulose acetate as filling and covering material in the construction of air craft.

In the treatment of cellulosic films according to the J. Brandenberger process[6], cellulose acetate or preferably viscose is made into film form with metallic powders, then attached in a moist or dry condition to paper or textile for decorative or imitative effects.

Knoll & Co.[7] advocated the use of nitrates as ammonium nitrate to neutralize the harmful effect of the contact agents used, on the theory that the small amount of nitric acid liberated would expend itself in forming nitrated cel-

1. Rev. gen, Chim. et Appl. 1907, **10**, 177; abst. Chem. Zentr. 1907, **78**, II, 858.

2. Zts. ang. Chem. 1908, **21**, 340; Bull. Soc. Chim. 1908, **4**, 635. Faerber Ztg. 1907, **18**, 146, 166, 182; abst. C .A. 1907, **1**, 2493; J. S. C. I. 1907, **26**, 430; Chem. Zentr. 1907, **78**, I, 1557.

3. Zts. ang. Chem. 1907, **20**, 743; Chem. Ztg. 1907, **31**, 302; abst. C. A. 1907, **1**, 1359, 2178; Bull. Soc. Chim. 1907, **2**, 908; Chem. Zentr. 1907, **78**, I, 1736; Jahr. Chem. 1905-8, II, 983.

4. E. P. 19735, 1908; abst. C. A. 1910, **4**, 2203; Chem. Ztg. 1909, **33**, 1293; J. S. C. I. 1910, **29**, 18. F. P. 393963, 1908; abst. J. S. C. I. 1909, **28**, 257; Mon. Sci. 1910, **72**, 450. D. R. P. 223793 (Addn. to 210519); abst. Wag. Jahr. 1910, **56**, II, 483; Kunst. 1911, **1**, 15. Swiss P. 44833, 51094.

5. D. R. P. 241963, 1908; abst. C. A. 1912, **6**, 2315; Chem. Ztg. Rep. 1912, **36**, 110.

6. E. P. 24811, 1908; abst. J. S. C. I. 1910, **29**, 17. F. P. 405429, 1908; abst. J. S. C. I. 1910, **29**, 345.

7. U. S. P. 981574, 1911; abst. J. Soc. Dyers Col. 1911, **27**, 74; Mon. Sci. 1912, **77**, 29; Kunst. 1911, **1**, 174; C. A. 1911, **5**, 1192. E. P. 8727, 1908; abst. Chem. Ztg. 1908, **32**, 944; J. S. C. I. 1908, **27**, 996; C. A. 1909, **3**, 1214; J. Soc. Dyers Col. 1909, **25**, 16. F. P. 376578, 1907; abst. J. S. C. I. 1907, **26**, 988, 1213; Mon. Sci. 1910, **73**, 452; Chem. Ztg. Rep. 1907, **31**, 449; C. A. 1908, **2**, 2620. F. P. Addn. 9194 (to F. P. 376578), 1907; abst. J. S. C. I. 1908, **27**, 996; Mon. Sci. 1910, **73**, 452. D. R. P. 201910, 1907, (Addn. to D. R. P. 196730); abst.

lulose, a statement enunciated by Haeussermann in 1905 (see p. 353, n. 2). The combined aceto-nitrocellulose plastic masses of L. Berend[1] comprises glue or glycerol indurated with formaldehyde. Mixed esters of cellulose as acetobenzoates and nitrobenzoyl nitrates have been investigated[2], but their stability, in general, is low.

Hydrolyzed cellulose acetates soluble in water (and hence worthless) are described by C. Claessen[3], in which acetated cellulose is hydrolyzed with pyridine sulfate, or quinoline sulfate until water-soluble products are formed. It is stated that aniline sulfate under the same conditions does not give water-soluble esters. Any acetated cellulose hydrolyzed to the point of solubility without turbidity in water is commercially worthless. In this year (1908) also, appears the process for water-proofing asbestos fibers by cellulose acetate[4], and the manufacture of incombustible

Chem. Ztg. 1908, **32**, 855; Chem. Zentr. 1908, **79**, II, 1310; Chem. Ztg. Rep. 1908, **32**, 526; Chem. Zts. 1909, **8**, No. 1052; Wag. Jahr. 1908, **54**, II, 365; Zts. ang. Chem. 1908, **21**, 2333. D. R. P. 234028, 1908; abst. C. A. 1911, **5**, 2948; Kunst. 1911, **1**, 215; Wag. Jahr. 1911, **57**, II, 422; Chem. Zentr. 1911, **82**, I, 1471; Chem. Ztg. Rep. 1911, **35**, 250; Zts. ang. Chem. 1911, **24**, 1151; Chem. Zts. 1911, **10**, No. 2574. Belg. P. 207839, 1908; abst. Chem. Ztg. 1908, **32**, 611. Aust. P. 36126, 37138; Chem. Ztg. 1909, **33**, 431.

1. U. S. P. 952724, 1910; abst. J. S. C. I. 1910, **29**, 503; Mon. Sci. 1910, **73**, 140; C. A. 1910, **4**, 1530. E. P. 4154, 1909; abst. J. S. C. I. 1910, **29**, 100. D. R. P. 242467, 1908; abst. Chem. Ztg. 1911, **35**, 1442; C. A. 1912, **6**, 2315; Wag. Jahr. 1912, **62**, II, 616; Chem. Ztg. Rep. 1912, **36**, 111; Kunst. 1912, **2**, 59. F. P. (Commercial Products Co.) 402028, 1909; abst. J. S. C. I. 1909, **28**, 1212; Mon. Sci. 1912, **77**, 14.

2. C. Cross, E. Bevan and R. Jenks, Ber. 1901, **34**, 2496; abst. J. S. C. I. 1901, **20**, 1133; Chem. News, 1901, **84**, 61.

3. D. R. P. 184229, 1905; abst. Wag. Jahr. 1907, **53**, II, 34; Chem. Ztg. Rep. 1907, **31**, 267; Zts. ang. Chem. 1907, **20**, 1194; Chem. Zentr. 1907, **78**, II, 366; Jahr. Chem. 1905-8, II, 160; Zts. Schiess. Spreng. 1907, **2**, 195; J. S. C. I. 1908, **27**, 183; Mon. Sci. 1909, **71**, 71; C. A. 1907, **1**, 2524. D. R. P. 222450,, 1908; abst. Wag. Jahr. 1910, **56**, II, 434; C. A. 1910, **4**, 2875; J. S. C. I. 1910, **29**, 811; Zts. ang. Chem. 1910, **23**, 1389; Chem. Zentr. 1910, **81**, II, 48; Chem. Zts. 1910, **9**, No. 1902; Chem. Ztg. Rep. 1910, **34**, 301; Mon. Sci. 1914, **81**, 91. Aust. P. 25335, 27060, 1906.

4. K. Goldstein, D. R. P. 219116, 1908; abst. C. A. 1910, **4**, 2048; Chem. Zentr. 1910, **81**, I, 970; Wag. Jahr. 1910, **56**, I, 396; Chem. Ztg. Rep. 1910, **34**, 120.

photographic pellicles by the employment of cellulose acetate with gelatin, fish-glue or agar-agar[1]. The Raison Sociale Siebert (Gebr. Siebert)[2] replaces glue in the manufacture of wax paper or cloth by means of cellite (acetylcellulose).

The H. Manissadjian plastic[3] for making dies, moulds and similar solids is formed by dissolving acetylcellulose in ethyl acetate or chloroform and adding non-drying oils and phenol, cresol or naphthol esters, the plasticity being increased in proportion to the percentage of aromatic esters added. The continuous film manufacturing process of G. Bonwitt[4] involves the flowing of a cellulose acetate solution on an endless band where it is there precipitated in a *transparent* condition, according to the statement of the patentee.

It was in 1908 that W. Doerflinger[5] introduced Ausperite, a cellulose acetate bronzing fluid containing acetone, with a small amount of sodium carbonate as an antacid. The essence of originality in the insulating method for electrical machines and transformers of Felten & Guilleaume-Lahmeyerwerke Akt. Ges.[6] involves the use of cellulose

1. Soc. anon. des Plaques et Papiers Photographiques A. Lumiere et ses Fils, F. P. 401228, 1908; abst. J. S. C. I. 1909, **28**, 1064; C. A. 1910, **4**, 3045.

2. F. P. 396467, 1908; abst. J. S. C. I. 1909, **28**, 598; Mon. Sci. 1909, **71**, 150; C. A. 1910, **4**, 109.

3. E. P. 27201, 1908; abst. C. A. 1911, **5**, 197; Chem. Ztg. 1911, **35**, 366. F. P. 397429, 1908; abst. J. S. C. I. 1909, **28**, 812; Mon. Sci. 1913, **79**, 392, 551. Span. P. 44590, 1909; abst. Chem. Ztg. 1909, **33**, 234. Swiss P. 43330, 1907.

4. D. R. P. 237151, 1911; abst. Zts. Chem. Ind. Koll. 1911, **9**, 318; J. S. C. I. 1911, **30**, 1232; C. A. 1912 ,**6**, 1526; Wag. Jahr. 1911, **57**, II, 506; Chem. Zentr. 1911, **82**, II, 500; Chem. Ztg. Rep. 1911, **35**, 456; Zts. ang. Chem. 1911, **24**, 1838; Kunst. 1911, **1**, 340.

5. U. S. P. 884475, 1908; abst. J. S. C. I. 1908, **27**, 512; Mon. Sci. 1909, **71**, 144.

6. E. P. 19263, 1908; abst. J. S. C. I. 1909, **28**, 1206.

acetate. G. Ekstroem[1] described a method of acetylcellulose manufacture; E. Fischer disclosed new methods for forming acetated cellulose solutions[2]; while C. Schwalbe[3] discussed problems of the cellulose and artificial silk industries with especial emphasis placed on the applications of the uninflammable cellulose esters.

As a result of his investigations up to that time, A. Eichengruen[4] concluded that the product of the acetylation of cellulose is not a simple triacetate, but apparently a complex mixture consisting of acetyl derivatives formed by the entrance of the acetyl group into different positions in the cellulose molecule, and of intermediate compounds produced by the addition of water or by internal anhydride formation. He maintained—and truly—that a large number or series of acetates must exist which do not essentially differ from the triacetate analytically, although differing materially in mechanical properties, and especially stability and solubility. According to his experiments, Cellit is a definite acetate soluble in acetone, a statement to which the author does not subscribe.

D. Law investigated the action of the acetylating agent recommended by C. Cross, E. Bevan and J. Briggs (see p. 324, n. 2), obtained by adding 100 gm. acetic anhydride to a solution of 50 gm. zinc chloride in 100 gm. glacial acetic acid, and found, that while with cellulose a triacetate is

1. Swed. P. 24249, 1908; abst. Chem. Ztg. 1908, **32**, 611. In a later process (P. Ekstroem, Swed. P. 33546, 1911; abst. C. A. 1913, **7**, 1289) cellulose is exposed in vacuo to the action of concentrated formic or acetic acid, the period of reaction being so regulated that the resulting acids may be distilled off and collected.

2. D. R. P. Anm. F-22850, 1908; abst. Chem. Ztg. 1908, **32**, 760.

3. Zts. ang. Chem. 1908, **21**, 2401; abst. C. A. 1910, **4**, 1105; Chem. Zentr. 1909, **80**, I, 473; Chem. Ztg. Rep. 1908, **32**, 686; Wag. Jahr. 1908, **54**, II, 368.

4. Zts. ang. Chem. 1908, **21**, 1729; Chem. Ztg. 1908, **32**, 583; abst. C. A. 1908, **2**, 2990; J. S. C. I. 1911, **30**, 413; Chem. Zentr. 1908, **79**, II, 1215; Oest. Chem. Ztg. 1911, **24**, 59; Wag. Jahr. 1908, **54**, II, 500; Phot. Wochenbl, 1908, **34**, 269.

formed, with starch no reaction takes place[1]. In acetation, A. Wohl attempted to correlate the relation between the time of reaction and the amount of sulfuric acid required as catalyst[2], and found when treating cellulose containing no ash, 0.2% or less sulfuric acid is sufficient, whereas with ordinary filter paper, about 0.4% is required, with correspondingly higher percentages for celluloses containing more ash. With these amounts of acid the whole of the cellulose can be converted into acetate by acetic anhydride after 1-2 hours at a temperature of 100°-120°.

In 1908 E. Knoevenagel pointed out that when cellulose is acetylated in the presence of sulfuric acid, solutions of acetylcellulose are obtained, which, after days or weeks according to the quantities of reagents employed, undergo a considerable change characterized externally by the fact that the solutions which are first viscous, become mobile[3]. If, on the other hand, the acetylation is conducted in the presence of inorganic salts as ferrous sulfate, viscous solutions of great stability result, which may be spun into

1. Chem. Ztg. 1908, **32**, 365; abst. J. C. S. 1908, **94**, i, 321; Bull. Soc. Chim. 1909, **6**, 157; Chem. Zentr. 1908, **79**, I, 1831; Jahr. Chem. 1905-8, II, 55; Zts. ang. Chem. 1908, **21**, 1377. This acetylating mixture converts sucrose into the octoacetyl derivative and dextrose into the tetra-acetyl compound, indefinite crystals, m. pt. 98°. Added in slight excess to benzaldehyde a violent reaction takes place; and when after some time the fluorescent solution is poured into cold water, crystals of a diacetate $C_6H_5.CH\ (OC_2H_3O_2)_2$ are obtained, which crystallizes from alcohol, of m. pt. 43°, and b. pt. 225-230°. When furfuraldehyde dissolved in glacial acetic acid is treated with an excess of the reagent and the mixture cooled in a freezing mixture a dark solution is obtained, which, when poured into water gradually separates an oil which crystallizes to a diacetyl derivative, $C_4OH_3.CH(OC_2H_3O_2)_2$, m. pt. 45°, b. pt. 220°. If the reagent is allowed to react with furfuraldehyde at the ordinary temperature, a black substance is obtained which is not attacked by acids or alkalis.

2. D. R. P. 243581, 1908; abst. C. A. 1912, **6**, 2316; J. S. C. I. 1912, **31**, 381; Chem. Zentr. 1912, **83**, I, 695; Chem. Ztg. Rep. 1912, **36**, 196; Wag. Jahr. 1912, **58**, II, 17; Zts. ang. Chem. 1912, **25**, 654. In this connection see also F. Klein, Zts. ang. Chem. 1912, **25**, 1409; abst. C. A. 1913, **7**, 2303; J. C. S. 1912, **102**, i, 679; J. S. C. I. 1912, **31**, 713; Chem. Zentr. 1912, **83**, II, 1196; Chem. Ztg. Rep. 1912, **36**, 532; Kunst. 1912, **2**, 311; Meyer Jahr. Chem. 1912, **22**, 178; Wag. Jahr. 1912, **58**, II, 560.

3. Chem. Ztg. 1908, **32**, 810; Zts. ang. Chem. 1908, **21**, 2057; abst. J. S. C. I. 1908, **27**, 937.

threads, and may be dyed in the usual manner, after suitable preliminary treatment, as softening in alcohol.

In the treatment of cotton to resist the action of direct or substantive dyestuffs, C. Cross and J. Briggs[1] superficially acetylate the yarn without changing its appearance. W. Walker contributed observations on the apparent advantage of benzenesulfonic acid as a catalyst in acetylation[2]; R. Flemming on the use of cellulose acetate in the insulation of fine wire[3]; and A. Smith and K. Orton[4] closed the year's work with their observations upon the acetylation of various bodies.

The year 1909 was also prolific in advancement, both in technical methods and in academic investigations. V. Pauthonier[5] recommends that cellulose acetation be conducted in the presence of sulforicinic acid from castor oil, or sulfopalmitic acid from palm oil in order to minimize the harmful action of the catalyst. K. Hofmann[6] acetates in the presence of phosphoric or pyrophosphoric acid (see L. Landsberg, p. 339, n. 1). The Farbenfabriken vorm. F. Bayer & Co. employ either sulfuryl chloride[7] or chlorosul-

1. J. Soc. Dyers Col. 1908, **24**, 189; abst. C. A. 1908, **2**, 2996; J. S. C. I. 1908, **27**, 802; Wag. Jahr. 1908, **54**, II, 473; Zts. ang. Chem. 1908, **21**, 2189.

2. J. Frankl. Inst. 1907, **164**, 131; abst. C. A. 1908, **2**, 318, 2619; Mon. Sci. 1908, **68**, 461; Jahr. Chem. 1905-8, II, 958; Text. Col. 1907, **29**, 247.

3. General Electric Review, Jan. 1908.

4. Proc. Chem. Soc. 1909, **25**, 166; J. C. S. 1909, **95**, 1060; abst. J. S. C. I. 1909, **28**, 678; Chem. Zentr. 1909, **80**, II, 515; Jahr. Chem. 1909, **62**, 607.

5. E. P. 27102, 1909; abst. J. S. C. I. 1911, **30**, 19; Chem. Ztg. Rep. 1911, **35**, 59; C. A. 1911, **5**, 2947; Mon. Sci. 1915, **82**, 55. F. P. 409465, 1909; abst. J. S. C. I. 1910, **29**, 751; Mon. Sci. 1910, **72**, 452; 1911, **74**, 147; 1913, **79**, 551; Chem. Ztg. 1911, **35**, 301.

6. D. R. P. 227198, 1909; abst. J. S. C. I. 1910, **29**, 1300; Chem. Zts. 1910, **9**, No. 2102; Chem. Zentr. 1910, **81**, II, 1349; Kunst. 1911, **1**, 16; C. A. 1911, **5**, 1514; Jahr. Chem. 1910, **63**, II, 429; Wag. Jahr. 1910, **56**, II, 431; Mon. Sci. 1916, **83**, 47; Chem. Ztg. Rep. 1910, **34**, 544.

7. D. R. P. 237765, 1909; abst. C. A. 1912, **6**, 1672; Zts. ang. Chem. 1911, **24**, 2084; Chem. Zentr. 1911, **62**, II, 1079; Chem. Ztg. Rep. 1911, **35**, 520; Wag. Jahr. 1911, **57**, II, 420.

fonic acids[1] as condensing agents in cellulose acetation. They[2] also have described methods for the coating of threads, ribbons and bands with cellulose acetate to which pigments and bronze powders may be added to produce selective effects. To increase the pliability of the filaments, L. Lederer[3] recommended resorcinol diacetate, he previously (see p. 340, n. 1) having described the usefulness of resorcinol for this purpose. Resorcinol diacetate is an excellent solvent for the hydrated acetylcelluloses. The other two iso-

1. D. R. P. 237766, 1909; abst. C. A. 1912, **6**, 1672; Zts. ang. Chem. 1911, **24**, 2084; Chem. Zentr. 1911, **82**, II, 1079; Chem. Ztg. Rep. 1911, **35**, 520; Wag. Jahr. 1911, **57**, II, 420; Chem. Zts. 1912, **11**, No. 2745.

2. P. Benrath, E. Damm and O. Stephani (assignors to Farben f. vorm. F. Bayer & Co., U. S. P. 1031616, 1912; 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, 1909; 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, 1910, to F. P. 408370, 1910; abst. J. S. C. I. 1910, **29**, 1299. Second Addn. 12755, 1910, to F. P. 408370, 1910; abst. J. S. C. I. 1910, **29**, 1371. F. P. 415048, 1910; abst. J. S. C. I. 1910, **29**, 1247; J. Soc. Dyers Col. 1910, **26**, 226. F. P. 417027, 1910; abst. J. S. C. I. 1910, **29**, 1373; Mon. Sci. 1913, **79**, 20; J. Soc. Dyers Col. 1910, **26**, 242. D. R. P. 227238, 1909; abst. Zts. ang. Chem. 1917, **30**, I, 76. D. R. P. 235357, 1910; abst. C. A. 1911, **5**, 3129; 1912, **6**, 1960; Zts. ang. Chem. 1911, **24**, 1435; Chem. Zentr. 1911, **82**, II, 171; Chem. Ztg. Rep. 1911, **35**, 348; Wag. Jahr. 1911, **57**, II, 97. D. R. P. 235381, 1910; abst. C. A. 1912, **6**, 1855; Chem. Ztg. Rep. 1911, **35**, 324; Wag. Jahr. 1911, **57**, II, 533; Chem. Ind. 1911, **34**, 390; J. Soc. Dyers Col. **27**, 217. D. R. P. 240188, 1909; abst. C. A. 1912, **6**, 2178; Zts. ang. Chem. 1911, **24**, 2336; Chem. Zentr. 1911, **82**, II, 1563; Chem. Ztg. Rep. 1911, **35**, 576; Wag. Jahr. 1911, **57**, II, 468; Chem. Zts. 1911, **10**, No. 2590. D. R. P. 243068, 1909; abst. C. A. 1912, **6**, 2310; Zts. ang. Chem. 1912, **25**, 560; Chem. Zentr. 1912, **83**, 534; Chem. Ztg. Rep. 1912, **36**, 110; Wag. Jahr. 1912, **58**, II, 502; Chem. Zts. 1912, **11**, No. 2739. D. R. P. 248946, 1909, (Addn. to D. R. P. 243068); abst. C. A. 1912, **6**, 2850; Zts. ang. Chem. 1912, **25**, 1758; Chem. Zentr. 1912, **83**, II, 296; Chem. Ztg. Rep. 1912, **36**, 439; Wag. Jahr. 1912, **58**, II, 502. Belg. P. 220225, 1909. Swiss P. 48975, 52903, 53888, 1910; abst. Chem. Ztg. 1912, **36**, 327. Aust. P. Appl. 4642 of 1910; abst. Chem. Ztg. 1910, **34**, 1362.

3. E. P. 8945, 1909; abst. J. S. C. I. 1909, **28**, 1271; Chem. Ztg. 1909, **33**, 1198. F. P. 402083, 1909; abst. C. A. 1911, **5**, 997; J. S. C. I. 1909, **28**, 1270; Chem. Ztg. 1909, **33**, 971; Mon. Sci. 1910, **73**, 168.

meric dihydroxybenzenes (pyrocatechol and hydroquinone) also form diacetates having solvent properties.

Knoll & Co.[1] claim to permanently increase the elasticity by treatment with solutions of inorganic acids as hydrochloric, and this is so, for by the partial hydration of an acetated cellulose by a mineral acid in the presence of water the elasticity is considerably augmented when the ester is dissolved in acetone, but this increase is only apparent up to a certain point in hydration, after which it diminishes if hydration is prolonged. A series of plastic inducing bodies was brought forward by A. Eichengruen in this year (1909)[2], in which he called attention to the possible usefulness of certain aromatic amines, phenols and ketones, including ethylacetanilid (manol), ethyl acetyltoluidine and methyl salicylate.

The impregnating composition disclosed by M. Krummling[3] for coating paper and textiles involves the employment of an acetone or acetic acid solution of acetylcellulose. Debauge et Cie[4] prefer tetrachlorethane and pyridine as a neutralizant in their insulating varnish for electrical construction, the viscosity of the cellulose acetate being increased by the addition of hexachlorethane (a solid). In the finishing of cellulose articles as artificial filaments, acetocellulose and nitrocellulose have been specified as coat-

1. E. P. 7743, 1909; abst. C. A. 1911, **5**, 206; J. S. C. I. 1910, **29**, 269; Chem. Ztg. 1911, **35**, 198; J. Soc. Dyers Col. 1909, **25**, 153; 1906, **26**, 90, 95. Addn. 10783, 1909, to F. P. 383636, 1907; abst. J. S. C. I. 1909, **28**, 1194; Chem. Ztg. 1909, **33**, 946; Mon. Sci. 1910, **73**, 451; J. Soc. Dyers Col. 1909, **25**, 270.

2. D. R. P. 238348, 1909; abst. C. A. 1912, **6**, 1672; Chem. Zentr. 1911, **72**, II, 1085; Chem. Ztg. 1911, **35**, 1001; Chem. Ztg. Rep. 1911, **35**, 520; Wag. Jahr. 1911, **57**, II, 552; Kunst. 1911, **1**, 416. Swiss P. 52115, 1910; abst. Kunst. 1912, **2**, 99.

3. E. P. 10578, 1909.

4. F. P. 418347, 1909; abst. J. S. C. I. 1911, **30**, 96; Kunst. 1912, **2**, 316. Addn. 15217, 1911, to F. P. 418347, 1909; abst. J. S. C. I. 1912, **6**, 651; Kunst. 1912, **2**, 316. F. P. 450886, 1912; abst. C. A. 1913, **7**, 3227; J. S. C. I. 1913, **32**, 596; Chem. Ztg. 1913, **37**, 284; Chem. Ztg. Rep. 1913, **37**, 388; Kunst. 1913, **3**, 195. F. P. 453464, 1913; abst. C. A. 1914, **8**, 24; Chem. Ztg. Rep. 1913, **37**, 544. See also A. Douque, waterproofing cloth with cellulose acetate, E. P. 17449, 1909; abst. J. S. C. I. 1910, **29**, 1007; F. P. 403761, 1909; abst. J. S. C. I. 1910, **29**, 19.

ing materials for the thread in order to increase the strength and water-repellent qualities[1].

The plastic mass of the Commercial Products Co. brought out in 1909[2], replaces camphor by anhydroformaldehyde aniline or a resinate, cellulose acetate being used as the ester. In another patent[3], phthalic acid esters as dimethyl and diethyl phthalates are specified. P. Krais puts a Schreiner finish on textile fabrics by means of cellulose acetate[4], the solution being applied by spraying. In an improvement on the acetylation of starch made by A. Militz and the Farbenfabriken[5] (see p. 363, n. 3), the starch is treated with glacial acetic acid and nitric acid until a sample of the product completely dissolves in hot water, at which time it is insoluble in glacial acetic acid.

The P. Prost and Les Fils Pinay process for cellulose acetylation[6] depends upon the esterification of tissue paper in loosely corrugated cylinders in closed stoneware pots.

1. Cie. Francaise des Applications de la Cellulose, F. P. 417599, 1909; abst. J. S. C. I. 1911, **30**, 19. Belg. P. 237056, 1911.

2. L. Berend, U. S. P. 952724, 1910; abst. J. S. C. I. 1910, **29**, 503; Mon. Sci. 1910, **73**, 140; C. A. 1910, **4**, 1530. Commercial Products Co., E. P. 4154, 1909; abst. J. S. C. I. 1910, **29**, 100. D. R. P. 242467, 1908; abst. Chem. Ztg. 1911, **35**, 1442; C. A. 1912, **6**, 2315; Wag. Jahr. 1912, **62**, II, 616; Chem. Ztg. Rep. 1912, **36**, 111; Kunst. 1912, **2**, 59. F. P. 402028, 1909; abst. J. S. C. I. 1909, **28**, 1212; Mon. Sci. 1912, **77**, 14.

3. 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, 1909; abst. C. A. 1911, **5**, 2155; J. S. C. I. 1910, **29**, 1398; Zts. ang. Chem. 1910, **23**, 2348; Chem. Zentr. 1910, **81**, II, 1579; Jahr. Chem. 1910, **63**, II, 867; Chem. Tech. Rep. 1910, **34**, 596; Chem. Zts. 1911, **10**, No. 2167; Kunst. 1911, **1**, 90. F. P. 416806, 1909; abst. J. S. C. I. 1910, **29**, 1398. U. S. P. 1003741, 1911; abst. C. A. 1911, **5**, 3922; J. S. C. I. 1911, **30**, 1223; Mon. Sci. 1912, **77**, 165; Kunst. 1912, **2**, 77.

4. U. S. P. 922295, 1909; abst. J. S. C. I. 1909, **28**, 653; Chem. Ztg. Rep. 1909, **33**, 376. E. P. 25463, 1903; abst. J. Soc. Dyers Col. 1904, **20**, 29.

5. U. S. P. 941159, 1909; abst. C. A. 1910, **4**, 525; J. S. C. I. 1909, **28**, 1322. E. P. 25274, 1907; abst. C. A. 1909, **3**, 386; J. S. C. I. 1908, **27**, 761; J. Soc. Dyers Col. 1908, **24**, 218. F. P. 383902, 1907; abst. C. A. 1909, **3**, 1105; J. S. C. I. 1908, **27**, 415; Chem. Ztg. Rep. 1908, **32**, 300. D. R. P. 200145, 1907; abst. C. A. 1908, **2**, 3167; Zts. ang. Chem. 1908, **21**, 2285; Chem. Zentr. 1908, **79**, II, 560; Jahr. Chem. 1905-8, II, 941; Chem. Tech. Rep. 1908, **32**, 454; Wag. Jahr. 1908, **54**, II, 190; Mon. Sci. 1911, **75**, 95.

6. F. P. 421854, 1909; abst. J. S. C. I. 1911, **30**, 416; Mon. Sci. 1913, **79**, 30.

The celluloid substitute of W. Parkin and A. Williams[1] lays claim to originality primarily from the employment of nitric acid as an aid to partial hydration (see Knoll & Co., p. 354, n. 1), coupled with combination of the acetated cellulose with chloral alcoholate (see p. 355, n. 1), triphenyl or trinaphthyl phosphates (see p. 162, n. 4) or glyceryl esters. The H. Reeser acetate plastic[2] discloses an observation of the first importance in this field. He proposes to take acetone-soluble acetylcellulose and combine this with a fluid which is a non-solvent when cold but dissolves when the solvent is heated to near its boiling point, specifying for this purpose a mixture of ethyl alcohol and benzene. The acetic ester upon cooling from such a solution jellifies, and after pouring the liquid from such a colloid, camphor or other plastic-inducing body is mechanically admixed with the precipitated ester. This observation has been materially extended since in a number of processes and in some instances with very satisfactory results.

In enameling cinematograph films according to the directions of F. Thompson[3] by means of a special apparatus which he has devised[4] the films are either covered with a nitrocellulose solution in amyl acetate and castor oil or an acetylcellulose solution. W. Biber[5] impregnates tissues with solutions of cellulose acetate in order to increase their waterproofing qualities; G. Gawlich[6] agglutinated pieces of

1. 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, 1910; abst. J. S. C. I. 1911, **30**, 416; Mon. Sci. 1913, **79**, 30, 392.

2. E. P. 12976, 1909, (not granted); abst. J. S. C. I. 1910, **29**, 147; Chem. Ztg. 1911, **35**, 94; Gummi Ztg. 1910, **10**, 65. F. P. 411126, 1909; abst. J. S. C. I. 1910, **29**, 875; Chem. Ztg. 1910, **34**, 432; Mon. Sci. 1912, **77**, 8; 1913, **78**, 392. Aust. P. Appl. 9533, 1909; abst. Chem. Ztg. 1910, **34**, 1362. Belg. P. 216668, 1909. Hung. P. Appl. R-2398, 1909. Port. P. 7102, 1909; abst. Chem. Ztg. 1911, **35**, 290. See also Elec. Engineering, 1909, **44**, 308.

3. E. P. 20965, 1909. U. S. P. 960437, 1910. U. S. P. 970972, 1910; abst. J. S. C. I. 1910, **29**, 1228; C. A. 1910, **4**, 3170.

4. See W. Daniels, E. P. 24556, 1909; abst. J. S. C. I. 1910, **29**, 1228.

5. **Belg. P. 219965, 1909.**

6. E. P. 16199, 1909; abst. J. S. C. I. 1910, **29**, 420; J. Soc. Dyers Col. 1910, **26**, 139. Aust. P. 46036; abst. Kunst. 1911, **1**, 136.

fabrics with the same material thus building up compound fabrics from smaller pieces; and J. and C. Bedfors and J. Kirk[1] prepared a linoleum material for the covering of spinning rollers of cotton cemented with acetylcellulose. A process for the manufacture of impermeable and washable linen by means of an acetylcellulose and nitrocellulose coating[2], was described by E. Roggenkaemper.

E. Grandmougin[3] has observed that although H. Ost regards[4] acetylcellulose as a triacetate, it must be remembered that it is always the case of an acetyl derivative of an already hydrolytically split cellulose, and that an acetyl compound of normal cellulose has apparently not as yet been made. In any event, it would be difficult to determine as to whether it was or was not, for although the solubility of the product and the elasticity of the films obtained by evaporation may be a deciding factor from the technical point of view, it adds nothing whatever to the problem of the *constitution* of the product obtained.

In the preliminary treatment of cellulose for purposes of esterification, E. Berl has observed[5] that those methods which increase the reaction of cellulose, do so by a decrease of the size of the molecule, and these relative differences in molecular magnitude can be established by measuring the internal friction of solutions of the same percentage composition of the esters formed from the cellulose. He recommends in the preparation of cellulose acetate, a pre-

1. E. P. 28393, 1909.

2. F. P. 407932, 1909; abst. J. S. C. I. 1910, **29**, 623; Mon. Sci. 1910, **73**, 300. D. R. P. 234500, 1910; abst. C. A. 1911, **5**, 2975. D. R. P. Anm. R-47445, 1919; abst. Chem. Ztg. 1920, **44**, 277.

21. Chem. Ztg. 1908, **32**, 241; abst. J. C. S. 1908, **94**, i, 250; Bull. Soc. Chim. 1909, **6**, 231; Chem. Zentr. 1908, **79**, I, 1617; Jahr. Chem. 1905-8, II, 959.

3. Zts. ang. Chem. 1906, **19**, 994; abst. J. C. S. 1906, **90**, i, 560; J. S. C. I. 1906, **25**, 606; Bull. Soc. Chim. 1906, **36**, 1053; Chem. Centr. 1906, **77**, II, 672; Jahr. Chem. 1905-8, II, 983; Meyer Jahr. Chem. 1906, **16**, 219; Wag. Jahr. 1906, **52**, II, 484.

4. Zts. Schiess Spreng. 1909, **4**, 81; abst. C. A. 1909, **3**, 1926; J. S. C. I. 1909, **28**, 380; Chem. Zentr. 1909, **80**, I, 1275; Chem. Ztg. Rep. 1909, **33**, 195; Jahr. Chem. 1909, **62**, II, 384; Meyer Jahr. Chem. 1909, **19**, 335; Wag. Jahr. 1909, **55**, II, 398.

vious treatment with dilute acids for hydrocellulose formation, and this means an essential diminution in the molecular size of the cellulose. It is well known that cellulose nitrates become more soluble by long heating, but the nitrogen content is not apparently diminished as the result of the treatment. With cellulose acetate, however, exposure to elevated temperature for periods which show marked changes in solubility, also invariably indicate a lower acetyl percentage, so the comparison is not strictly analogous. E. Berl depolymerizes cellulose by heating to 100° in the presence of an inert gas[1].

E. Knoevenagel[2] in referring to the degradation of cellulose to cellobioseoctoacetate as effected by Z. Skraup and his co-workers when working with acetic anhydride in the presence of sulfuric acid (a process which has since been designated as acetolysis[3]), observes that such acetolytic change evidently occurs in many cases when employing acetic anhydride in presence of various catalytic substances. For instance, when cineol is treated with acetic anhydride using sulfuric acid, iron chloride or other catalyst, terpine diacetate and terpineol acetate are formed; similarly, ethyl acetate results from diethyl ether. The acetolysis of cellulose to the octoacetate does not necessarily lead to the assumption that there are no oxygen linkages in the cellulose molecule, as the supposed presence of such linkages satisfactorily explains many points in connection with cellulose

1. D. R. P. 199885, 1907; abst. C. A. 1908, **2**, 3154; J. S. C. I. 1908, **27**, 937; Mon. Sci. 1911, **74**, 93; 1916, **83**, 180; Chem. Zentr. 1908, **79**, II, 466; Chem. Ind. 1908, **31**, 454; Chem. Ztg. Rep. 1908, **32**, 382; Jahr. Chem. 1905-8, II, 309; Wag. Jahr. 1908, **54**, II, 355; Zts. ang. Chem. 1908, **21**, 2233; Zts. Schiess Spreng. 1909, **4**, 81. See also Technology of Cellulose Esters, 1921, **1**, 29, 43, 55, 562, 567, 613, 1673, 2017, 2623, 2625.

2. Zts. ang. Chem. 1909, **22**, 281; Chem. Ztg. 1909, **33**, 104. For the cellulose acetate solution of G. Muth see Belg. P. 228668, 1909; abst. Chem. Ztg. 1910, **34**, 1162.

3. See Technology of Cellulose Esters, 1921, **1**, 181, 187.

chemistry; but it does lead to a lack of certainty in the determination of the number of hydroxyl groups in organic compounds as usually carried out with acetic anhydride, if any contact substance happens to be present.

R. Lowenthal[1] published a review of the recent articles and patents issued covering this general field.

In the contemplation of the significance of the hundred twenty-five patents and contributions mentioned herein during the semi-decennial period 1905-1909, the following stand out as especially significant points of this transition period, as viewed in the perspective of elapsed time:

1. Miles disclosed and others worked on various angles of the observation that a substantially normal cellulose acetate by the introduction of hydroxyl by treatment with hydroxyl-containing bodies (water, glycol, glycerol) could be changed to a number of indefinitely characterized esters by a diminution of acetic acid content in the ester, whereby an increase in tensile strength, resiliency and stability of the formed product results, and the use of cheaper, less toxic and more widely applicable solvents is possible.

2. Attempts to diminish the inflammability of nitrocellulose by co-esterification with acetic acid and nitric acid or otherwise, whereby mixed esters result was given careful consideration, especially from the viewpoint of their technical production in large quantities.

3. The drastic action of sulfuric acid as a condensing agent was generally recognized, and many attempts made to minimize or temper this action in various ways, the majority of which have been commercially unsuccessful. Some of the methods proposed appear to be but attempts at patent circumlocution.

1. Chem. Ztg. 1909, **33**, 753, 770; abst. C. A. 1910, **4**, 1811; Bull. Soc. Chim. 1910, **8**, 59; Chem. Zentr. 1909, **80**, II, 484.

4. The hope that camphor would induce with acetylcellulose the same or similar properties of thermoplasticity as is imparted to nitrocellulose was virtually abandoned, and investigators began to turn their attention to the possible applicability of "camphor substitutes" for this purpose —a search which has been unremitting up to the present day.

5. Reeser, unwittingly or otherwise, made a valuable observation in attempting to employ solvent combinations which with cellulose acetate showed dissolving power when hot, but little or no power in this direction when cold, and this angle of cellulose ester technology has been considerably amplified from that time to now, as will appear in the survey of the next ten year period.

6. A well defined and logical co-ordinated effort is apparent in this period to extend the uses of the cellulose acetates to those fields where the corresponding nitric esters have been found useful, and this is reflected in the writings and processes looking toward new uses in photography, filament formation, plastics and general technical applications.

7. The peculiar and technically interesting results disclosed by the methods of partial hydration published in this period, caused men of reflection and research to ponder thoughtfully the physical chemistry involved in the various phases of depolymerization, esterification and hydration, but as yet without any generally accepted theory having been enunciated.

8. Endeavors to extend the usefulness of the cellulose formates were many but without any marked permanent advancement noticeable, primarily on account of the diminished stability of the formylcelluloses, and to the fact that the known solvents were few and generally unsatisfactory.

9. Everywhere is observed an exemplification of the statement that advancement is dependent upon solvents, upon increasing the range of dissolving simple and compound bodies which would have the desirable properties of non-hygroscopicity, non-toxicity, low cost, quick dissolving power, and obtainable in unlimited amounts.

Cellulose Acetate Advancement, Period 1910-1914. The five year period from 1910 to 1914 inclusive, in the number and variety of theoretical investigations and technical processes proposed and patented, indicates a very materially increased interest in this subject—especially from a practical point of view—over any preceding five year period. There appears a well marked indication of the reduction to tangible commercial practice of the more or less sporadic efforts of the past, and a successful attempt to correlate the work of those who have preceded, into a stable and enduring industry.

In the year 1910 was brought forward the composition for finishing and rendering impermeable, of J. Achard and C. Gonon[1], consisting of cellulose acetate mixed with its own volume of tetrachlorethane. The Viscose Development Co. and J. Morford in improving upon their process for the utilization of viscose for sealing bottles[2], found that cellulose acetate in glacial acetic acid is adapted for similar application by virtue of the fact that the ester may be separated from solution as a continuous film in combination with water of hydration[3].

1. F. P. 427562, 1910; abst. J. S. C. I. 1911, **30**, 1053; J. Soc. Dyers Col. 1911, **27**, 194; Mon. Sci. 1913, **79**, 23.
2. E. P. 2880, 1905.
3. E. P. 14194, 1910; abst. J. S. C. I. 1911, **30**, 888. D. R. P. 270314, 1911; abst. C. A. 1914, **8**, 2251; Chem. Ztg. Rep. 1914, **38**, 133; Kunst. 1914, **4**, 116. Aust. P. 66165; abst. Kunst. 1914, **4**, 274; 1915, **5**, 82. Swiss P. 56152, 1911. The N. V. Fabriek van Chemis. Produkten (E. P. 12042, 1913; Swiss P. 65920; F. P. 461540) produce mixed fatty anhydrides by heating an acylsulfate with a fatty acid salt. Sodium acetylsulfate and sodium propionate give acetic-propionic anhydride. The acidylsulfuric acid is prepared by heating (say) acetylsulfuric acid with sodium chloride, acetyl chloride being simultaneously formed.

In the process of the Farbenfabriken vorm. F. Bayer & Co. for the coating of threads[1], the cellulose acetate is combined with such bodies as ethylbenzoyl-*o*-toluidine, acetin and acetylbenzyl-*o*-toluidine. A. Bacigalupi[2] described the formation of printing plates of acetated cellulose with tetra- and penta-chlorethane, alcohol and benzene, while A. Zimmer[3] treated starched linen articles with cellulose acetate in trichlorethane or trichlorethylene, castor oil and camphor, or used cellulose butyrate dissolved in acetone. The artificial rubber of J. Scammel[4] combined cellulose treated with butyric acid, oil and sulfur chloride, which may have resulted in the formation of cellulose butyrate. In another process[5], cellulose acetate is rendered uninflammable by soaking in boric acid. An attempt was made to improve

1. 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, 1910; 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, 1910; 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.

2. E. P. 29273, 1910.

3. U. S. P. 1025731, 1912; abst. C. A. 1912, **6**, 1994; J. Soc. Dyers 1912, **28**, 248; Mon. Sci. 1913, **79**, 14; J. S. C. I. 1912, **31**, 533. E. P. 24006, 1909; abst. J. S. C. I. 1911, **30**, 21; J. Soc. Dyers, 1911, **27**, 63. E. P. 12406, 1910; abst. J. S. C. I. 1911, **30**, 206; C. A. 1911, **5**, 2963. See also E. P. 6519, 1910; abst. J. S. C. I. 1911, **30**, 206; C. A. 1911, **5**, 2962. F. P. 422763, 1910; abst. J. S. C. I. 1911, **30**, 53. D. R. P. 242786, 1910; abst. Wag. Jahr. 1912, **58**, II, 509; C. A. 1912, **6**, 2182; Chem. Ztg. Rep. 1912, **36**, 79; Zts. ang. Chem. 1912, **25**, 512; C. A. 1912, **6**, 2182. See p. 378, n. 2.

4. E. P. 9636, 1910; abst. C. A. 1911, **5**, 3174; J. S. C. I. 1911, **30**, 437; Kunst. 1911, **1**, 255; Chem. Ztg. Rep. 1911, **35**, 488. The manufacture of alcohol-soluble cellulose acetates has been described by C. Schwalbe, D. R. Anm. Sch. 36144, 1910; abandoned, Feb. 15, 1912.

5. F. Seaton-Snowden and D. Young, E. P. 28848, 1910; abst. J. S. C. I. 1911, **30**, 123; Chem. Ztg. 1912, **36**, 35; Chem. Ztg. Rep. 1912, **36**, 273; J. Soc. Dyers Col. 1912, **28**, 74; C. A. 1912, **6**, 1526. E. P. 16133, 1912; abst. J. S. C. I. 1912, **31**, xv. F. P. 436900, 1911;

on the process of F. Meyer (see p. 367, n. 2) for coating the tips of cigars with cellulose acetate[1], while A. Pellerin[2] described the use of hydrated cellulose from viscose manufacture as the basic material for acetation.

A series of patents were granted to A. Eichengruen in 1910 in this art embracing (1) the production of celluloid-like masses with camphor or its substitutes and finely powdered mica or similar materials[3], upon which a brilliant gloss is imparted by means of polished and heated plates[4]; (2) the employment of a mixture of alcohol and benzene as a precipitant preparatory to kneading and moulding the acetated cellulose with camphor[5]; (3) preparing brilliant, matt or decorated cellulose acetate coatings by the adhesion

abst. Kunst. 1912, **2**, 255; J. S. C. I. 1912, **31**, 428; Mon. Sci. 1913, **79**, 191. F. P. 437411, 1911; abst. J. S. C. I. 1912, **31**, 549; Chem. Ztg. 1912, **36**, 367. F. P. 437473, 1911; abst. Kunst. 1912, **2**, 255; J. S. C. I. 1912, **31**, 123; J. Soc. Dyers Col. 1912, **28**, 200. Belg. P. 241975. Ital. P. 122890; abst. Chem. Ztg. 1913, **37**, 32. Hung. P. Appl. S-6073, 1912; abst. Chem. Ztg. 1912, **36**, 1045.

1. U. S. P. 951582, 1910; abst. C. A. 1910, **4**, 1515. See Safety Celluloid Co., Ital. P. 134767.

2. E. P. 7748, 1910; abst. C. A. 1911, **5**, 3156; J. S. C. I. 1911, **30**, 533; J. Soc. Dyers, 1911, **27**, 161. See E. P. 983, 1881; 1753, 11734, 1903; 16598, 1906; 28743, 1907; 15306, 1909. J. Aylsworth (U. S. P. 1094830) has patented the use of acetylene tetrachloride as a lacquer solvent, and Knoll & Co. (Aust. P. 67814) cellulose acetate highly viscous in acetone by esterizing with potassium bisulfate and diethylamine. See D. R. P. 159524.

3. E. P. 18189, 1910; abst. C. A. 1911, **5**, 3340; J. S. C. I. 1911, **30**, 798; Kunst. 1911, **1**, 417. F. P. 418744, 1910; abst. J. S. C. I. 1911, **30**, 79; Mon. Sci. 1913, **78**, 551; Kunst. 1911, **1**, 92.

4. E. P. 1441, 1910; abst. J. S. C. I. 1910, **29**, 1005; C. A. 1911, **5**, 2177; Chem. Ztg. Rep. 1911, **35**, 340. E. P. 18076, 1910, (Addn. to E. P. 1441, 1910); abst. J. S. C. I. 1910, **29**, 1199; C. A. 1911, **5**, 2723. F. P. 412797, 1910; abst. Kunst. 1911, **1**, 57; Chem. Ztg. 1910, **34**, 606; J. S. C. I. 1910, **34**, 1005; Mon. Sci. 1913, **79**, 76. First Addn. 12388, 1910, to F. P. 412797, 1910; abst. J. S. C. I. 1910, **29**, 1199; Chem. Ztg. 1910, **34**, 842; Kunst. 1911, **1**, 57. See also Oest. Chem. Ztg. 1911, **24**, 59.

5. U. S. P. 1015156, 1912; abst. Mon. Sci. 1912, **77**, 163; C. A. 1912, **6**, 685; Kunst. 1912, **2**, 158. D. R. P. Anm. E-14630, 1909; abst. Kunst. 1911, **1**, 320; Chem. Ztg. 1911, **35**, 672. D. R. P. 238348, 1909; abst. C. A. 1912, **6**, 1672; Chem. Zentr. 1911, **82**, II, 1085; Chem. Ind. 1911, **34**, 637; Chem. Ztg. Rep. 1911, **35**, 520; Wag. Jahr. 1911, **57**, II, 552; Kunst. 1911, **1**, 416. D. R. P. 254385 ,1909; abst. Chem. Ztg. 1912, **36**, 1364; Kunst. 1912, **2**, 439; 1913, **3**, 50; C. A. 1913, **7**, 1288; Zts. ang. Chem. 1913, **26**, II, 32; Chem. Zentr. 1913, **84**, I, 361; Chem. Ztg. Rep. 1913, **37**, 20; C. A. 1913, **7**, 1288. D. R. P. 295764, 1916;

of thin films to textiles or leather[1]; (4) the employment of a mixture of tetrachlorethane and alcohol as a solvent combination[2]; (5) admixture of acetone-soluble acetylcellulose with methylacetanilid and methyl alcohol for the formation of hard plastics[3]; (6) transfusing cellulose acetate with benzene (toluene) and ethyl alcohol, then adding dichlorhydrin, acetochlorhydrin or diacetin (glyceryl diacetate) for thermoplastic products[4].

The Internationale Celluloseesterges. precipitate cellulose esters from the original esterifying solution by means of ethyl ether[5], or employ amyl acetate as the precipitant

abst. Chem. Zentr. 1917, **88**, I, 296; Chem. Ztg. 1916, **40**, 1004; Chem. Ztg. Rep. 1917, **41**, 64; Wag. Jahr. 1917, **63**, II, 256; Kunst. 1917, **7**, 24; Zts. ang. Chem. 1917, **30**, II, 19. Aust. P. 47899. Belg. P. 222416, 1910; abst. Chem. Ztg. 1910, **34**, 432. Can. P. 129265, 1910. Swiss P. 52115; abst. Kunst. 1912, **2**, 99.

1. E. P. 4959, 1910; abst. J. S. C. I. 1911, **30**, 19; Chem. Ztg. 1910, **34**, 501. F. P. 413901, 1910; abst. J. S. C. I. 1910, **29**, 1101. D. R. P. 254784, 1909; abst. Kunst. 1913, **3**, 60; 1914, **4**, 37; Wag. Jahr. 1912, **58**, II, 604; Chem. Zentr. 1913, **84**, I, 358; C. A. 1913, **7**, 1111; Chem. Ztg. Rep. 1913, **37**, 12; Zts. ang. Chem. 1912, **25**, 80; Mon. Sci. 1916, **83**, 46. Aust. P. Appl. 2906, 2907, 1910. Aust. P. Appl. 6220, 1910; abst. Kunst. 1912, **2**, 320. Aust. P. 57984; abst. Kunst. 1913, **3**, 218; Chem. Ztg. 1913, **37**, 262.

2. E. P. 27258, 1910; abst. Kunst. 1912, **2**, 34; C. A. 1912, **6**, 1526; Chem. Ztg. 1911, **35**, 982. F. P. 419530, 1910; 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, 1910. Swiss P. 51952, 1910; abst. Chem. Ztg. 1911, **35**, 965.

3. U. S. P. 1185074, 1916; 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, 1910; abst. J. S. C. I. 1911, **30**, 79; Mon. Sci .1913, **79**, 551. D. R. P. 287745, 1910; abst. C. A. 1916, **10**, 2145; Kunst. 1915, **5**, 274; Chem. Zentr. 1915, **86**, II, 864; Chem. Ztg. Rep. 1915, **39**, 422.

4. U. S. P. 1015155, 1912; abst. C. A. 1912, **6**, 684; Chem. Ztg. 1912, **36**, 209; Mon. Sci. 1912, **77**, 163; J. S. C. I. 1912, **31**, 184. D. R. P. 229450, 1909; abst. Chem. Ztg. Rep. 1911, **35**, 88; Mon. Sci. 1916, **83**, 47; Kunst. 1911, **1**, 90. Aust. P. Appl. 6220, 1910; Aust. P. 27258, 1910. Aust. P. 47889, 1910; 47899, 1910; abst. Chem. Ztg. 1911, **35**, 500; Kunst. 1911, **1**, 356. Aust. P. 55514, 1912; abst. Kunst. 1913, **3**, 38. Can. P. 129265, 1910; 139235, 1912. Swiss P. 52437, 1910; abst. Chem. Ztg. 1911, **35**, 1205; Kunst. 1912, **2**, 135.

5. D. R. P. 242289, 1910; Addn. to D. R. P. 163316, 1901; abst. Zts. Chem. Ind. Koll. 1912, **11**, 139; C. A. 1912, **6**, 2170; Chem. Zentr. 1912, **83**, I, 298; Chem. Ind. 1912, **35**, 87; Chem. Ztg. Rep. 1912, **36**, 47; Chem. Zts. 1912, **2**, No. 2798; Kunst. 1913, **3**, 35; Wag. Jahr. 1912, **58**, II, 17; Zts. ang. Chem. 1912, **25**, 286.

for cellulose formate or phosphoformate in the production of plastics[1]. In the preparation of formylcelluloses[2], the cellulose hydrates obtained from the precipitation or decomposition of the cellulose solutions employed in the artificial silk industry have been recommended as an unusually suitable source of the initial cellulosic material[3].

1. D. R. P. 249535, 1910; abst. C. A. 1912, **6**, 3183; Chem. Zentr. 1912, **83**, II, 467; Chem. Ztg. 1912, **36**, 817; Chem. Ztg. Rep. 1912, **36**, 485.

2. D. R. P. 254093, 1910; Addn. to D. R. P. 233589; abst. C. A. 1913, **7**, 1288; Chem. Zentr. 1913, **84**, I, 83; Chem. Ztg. Rep. 1912, **36**, 693; Chem. Ztg. 1912, **36**, 1332; Kunst. 1912, **2**, 420; 1913, **3**, 52; Wag. Jahr. 1912, **58**, II, 18; Zts. ang. Chem. 1913, **26**, 16.

3. Vereinigte Glanzstoff Fabriken, A.-G., D. R. P. 233589, 1909; abst. Mon. Sci. 1913, **78**, 389; Chem. Zentr. 1911, **82**, I, 1333; Chem. Ztg. Rep. 1911, **35**, 230; 1912, **36**, 675; Chem. Ztg. 1912, **36**, 1332; Chem. Zts. 1912, **11**, 2733; Kunst. 1911, **1**, 173; Wag. Jahr. 1911, **57**, II, 421; Zts. ang. Chem. 1911, **24**, 860. E. Bronnert, assignor to Vereinigte Glanzstoff Fabriken, A.-G. (dissolves cellulose hydrate in formic acid), U. S. P. 1061977, 1913; abst. C. A. 1913, **7**, 2471; J. S. C. I. 1913, **32**, 563; Mon. Sci. 1914, **81**, 23; Chem. Ztg. 1913, **37**, 712. Also E. Bronnert and the Vereinigte Glanzstoff Fabriken, E. P. 15700, 1910; abst. C. A. 1911, **5**, 2723; J. S. C. I. 1910, **29**, 1199; J. Soc. Dyers Col. 1910, **26**, 256; Mon. Sci. 1913, **78**, 389, 391; Chem. Ztg. Rep. 1911, **35**, 35; Kunst. 1911, **1**, 75. F. P. 420856, 1910; abst. J. S. C. I. 1911, **30**, 279; Mon. Sci. 1913, **78**, 389, 391; **79**, 113. Vereinigte Glanzstoff Fabriken, D. R. P. 233589, 1909; abst. Mon. Sci. 1913, **78**, 391; Chem. Zentr. 1911, **82**, I, 1333; Chem. Ztg. 1911, **35**, 377; Chem. Ztg. Rep. 1912, **36**, 693; Chem. Zts. 1912, **11** ,2733; Kunst. 1911, **1**, 173; Wag. Jahr. 1911, **57**, II, 421; Zts. ang. Chem. 1911, **24**, 860. Hung. P. Appl. 3096, 1910; abst. Chem. Ztg. 1911, **35**, 35. Aust. P. Anm. 5148, 1910; abst. Mon. Sci. 1913, **78**, 389; 2275, 1911; abst. Chem. Ztg. 1913, **37**, 481. Aust. P. 57421; abst. Kunst. 1913, **3**, 218. Belg. P. 229046, 1910; 234433, 1911. E. Bronnert dissolves waste from artificial silk manufacture in formic acid only, Can. P. 133197, 1911; abst. C. A. 1911, **5**, 2909. E. Bronnert and Vereinigte Glanzstoff Fabriken, U. S. P. 1046729, 1912; abst. C. A. 1913, **7**, 700; J. S. C. I. 1913, **32**, 19; Mon. Sci. 1913, **78**, 107; Chem. Ztg. 1913, **37**, 200. D. R. P. 274550, 1912; abst .Chem. Zentr. 1914, **85**, I, 2128; Chem. Ztg. 1914, **38**, 609; Chem. Ztg. Rep. 1914, **38**, 349; Wag. Jahr. 1914, **60**, I, 337. Addn. 13939, 1911, to F. P. 420856, 1910; abst .J. S. C. I. 1911, **30**, 1050; Chem. Zts. 1911, **35**, 709. E. P. 6241, 1911; abst. C. A. 1912, **6**, 2529; J. S. C. I. 1912, **31**, 279; Chem. Ztg. 1911, **35**, 142; 1912, **36**, 263. Belg. P. 233792, 1911. Aust. P. 60447; abst. Kunst. 1913, **3**, 395. Ital. P. 115772, 1911; abst. Chem. Ztg. 1912, **36**, 1083. Hung. P. Appl. 3306, 1911; abst. Mon. Sci. 1913, **78**, 389, 391; Chem. Ztg. 1911, **35**, 843. Swiss P. 53585, 1910; abst. Mon. Sci. 1913, **78**, 391; Chem. Ztg. 1909, **26**, 223. India P. Appl. 349, 1911. International Cellulose Ester Ges., D. R. P. 254093, 1910; abst. C. A. 1913, **7**, 1288; Chem. Zentr. 1913, **84**, I, 83; Chem. Ztg. Rep. 1912, **36**, 693; Kunst. 1913, **3**, 52; Wag. Jahr. 1912, **58**, II, 18; Zts. ang. Chem. 1913, **26**, 16. E. Bronnert dissolves cellulose in formic and phosphoric acid,

They find lactic acid (see p. 141, n. 3) to be valuable as a

U. S. P. 1055513, 1913; abst. C. A. 1913, **7**, 1608; J. S. C. I. 1913, **32**, 322; Mon. Sci. 1913, **78**, 151; Chem. Ztg. Rep. 1913, **37**, 273. Can. P. 133197, 134164, 1911. Vereinigte Glanzstoff Fabriken, E. P. 29246, 1910; abst. C. A. 1911, **5**, 3340; J. S. C. I. 1911, **30**, 888; Mon. Sci. 1913, **78**, 390; Chem. Ztg. Rep. 1911, **35**, 520; Kunst. 1911, **1**, 417. E. P. 309, 1911; abst. C. A. 1911, **5**, 3157; J. S. C. I. 1911, **30**, 484; J. Soc. Dyers Col. 1911, **27**, 179; Mon. Sci. 1913, **78**, 340. F. P. 423774, 1910; abst. C. A. 1911, **5**, 3340; J. S. C. I. 1911, **30**, 615; Mon. Sci. 1913, **78**, 393; 1913, **79**, 31; Kunst. 1911, **1**, 235. F. P. 424621, 1911; abst. J. S. C. I. 1911, **30**, 741; Mon. Sci. 1913, **78**, 393; 1913, **79**, 18. D. R. P. Anm. V-9653, 1910. Aust. P. Appl. 9782, 1910; abst. Chem. Ztg. 1912, **36**, 478. Aust. P. 54512, 1912; abst. Chem. Ztg. 1912, **36**, 935; Kunst. 1912, **2**, 393. Aust. P. 54819; abst. Kunst. 1912, **2**, 456. Belg. P. 231279, 1910; 231853, 1911. Swiss P. 53777; abst. Kunst. 1912, **2**, 255. Swiss P. 56146, 1911; abst. Chem. Ztg. 1912, **36**, 1197. E. Bronnert, U. S. P. 1153596, 1915; abst. C. A. 1915, **4**, 3129; J. S. C. I. 1915, **34**, 1049; Mon. Sci. 1917, **84**, 28; Kunst. 1919, **9**, 137. In connection with the development of this important series of processes, reference is directed to the following: Vereinigte Glanzstoff-fabriken, D. R. P. 233589, 1909; (abst. Mon. Sci. 1913, **78**, 389; Chem. Zentr. 1911, **82**, I, 1333; Chem. Ztg. Rep. 1911, **35**, 230; Chem. Zts. 1912, **11**, No. 2733; Kunst. 1911, **1**, 173; Wag. Jahr. 1910, **56**, II, 421; Zts. ang. Chem. 1911, **24**, 860) uses the waste obtained from the manufacture of artificial silk for the preparation of cellulose formate. See also D. R. P. 254093. Internationale Celluloseester Ges., D. R. P. 239701, 1910; (abst. C. A. 1912, **6**, 2169; Chem. Zentr. 1911, **82**, II, 1502; Chem. Ztg. Rep. 1911, **35**, 556; Kunst. 1911, **1**, 437; Wag. Jahr. 1911, **57**, II, 552), manufacture a plastic of formylcellulose and lactic acid. D. R. P. 241963, 1910; (abst. C. A. 1912, **6**, 2315; Chem. Ztg. Rep. 1912, **36**, 110) covers the use of cellulose acetate as a filling or covering material for aircraft. D. R. P. 242289, 1910; (abst. C. A. 1912, **6**, 2170; Chem. Zentr. 1912, **83**, I, 298; Chem. Ztg. Rep. 1912, **36**, 47; Chem. Zts. 1912, **11**, No. 2798; Kunst. 1913, **3**, 35; Wag. Jahr. 1912, **58**, II, 17; Zts. ang. Chem. 1912, **25**, 286), separation of cellulose esters from the original esterifying solution by means of ethyl ether. D. R. P. 249535, 1910; (abst. C. A. 1912, **6**, 3183; Chem. Zentr. 1912, **83**, II, 467; Chem. Ztg. Rep. 1912, **36**, 485; Kunst. 1912, **2**, 354); precipitation of a formic acid solution of cellulose formate or phosphoformate by amyl acetate. See also Neues Erfindungen und Erfahrungen, 1913, **40**, 155. (The Vereinigte Glanzstoff-fabriken, E. P. 29246, 1910, precipitates cellulose formate from a methyl acetate solution by means of amyl acetate.) D. R. P. 254093, 1910; Addn. to D. R. P. 235589; (abst. C. A. 1913, **7**, 1288; Chem. Zentr. 1913, **84**, I, 83; Chem. Ztg. Rep. 1912, **36**, 693; Kunst. 1913, **3**, 55; Wag. Jahr. 1912, **58**, II, 18; Zts. ang. Chem. 1913, **26**, II, 16) covers the use of cellulose hydrates obtained by the precipitation or decomposition of such cellulose solutions as are used in the artificial silk industry. D. R. P. 260984, 1912; (abst. C. A. 1913, **7**, 3228; J. S. C. I. 1913, **32**, 748; Chem. Zentr. 1913, **84**, II, 190; Chem. Ztg. Rep. 1913, **37**, 388; Kunst. 1913, **3**, 273; Wag. Jahr. 1913, **59**, II, 16; Zts. ang. Chem. 1913, **26**, II, 406): preparation of cellulose acetate solutions by diluting the original esterifying bath by means of acetone, ethyl acetate and dichlorethylene; the acetic acid being neutralized with carbonates. D. R. P. 265852, 1913; (abst. C. A. 1914,

solvent[1]. Whereas above in this paragraph is mentioned the use of amyl acetate as a cellulose formate precipitant from a formic acid solution, the Vereinigte Glanzstoff Fab.[2] use amyl acetate for this purpose, the formic ester being

8, 573; J. S. C. I. 1913, **32**, 1104; Chem. Zentr. 1913, **84**, II, 1635; Chem. Ztg. Rep. 1913, **37**, 645; Chem. Zts. 1914, **13**, No. 3348; Wag. Jahr. 1913, **59**, II, 447; Zts. ang. Chem. 1913, **26**, II, 700); manufacture of cellulose formate solutions by means of mono or polyhydric phenols. D. R. P. 265911, 1913; (abst. C. A. 1914, **8**, 573; J. S. C. I. 1913, **32**, 1104; Chem. Zentr. 1913, **84**, II, 1635; Chem. Ztg. Rep. 1913, **37**, 645; Chem. Zts. 1914, **13**, No. 3351; Kunst. 1913, **3**, 474; Wag. Jahr. 1913, **59**, II, 447; Zts. ang. Chem. 1913, **26**, II, 700): manufacture of cellulose formate solutions, using chloral hydrate or chloral alkyloxide (alcoholate) as solvents; (See also D. R. P. 265852). D. R. P. 266600, 1912; (abst. C. A. 1914, **8**, 573; Chem. Zentr. 1913, **84**, II, 1834; Chem. Ztg. Rep. 1913, **37**, 645; Chem. Zts. 1914, **13**, No. 3408; Wag. Jahr. 1913, **59**, II, 447): use of, as cellulose formate solvents, alkali iodides and bromides, calcium chloride, ammonium nitrate; alkaline earth and metallic nitrates, cupric chloride; alkali xanthates or alkali salts of aromatic mono- or poly-sulfonic acids. D. R. P. 267557, 1913; Addn. to D. R. P. 266600; (abst. C. A. 1914, **8**, 822; Chem. Zentr. 1914, **85**, I, 206; Chem. Ztg. Rep. 1913, **37**, 684; Chem. Zts. 1914, **13**, No. 3509; Kunst. 1914, **4**, 75; Wag. Jahr. 1913, **59**, II, 447; Zts. ang. Chem. 1914, **27**, II, 56): use of ammonium bichromate as a cellulose formate solvent. D. R. P. 277529, 1909; (abst. Chem. Zentr. 1914, **85**, II, 856; Chem. Ztg. Rep. 1914, **38**, 501; Kunst. 1914, **4**, 335; Wag. Jahr. 1914, **60**, II, 416; Zts. ang. Chem. 1914, **27**, II, 604; C. A. 1915, **9**, 862): use of resorcinol diacetate as a softener of cellulose acetate. (L. Lederer—E. P. 8945, 1909; F. P. 402083—has patented the same thing.) D. R. P. 300908, 1917; (abst. Chem. Zentr. 1917, **88**, II, 716; Chem. Ztg. Rep. 1918, **42**, 36; Wag. Jahr. 1917, **63**, II, 263; Zts. ang. Chem. 1917, **30**, II, 348) covers the manufacture of patent leather with the employment of cellulose acetate lacquers.

1. International Cellulose Ester Ges., D. R. P. 239701, 1910; abst. C. A. 1912, **6**, 2169; Mon. Sci. 1913, **78**, 393; Chem. Zentr. 1911, **82**, II, 1502; Chem. Ztg. 1911, **35**, 1114; Chem. Ztg. 1911, **35**, 1114; Chem. Ztg. Rep. 1911, **35**, 556; Kunst. 1911, **1**, 437; Wag. Jahr. 1911, **57**, II, 552. E. Bronnert, assignor to Vereinigte Glanzstoff Fabriken, U. S. P. 1029341, 1912; abst. C. A. 1912, **6**, 2528; J. S. C. I. 1912, **31**, 637; Mon. Sci. 1912, **77**, 164; 1913, **78**, 393. Vereinigte Glanzstoff Fabriken, E. P. 8313, 1911; abst. C. A. 1912, **6**, 3018; J. S. C. I. 1911, **30**, 1050; Mon. Sci. 1913, **78**, 393; Chem. Ztg. Rep. 1911, **35**, 556; 1912, **36**, 532. F. P. 428069, 1911; abst. J. S. C. I. 1911, **30**, 1156; Mon. Sci. 1913, **78**, 393; **79**, 124; Chem. Ztg. 1911, **35**, 809; Kunst. 1911, **1**, 398. Aust. P. Appl. 2994, 1911; abst. Chem. Ztg. 1912, **36**, 1242. Aust. P. 57421, 1912. Belg. P. 234433, 1911; abst. Mon. Sci. 1913, **78**, 389; Chem. Ztg. 1911, **35**, 790. Swiss P. 53777, 1910; abst. Kunst. 1912, **2**, 255; Chem. Ztg. 1912, **36**, 327. Swiss P. 55942, 1911.

2. E. P. 29246, 1910; abst. C. A. 1911, **5**, 3340; J. S. C. I. 1911, **30**, 888; Mon. Sci. 1913, **78**, 390; Chem. Ztg. Rep. 1911, **35**, 520; Kunst. 1911, **1**, 417.

dissolved in methyl formate. The Farbenfabriken[1] prepare cellulose formates by means of sulfuryl chloride or chlorosulfonic acid, the reaction being facilitated by the presence of zinc chloride.

In this same year (1910) appeared the first of the numerous W. Lindsay patents in the cellulose ester field, benzyl benzoate and ethyl alcohol being specified as an advantageous cellulose ester solvent[2]. B. Borzykowski[3] disclosed his method for the manufacture of a glass substitute from acetylcellulose sheets, and for the production of artificial bristles from the same material[4].

In the dyeing of cellulose acetate two additional methods were proposed by A. Sansone[5] and by the Farben-

1. E. P. 24980, 1910; abst. J. S. C. I. 1911, **30**, 1112; J. Soc. Dyers Col. 1911, **27**, 241; Mon. Sci. 1913, **78**, 391. F. P. 422542, 1910; abst. C. A. 1912, **6**, 1990; J. S. C. I. 1911, **30**, 532, 1112; Mon. Sci. 1913, **79**, 116; Chem. Ztg. 1911, **35**, 233; Chem. Ztg. Rep. 1911, **35**, 250. D. R. P. 237765, 237766, 1909; abst. C. A. 1912, **6**, 1672; Mon. Sci. 1913, **78**, 390; Chem. Zentr. 1911, **82**, 1079; Chem. Ztg. 1911, **35**, 866; Chem. Ztg. Rep. 1911, **35**, 520; Chem. Zts. 1912, **11**, 2745; Wag. Jahr. 1911, **57**, II, 420; Zts. ang. Chem. 1911, **24**, 2084. Aust. P. Appl. A-8776, 1910; abst. Mon. Sci. 1913, **78**, 391. U. S. P. 1093247, 1914; abst. C. A. 1914, **8**, 2060; J. S. C. I. 1914, **33**, 546; Mon. Sci. 1914, **81**, 146; Kunst. 1914, **4**, 379; Chem. Ztg. 1914, **38**, 608. It will be remembered that this firm in 1909 patented the use of sulfuryl chloride (D. R. P. 237765) and chlorosulfonic acid (D. R. P. 237766) for the manufacture of cellulose acetate.

2. U. S. P. 961360, 1910; abst. C. A. 1910, **4**, 2581; J. S. C. I. 1910, **29**, 875; 1911, **30**, 279; Mon. Sci. 1910, **73**, 135; 1913, **78**, 392; Kunst. 1911, **1**, 235. E. P. 13692, 1910; abst. C. A. 1911, **5**, 2952; J. S. C. I. 1911, **30**, 279; Mon. Sci. 1913, **78**, 392; Chem. Ztg. Rep. 1911, **35**, 199. F. P. 416843, 1910; abst. Kunst. 1911, **1**, 73. D. R. P. Anm. L. 30386, 1910. Ital. P. 120751, 136231, 136232.

3. E. P. 21719, 1910; abst. C. A. 1912, **6**, 1510; J. S. C. I. 1911, **30**, 1213; Kunst. 1912, **2**, 76. F. P. 420555, 1910; abst J. S. C. I. 1911, **30**, 363; Kunst. 1911, **1**, 156. F. P. 420745, 1910; abst. J. S. C. I. 1911, **30**, 363, 1213. Belg. P. 229404. Span. P. 48887. Swiss P. 54146. Hung. P. 55647. Ital. P. 112260.

4. U. S. P. 1010222, 1911; abst. C. A. 1912, **6**, 414; J. S. C. I. 1912, **31**, 24; E. P. 30398, 1910; abst. J. S. C. I. 1913, **32**, 597. F. P. 424428, 1910; abst. J. S. C. I. 1911, **30**, 740; Kunst. 1911, **1**, 339. Belg. P. 232255. Ital. P. 115139. Swiss P. 56107. Span. P. 49719.

5. D. R. P. Anm. S-31390, 1910; abst. Chem. Ztg. 1911, **35**, 534. This patent was refused.

fabriken vorm. F. Bayer & Co.[1] In the latter, the cellulose is dyed before acidylation by means of such dyestuffs as the indanthrenes which are unaffected by the esterizing bath.

In 1910 appeared the first of the multitude of Dreyfus patents which in their entirety cover the whole field of cellulose acetate formation and including the preparation of acetic anhydride, acetaldehyde and synthetic acetic acid. C. Dreyfus[2] described a method for acetation of cellulose at low temperatures in the presence of ethylsulfuric acid as catalyst, while H. Dreyfus advocated the employment of lead chamber crystals for the same purpose[3], the product obtained being applied to the manufacture of artificial silk[4].

In advancement along lines of endeavoring to produce a satisfactory cellulose acetate plastic, J. Aylsworth[5] introduced the methyl, ethyl, butyl or amyl esters of chlorinated stearic, myristic or palmitic acids, of especial value when applied to the production of photograph sound rec-

1. E. Friedman, Assignor to F. Bayer & Co., U. S. P. 994738, 1911; abst. C. A. 1911, **5**, 2726; J. S. C. I. 1911, **30**, 888, 1051; J. Soc. Dyers Col. 1911, **27**, 206; Mon. Sci. 1912, **77**, 31; 1913, **78**, 390; Chem. Ztg. 1911, **35**, 809; Chem. Ztg. Rep. 1911, **35**, 538. E. P. 1556, 1911; abst. C. A. 1912, **6**, 1853; J. S. C. I. 1911, **30**, 1236, 1309; J. Soc. Dyers Col. 1911, **27**, 73, 302, 312; Mon. Sci. 1913, **78**, 390. F. P. 427445, 1911; abst. J. S. C. I. 1911, **30**, 1051; Mon. Sci. 1913, **79**, 19; Chem. Ztg. 1911, **35**, 709. D. R. P. Anm. F-29595, 1910; abst. Chem. Ztg. 1911, **35**, 474. D. R. P. 237210, 1910; abst. C. A. 1912, **6**, 1536; Mon. Sci. 1913, **78**, 390; Chem. Zentr. 1911, **82**, II, 497; Chem. Ind. 1911, **34**, 535; Chem. Ztg. 1911, **35**, 818; Chem. Ztg. Rep. 1911, **35**, 455; Kunst. 1911, **1**, 338; Wag. Jahr. 1911, **57**, II, 468; Zts. ang. Chem. 1911, **24**, 1837. Belg. P. 233876, 1911; abst. Chem. Ztg. 1911, **36**, 699. Aust. P. Appl. A-2376, 1911; abst. Chem. Ztg. 1912, **36**, 252.

2. D. R. P. Anm. D-23457, 1910; abst. Chem. Ztg. 1911, **35**, 930; Kunst. 1921, **11**, 4.

3. F. P. 413671, 1910; abst. J. S. C. I. 1910, **29**, 1101; Mon. Sci. 1913, **79**, 78; Chem. Ztg. 1910, **34**, 487, 786; Chem. Ztg. Rep. 1910, **34**, 250; Kunst. 1911, **1**, 58. D. R. P. Anm. D-24819, 1911; abst. Chem. Ztg. 1911, **35**, 1234; Kunst. 1921, **11**, 4.

4. H. Dreyfus and L. Schneeberger, F. P. 413787, 1910; abst. J. S. C. I. 1910, **29**, 1101; Mon .Sci. 1911, **75**, 155; Kunst. 1911, **1**, 34.

5. U. S. P. 962877, 1910; abst. C. A. 1910, **4**, 2570; J. S. C. I. 1910, **29**, 940; Mon. Sci. 1911, **75**, 11; 1913, **78**, 393; Kunst. 1911, **1**, 235. See U. S. P. 855556, 1907.

ords[1]. The W. Merckens and H. Manissadjian uninflammable plastic[2] depends upon the use of the phenol, cresol and naphthol esters of phosphoric, thiophosphoric and sulfoacetic acids, while that of the Compagnie Francaise du Celluloid[3] combines monoacetylethylaniline also with cellulose acetate, or the above in which acetyl has been replaced by propionyl, butyryl or valeryl radicles, and ethyl has been replaced by methyl, propyl, butyl or amyl. In another method for plastic formation also disclosed this same year (1910)[4], acetylcellulose in tetrachlorethane and caoutchouc dissolved in ethylene dichloride are combined for the manufacture of combs.

In new methods of manufacturing cellulose acetate which were disclosed, that of the Chemische Fabrik von

1. J. Aylsworth, U. S. P. 953454, 1910; abst. C. A. 1910, **4**, 1530.

2. F. P. 413657, 1910; abst. J. S. C. I. 1910, **29**, 1101, 1199; Mon. Sci. 1912, **77**, 8; Chem. Ztg. 1910, **34**, 786; Kunst. 1911, **1**, 57. Belg. P. 223996, 1910; abst. Chem. Ztg. 1910, **34**, 842. Aust. P. Appl. A-2118, 1910. Aust. P. 47244, 47679, 1910; abst. Kunst. 1911, **1**, 235, 256. E. P. 6608, 1910; (patent not granted) abst. Chem. Ztg. 1910, **34**, 432, specifies triphenyl phosphate, naphthyl phosphate and cresyl phosphate. F. P. 413657, 413658, 1910; abst. J. S. C. I. 1910, **29**, 1101, 1134; Mon. Sci. 1912, **77**, 8; Kunst. 1911, **1**, 57, 58. F. P. 413658 covers the use of sulfacetic esters only. E. P. 8646, 8647, 1910; abst. C. A. 1911, **5**, 3156; J. S.C. I. 1911, **30**, 533, 616; Mon. Sci. 1916, **83**, 47; Chem. Ztg. 1910, **34**, 501; Chem. Ztg. Rep. 1911, **35**, 307; Kunst. 1911, **1**, 316. E. P. 8646, 1910, is the same as F. P. 414679, covering sulfacetates and phosphates of cellulose with the esters of phenols, cresols or naphthols. E. P. 8647, 1910, is the same as F. P. 414680, covers cellulose acetate and a cellulose ester of different radical from acetic acid with esters of phenols, cresols or naphthols. F. P. 414679, 414680, 1910; abst. J. S. C. I. 1910, **29** ,1199, 1228; 1911, **30**, 533, 616; Mon. Sci. 1912, **77**, 13; Chem. Ztg. 1910, **34**, 878; Kunst. 1911, **1**, 58, 72. D. R. P. Anm. M-39103, 1909; abst. Chem. Ztg. 1910, **34**, 1266. Belg. P. 223996, 224741, 1910; abst. Chem. Ztg. 1910, **34**, 878. Aust. P. 53109; abst. Kunst. 1912, **2**, 255. Swiss P. 51644, 51910, 51960, 51970, 1910; abst. Chem. Ztg. 1911, **35**, 909, 965; Kunst. 1912, **2**, 77, 99. Aust. P. Appl. A-2858, 1910 .

3. F. P. 427804, 1910; 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, 1911; abst. J. S. C. I. 1912, **31**, 812; Mon. Sci. 1914, **81**, 14; Kunst. 1912, **2**, 355.

4. G. Convert, F. P. 421843, 1910; abst. J. S. C. I. 1911, **30**, 415; Kunst. 1911, **1**, 174.

Heyden[1] depends upon the treatment of cellulose with acetic anhydride in the presence of sulfuryl chloride, pyrosulfuryl chloride or chlorosulfonic acid (see Farbenfabriken, p. 373, n. 7), an alleged improvement on this process[2] being that where sufficient sulfuryl chloride is used the reaction may be caused to take place without warming. In further attempts to replace sulfuric acid as catalyst in cellulose acetation[3], aniline bisulfate or toluidine bisulfate have been recommended for this purpose. However, C. Schwalbe[4] in a careful experimental exposition of the subject, has shown specifically that with phenolsulfonic acid, and with sulfonic acids in general, their catalytic action is due to

1. U. S. P. 1051165, 1913; abst. C. A. 1913, **7**, 889; J. S. C. I. 1913, **32**, 192; Mon. Sci. 1913, **79**, 107; Chem. Ztg. 1913, **37**, 245; Kunst. 1913, **3**, 275. E. P. 24382, 1910; abst. C. A. 1911, **5**, 3157; J. S. C. I. 1911, **30**, 616; Mon. Sci. 1913, **78**, 390; Chem. Ztg. 1911, **35**, 500. F. P. 423197, 1910; abst. C. A. 1912, **6**, 1990; J. S. C. I. 1911, **30**, 615; Mon. Sci. 1913, **78**, 390; **79**, 117; Chem. Ztg. 1911, **35**, 270; Chem. Ztg. Rep. 1911, **35**, 307. D. R. P. 269193, 1909; abst. C. A. 1914, **8**, 2251; Chem. Zentr. 1914, **85**, I, 506; Chem. Ztg. 1914, **38**, 22; Chem. Ztg. Rep. 1914, **38**, 111; Kunst. 1914, **4**, 20, 97; Wag. Jahr. 1914, **60**, II, 16; Zts. ang. Chem. 1914, **27**, 110. Aust. P. Appl. 8062, 1910; 327, 1911; abst. Chem. Ztg. 1912, **36**, 72; Kunst. 1912, **2**, 460. Aust. P. 65834, 1912; abst. Chem. Ztg. 1914, **38**, 847. Swiss P. 54497, 1910; abst. Mon. Sci. 1913, **78**, 390; Chem. Ztg. 1912, **36**, 643. Span. P. 49118, 1910; abst. Chem. Ztg. 1911, **35**, 318. Belg. P. 229995, 1910; abst. Mon. Sci. 1913, **78**, 390; Chem. Ztg. 1911, **35**, 81; Belg. P. 244950, 1912; abst. Kunst. 1912, **2**, 399.

2. D. R. P. 273029, 1910; Addn. to D. R. P. 269193, 1909; abst. C. A. 1914, **8**, 2806; Chem. Zentr. 1914, **85**, I, 1716; Chem. Ztg. Rep. 1914, **38**, 301; Kunst. 1914, **4**, 179, 234; Wag. Jahr. 1914, **60**, II, 16; Zts. ang. Chem. 1914, **27**, 321.

3. O. Bonhoeffer and H. Guntrum (Assigned to F. Bayer & Co.), U. S. P. 987692, 1911; abst. C. A. 1911, **5**, 1994; J. S. C. I. 1911, **30**, 485; Mon. Sci. 1912, **77**, 29; Chem. Ztg. 1911, **35**, 429; Chem. Ztg. Rep. 1911, **35**, 250. F. Bayer & Co., E. P. 14271, 1910; abst. C. A. 1911, **5**, 3156; J. S. C. I. 1911, **30**, 485; Chem. Ztg. 1911, **35**, 377. F. P. 417274, 1910; abst. C. A. 1915, **9**, 2311; J. S. C. I. 1911, **30**, 19, 485; Mon. Sci. 1913, **79**, 84; Chem. Ztg. 1910, **34**, 1026; Chem. Ztg. Rep. 1915, **39**, 77; Addn. 18345, 1913, to F. P. 417274, 1910; abst. C. A. 1915, **9**, 2311; J. S. C. I. 1914, **33**, 478; Chem. Ztg. 1914, **38**, 216; Kunst. 1914, **4**, 235. Aust. P. 50331 ,1911; abst. Chem. Ztg. 1911, **35**, 1070.

4. Zts. ang. Chem. 1910, **23**, 433; abst. C. A. 1910, **4**, 1603; J. C. S. 1910, **88**, i, 224; J. S. C. I. 1910, **29**, 415; Bull. Soc. Chim. 1910, (4), **8**, 694; Chem. Zentr. 1910, **81**, I, 1964; Jahr. Chem. 1910, **63**, I, 648.

the fact that free sulfuric acid is liberated during the course of the reaction.

H. Danzer[1] ripens the acetated cellulose by a "special" process of hydrolysis characterized by a chemical reaction which produces water. He esterifies ethyl alcohol with acetic acid, and uses the water given off in the course of the reaction. It would appear that ordinary tap water ought to be cheaper, and is certainly equally efficient for the purpose. He[2] prepares cinematographic bands and films and renders them impermeable to water by superficially acetylating or nitrating them.

In the waterproofing of linen, H. Peters employs "sodium casein" and then dips the fabric in a cellulose acetate lacquer[3], or[4], dissolves the cellulose ester directly in methylated ether and amyl alcohol and applies to the collar or cuff. W. Doerflinger[5] described the usefulness of diacetone alcohol as a cellulose acetate solvent, this being one of the comparatively few liquids which are efficient in their dissolving power for both cellulose acetate and nitrate[6].

1. F. P. 428554, 1910; abst. C. A. 1912, **6**, 2169; J. S. C. I. 1911, **30**, 1155; Mon. Sci. 1913, **79**, 125; Chem. Ztg. 1911, **35**, 902; Chem. Ztg. Rep. 1911, **35**, 576.

2. E. P. 3603, 1910; abst. J. S. C. I. 1910, **29**, 978.

3. E. P. 870, 1910; abst. C. A. 1911, **5**, 2980; J. S. C. I. 1911, **30**, 206. F. P. 420127, 1910; abst. J. S. C. I. 1911, **30**, 280; Mon. Sci. 1913, **79**, 21.

4. E. P. 14293, 1910; abst. C. A. 1911, **5**, 3347; J. S. C. I. 1911, **30**, 1171.

5. U. S. P. 1003438, 1911; abst. C. A. 1911, **5**, 3922; J. S. C. I. 1911, **30**, 1398; Mon. Sci. 1913, **78**, 392. E. P. 11728, 1911; abst. C. A. 1912, **6**, 3183; J. S. C. I. 1911, **30**, 1447; J. Soc. Dyers Col. 1912, **28**, 39; Mon. Sci. 1913, **78**, 392; Chem. Ztg. 1911, **35**, 1349. F. P. 429754, 1911; abst. J. S. C. I. 1911, **30**, 1398; Mon. Sci. 1913, **78**, 392. D. R. P. Anm. D-23476, 1910; abst. Chem. Ztg. 1912, **36**, 152. D. R. P. 246967, 1910; abst. C. A. 1912, **6**, 2529; Mon. Sci. 1913, **78**, 392; Chem. Zentr. 1912, **83**, I, 1938; Chem. Ind. 1912, **35**, 57; Chem. Ztg. 1912, **36**, 42; Chem. Ztg. Rep. 1912, **36**, 332; Kunst. 1916, **6**, 113; Wag. Jahr. 1912, **58**, II, 603; Zts. ang. Chem. 1912, **25**, 1550. Can. P. 136538, 1911; abst. C. A. 1912, **6**, 303; J. S. C. I. 1911, **30**, 1398; Mon. Sci. 1912, **77**, 160; 1913, **78**, 392.

6. Technology of Cellulose Esters, 1921, **1**, IV, 2382, 2401.

In advancement in acetate film formation should be mentioned the disclosures of Knoll & Co.[1] and C. Mijnssen[2]. In the process of the former the cellulose ester is used directly from the esterifying bath without previous precipitation, while in the latter the films are produced by successively depositing layers of acetylcellulose one upon the other, phenol being a useful addition. C. Schwalbe proposed to overcome the tendency of cylinders for drying paper to rust by the application thereto of an acetylcellulose solution such as Cellit[3].

In the preparation of acetate lacquers and varnishes, Leduc, Heitz & Co.[4] recommend dilute acetone solutions with a mixture of alcohol and benzene to which a small amount of *b*-naphthol or hexachlorethane is added, the preparation being intended primarily for the coating of balloon fabrics. Another lacquer designed for a similar purpose[5] combines caoutchouc with cellulose acetate and is said to greatly minimize the permeability of the fabric by hydro-

1. E. P. 3559, 1910; abst. Chem. Ztg. 1910, **34**, 889; J. S. C. I. 1910, **29**, 1082. F. P. 412503, 1910; abst. J. S. C. I. 1910, **29**, 1038; Chem. Ztg. 1910, **34**, 589; Phot. Ind. 1910, 509; Eder's Jahr. Phot. 1911, 498; Kunst. 1911, **1**, 57. D. R. P. Anm. K-48996, 1911; abst. Kunst. 1912, **2**, 379; Chem. Ztg. 1912, **34**, 1174.

2. U. S. P. 1005454, 1911; abst. J. S. C. I. 1911, **30**, 1249; C. A. 1912, **6**, 153. E. P. 476, 1910; abst. J. S. C. I. 1910, **29**, 1082; Mon. Sci. 1913, **78**, 392. F. P. 411298, 1910; abst. J. S. C. I. 1910, **29**, 978; Phot. Ind. 1910, 1221; Eder's Jahr. Phot. 1911, 526; Mon. Sci. 1913, **78**, 392. D. R. P. Anm. dated Jan. 9, 1909. Aust. P. Appl. 9777, 1909. Aust. P. 50656; abst. Kunst. 1912, **2**, 77. Belg. P. 222106, 1910; abst. Chem. Ztg. 1910, **34**, 450; Mon. Sci. 1913, **78**, 392. Hung. P. Appl. M-3691, 1909. Ital. P. 115776, 1911; abst. Chem. Ztg. 1912, **36**, 817. Swiss P. 51839, 1910; abst. Chem. Ztg. 1911, **35**, 930; Kunst. 1912, **2**, 77; Mon. Sci. 1913, **78**, 392.

3. Chem. Ztg. 1910, **34**, 1351.

4. E. P. 6798, 1911; abst. C. A. 1913, **7**, 3032; J. S. C. I. 1912, **31**, 1026. E. P. 21426, 1911; abst. C. A. 1913, **7**, 1108; J. S. C. I. 1912, **31**, 1027; (no patent granted). F. P. 429788, 1911; abst. J. S. C. I. 1911, **30**, 1267; C. A. 1912, **6**, 2186; Chem. Ztg. Rep. 1912, **36**, 63; Mon. Sci. 1913, **79**, 39; Oil. Paint and Drug Review April 24, 1912. F. P. 431692, 1911, and Addn. 14580, 1911, thereto. F. P. 446627, 1912; abst. Kunst. 1913, **3**, 475; J. S. C. I. 1913, **32**, 132. Belg. P. 229396, 1910; 251795, 1912; 261464, 1913; abst. Chem. Ztg. 1913, **37**, 254; 1914, **38**, 11. D. R. P. Anm. L-32835, 1911; abst. Kunst. 1913, **3**, 100.

5. Soc. Francaise des Tissus Biaises, F. P. 427818, 1910, and Addn. 14044 thereto; abst. Kunst. 1911, **1**, 455.

gen. The R. Weeber coating composition comprises alternate layers of varnish and acetylcellulose in conjunction with finely powdered wood meal[1].

In connection with explosives, C. van Pittius[2] has proposed to combine dinitroacetinglycerol, trinitrotoluene, acetylcellulose and nitrocellulose, while H. Mork[3] described the uses of methyl formate as a cellulose acetate solvent. A study of acetylation with sulfuric acid and acetic anhydride was made by J. Blanksma[4], and C. Schwalbe[5] critically reviewed the art up to this time, as did F. Beltzer[6]. The appearance of the inaugural dissertation of W. Cross on the acetyl groups in lignin[7] closed the contributions on the uninflammable cellulose esters of 1910, the fifty-five references to processes and products given in the foregoing resume indicating the breadth of advancement of the art at this time.

The succeeding year (1911) was fully as prolific in contributions—both patent and literary—as the preceding

1. E. P. 951, 1910.
2. E. P. 25274, 1910; abst. J. S. C. I. 1911, **30**, 1281; C. A. 1912, **6**, 1527.
3. U. S. P. 972464, 1910; abst. C. A. 1911, **5**, 197; J. S. C. I. 1911, **30**, 1245; Mon. Sci. 1911, **75**, 12; 1913, **78**, 392; Chem. Ztg. 1910, **34**, 1230; Chem. Ztg. Rep. 1911, **35**, 152; Kunst. 1911, **1**, 174. E. P. 20672, 1910; abst. C. A. 1911, **5**, 2947; J. S. C. I. 1911, **30**, 354; Chem. Ztg. 1911, **35**, 218.
4. Chem. Weekblad, 1909, **6**, 717; abst. C. A. 1910, **4**, 752; J. C. S. 1909, **96**, i, 779; Rep. Chim. 1910, **10**, 38; Chem. Zentr. 1909, **80**, II, 1219; Jahr. Chem. 1909, **62**, II, 494; Meyer Jahr. Chem. 1909, **19**, 240.
5. Zts. ang. Chem. 1910, **23**, 433; 1911, **24**, 1256; abst. C. A. 1910, **4**, 1603; 1911, **5**, 3154; J. C. S. 1910, **98**, i, 224; 1911, **100**, i, 712; J. S. C. I. 1910, **29**, 415; 1911, **30**, 948; Bull. Soc. Chim. 1910, **8**, 694; Chem. Zentr. 1910, **81**, I, 1964; 1911, **82**, II, 670; Chem. Ztg. Rep. 1910, **34**, 180; 1911, **35**, 369; Jahr. Chem. 1910, **63**, I, 648; Kunst. 1911, **1**, 452.
6. Rev. Chim. 1906, **9**, 421; abst. C. A. 1907, **1**, 640; Chem. Zentr. 1907, **78**, I, 853; Jahr. Chem. 1905-8, II, 983, 990; Zts. ang. Chem. 1907, **20**, 1537. Mon. Sci. 1910, **72**, 145; abst. C. A. 1910, **4**, 1238; Chem. Zentr. 1910, **81**, II, 509; Jahr. Chem. 1910, II, 428; Zts. ang. Chem. 1911, **24**, 1456; Zts. Kolloid. 1911, **8**, 177.
7. Dissertation, Göttingen, 1910. Ber. 1910, **43**, 1526; J. S. C. I. 1910, **29**, 750. See also W. Cross and B. Tollens, J. Landw. 1911, **59**, 185; abst. Chem. Zentr. 1911, **82**, II, 970; C. A. 1912, **6**, 2599; Zts. ang. Chem. 1911, **24**, 1660.

twelve month period, and contains many advancements of a noteworthy character. C. Dreyfus[1] described the advantages of the use of ethylsulfuric acid as catalyst, and A. Wohl[2] those of methyl formate as solvent for formyl-, acetyl-, and nitro-celluloses.

H. Dreyfus on July 5, 1911, deposited with the French government a communication[3] which later issued in patent form, which, with the eight additions thereto[4] and the nearly 100 corresponding patents in other countries[5], in their

1. F. P. 430606, 1911; abst. J. S. C. I. 1911, **30**, 1375; Mon. Sci. 1913, **78**, 390, 391, 551; **79**, 127; Chem. Ztg. 1911, **35**, 1001. D. R. P. Anm. June 8, 1910 (withdrawn).

2. E. P. 3139, 1911; abst. C. A. 1911, **5**, 3340; J. S. C. I. 1911, **30**, 888; Chem. Ztg. 1911, **35**, 843; Chem. Ztg. Rep. 1911, **35**, 520. F. P. 425900, 1911; abst. J. S. C. I. 1911, **30**, 951; Mon. Sci. 1913, **79**, 121; Chem. Ztg. 1911, **35**, 553; Kunst. 1911, **1**, 295. D. R. P. 246651, 1910; abst. C. A. 1912, **6**, 2529; Chem. Zentr. 1912, **83**, I, 1742; Chem. Ztg. Rep. 1912, **36**, 332; Kunst. 1912, **2**, 232; Wag. Jahr. 1912, **58**, II, 445; Zts. ang. Chem. 1912, **25**, 1549. Belg. P. 232699, 1911. Hung. P. Appl. W-2966, 1911; abst. Chem. Ztg. 1911, **35**, 510. F. P. 435742, 1912; abst. J. S. C. I. 1912, **31**, 329; Mon. Sci. 1913, **78**, 133.

3. F. P. 432046, 1911; abst. J. S. C. I. 1912, **31**, 24; Chem. Ztg. 1912, **36**, 141. See also F. P. 478023, 1914. Knoll & Co. (Ital. P. 124854) described a method for cellulose acetate manufacture the ester being insoluble in acetic acid and in chloroform. If this is so, then he must have produced a fibrous cellulose acetate. A. Eichengruen (Ital. P. 122428) disclosed his method for preparing celluloid substituted with acetylcellulose. L. Lederer (Ital. P. 130002) a method of separating cellulose esters from their esterizing solution. For pentachlorethane manufacture, see Salzbergwerke Neustassfurt, Ital. P. 122600, and acetic acid manufacture, Chemische Fabrik Griesheim Elektron, Ital. P. 123252.

4. F. P. Addn. 14558, 1911; abst. J. S. C. I. 1912, **31**, 225. F. P. Addn. 14559, 1911. F. P. Addn. 14783, 1911; abst. J. S. C. I. 1912, **31**, 329. F. P. Addn. 15894, 1912; abst. Kunst. 1913, **3**, 434. F. P. Addn. 15933, 1912; abst. Kunst. 1913, **3**, 435. F. P. Addn. 16316, 1912; abst. J. S. C. I. 1913, **32**, 283; Kunst. 1913, **3**, 435. F. P. Addn. 16494, 1912; abst. J. S. C. I. 1913, **32**, 420. (all 7 to F. P. 432046, 1911). F. P. 461544, 1913; abst. C. A. 1914, **8**, 3859; J. S. C. I. 1914, **33**, 196; Chem. Ztg. Rep. 1914, **38**, 349; Kunst. 1914, **4**, 137.

5. U. S. P. 1181857, 1916; abst. C. A. 1916, **10**, 1790; J. S. C. I. 1916, **35**, 686; Mon. Sci. 1917, **84**, 29; Chem. Ztg. 1916, **40**, 659. U. S. P. Re-14338, 1917 (of U. S. P. 1181857, 1916); abst. C. A. 1917, **11**, 2610; J. S. C. I. 1917, **36**, 1004. E. P. 20977, 1911; abst. C. A. 1913, **7**, 891; J. S. C. I. 1913, **32**, 133; Chem. Ztg. 1913, **37**, 200; Chem. Ztg. Rep. 1913, **37**, 287; Kunst. 1913, **3**, 194. Aust. P. Appl. Mar. 9, 1911. Belg. P. 241250, 1911; abst. Mon. Sci. 1913, **78**, 392; Chem. Ztg. 1912, **36**, 338, 975; Kunst. 1912, **2**, 399. Belg. P. 246250, 246251, 1912. Can. P. 155724, 1914; abst. C. A. 1914, **8**, 2947. D. R. P. Anm. D-25442, 1911 (withdrawn); abst. Chem. Ztg. 1913, **37**, 1186;

entirety constitute an advancement of the first magnitude in importance in the manufacture of cellulose acetates. By modifying the proportion of constituents in the normal esterizing bath, Dreyfus demonstrated that a whole series of acetated celluloses could be prepared, analytically indistinguishable as to percentage composition, but possessing varied solubilities in different reagents depending upon the method of procedure in acetylation and subsequent partial hydrolysis or hydration.

He described methods whereby esters are obtained which are insoluble or sparingly soluble in chloroform, but readily soluble in a mixture of alcohol and chloroform or alcohol and tetrachlorethane, or alcohol and benzene, and laid down definite methods of procedure whereby these different classes of cellulose esters may be obtained. He it was who emphasized the fact that in artificial filament and film formation, high viscosity and high tensile strength, elasticity and resiliency are complimentary in an acetated cellulose, and showed that these valuable properties may be obtained by a minimum depolymerization of the cellulose preceding, coincident with, or subsequent to, the normal acetylation process.

In improvements in the manufacture of celluloid and similar compositions, H. Dreyfus combines cellulose acetate with tetrachlorethane, pentachlorethane, and di-, and trichlorethylene[1]. In another patent with its six additions,

Kunst. 1921, **11**, 4. Hung. P. Appl. D-2145, 1912; abst. Chem. Ztg. 1914, **38**, 608. Ital. P. 126542, 148762, 151294. Port. P. 8348, 1912; abst. Chem. Ztg. 1912, **36**, 1442. Swiss P. 67113, 1911; abst. Chem. Ztg. 1914, **38**, 1176; Kunst. 1915, **5**, 57, 95; Zts. ang. Chem. 1916, **29**, I, 51. Swiss P. 68001; abst. Kunst. 1915, **5**, 131. Swiss P. 78274; abst. Kunst. 1919, **9**, 67.

1. U. S. P. 1181858, 1916 abst. C. A. 1916, **10**, 1789; J. S. C. I. 1916, **35**, 686 Mon. Sci. 1917, **84**, 29; Chem. Ztg. 1916, **40**, 659. U. S. P. 1242783, 1917; abst. C. A. 1918, **12**, 224; J. S. C. I. 1917, **36**, 1232; Mon. Sci. 1918, **85**, 36. E. P. 20976, 1911; abst. C. A. 1913, **7**, 890; J. S. C. I. 1913, **32**, 810; Chem. Ztg. 1913, **37**, 163; Chem. Ztg. Rep. 1913, **37**, 890; Kunst. 1913, **3**, 175. F. P. 432047, 1911;

are specified a series of plastic-inducing bodies[1] of especial applicability in conjunction with cellulose acetate, and including methylal, trichlorphenol, benzyl benzoate, phenyl, cresyl and naphthyl acetates; mono-, di-, and tri-acetin; toluenesulfonic esters, chloral hydrate, chlorbenzene, dichlorbenzene, chlor- and dichlor-toluene, trichlorbenzene, chlornaphthalenes, benzyl chloride, chlornitrobenzene, dichlornitrobenzene, phenyl bromide, nitronaphthalin, resorcin, pyrocatechin, phenetol, cresol methyl or ethyl ethers, naphthol methyl or ethyl ethers, benzylethyl ether, benzylmethyl ether, benzyl ether (dibenzyl ether), veratrol, pyrocatechin dimethyl ether, safrol, *iso*-safrol, chlorphenetol, dichlorphenetol, nitroanisol, chlornitroanisol, monochloride and monobromide of camphor, acetophenone, benzophenone, dichloracetone, benzyl alcohol, chlorbenzyl alcohol, benzhydrol, diphenylcarbinol, amidophenol, manol, and similar compounds[2]. This patents with its numerous additions constitutes an unusually comprehensive survey of the various high boilers and plasticizers of possible applicability with the cellulose acetates.

abst. J. S. C. I. 1912, **31**, 24; Mon. Sci. 1913, **78**, 392; **79**, 40; Chem. Ztg. 1912, **36**, 141; Kunst. 1912, **2**, 76, 415. F. P. Addns. 15719, 1912; 19679, 1916, to F. P. 432047. Belg. P. 241252, 1911; abst. Mon. Sci. 1913, **78**, 392; Chem. Ztg. 1912, **36**, 350. F. P. Addn. 16854, 1912, to F. P. 432264, 1911; abst. C. A. 1913, **7**, 3414; J. S. C. I. 1913, **32**, 652; Chem. Ztg. 1913, **37**, 537; Kunst. 1913, **3**, 258. D. R. P. Anm. D-29439, 1913 (withdrawn); abst. Chem. Ztg. 1913, **37**, 1406; Kunst. 1913, **3**, 439; 1921, **11**, 4. Swiss P. 63584, 1911; abst. C. A. 1914, **8**, 2252; Chem. Ztg. 1914, **38**, 106; Kunst. 1914, **4**, 216.

1. F. P. 432264, 1911; 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; Kunst. 1914, **8**, 370.

2. F. P. Addns. 16854, 1912; abst. Kunst. 1913, **3**, 258; 19678, 1913; 19680, 1914; 19685, 1914; 19687, 1914; abst. Kunst. 1918, **8**, 95; 20264, 1915, all to F. P. 432264.

In a modification of a previous process[1], the Farbenfabriken[2] described methods for preparing alcoholic acetylcellulose solutions by dissolving the cellulose ester in the presence of thiocyanates or the chlorides of zinc, tin or antimony with ethyl alcohol, a clear solution being obtained. The A. Wohl process for recovering volatile solvents from cellulose esters was disclosed in this year (1911), whereby the vapors to be recovered are led over the solid cellulose ester and thereby again absorbed[3].

The Societe Chimique des Usines du Rhone[4] have described a method of acetylating by means of acetic anhy-

1. D. R. P. 256922, 1911; abst. C. A. 1913, **7**, 2116; J. S. C. I. 1913, **32**, 530; Chem. Zentr. 1913, **84**, I, 1156; Chem. Ztg. Rep. 1913, **37**, 144; Kunst. 1913, **3**, 213; 1916, **6**, 113; Wag. Jahr. 1913, **59**, II, 585; Zts. ang. Chem. 1913, **26**, II, 290.

2. D. R. P. 268627, 1911 (Addn. to D. R. P. 256922); abst. C. A. 1914, **8**, 2060; Chem. Zentr. 1914, **85**, I, 317; Chem. Ztg. Rep. 1914, **38**, 66; Kunst. 1914, **4**, 96; Wag. Jahr. 1913, **59**, II, 585; Zts. ang. Chem. 1914, **27**, II, 100. D. R. P. Anm. E-17505, 1911; D. R. P. 281374, 1911; abst. C. A. 1915, **9**, 2312; Chem. Zentr. 1915, **86**, I, 235; Chem. Ztg. 1913, **37**, 1304; 1914, **38**, 1235; Chem. Ztg. Rep. 1915, **38**, 44; Kunst. 1913, **3**, 420; Wag. Jahr. 1915, **61**, II, 368; Zts. ang. Chem. 1913, **26**, II, 700; 1915, **28**, II, 85. D. R. P. 322586, 1912; abst. Chem. Ztg. 1920, **44**, 350; Kunst. 1920, **10**, 212. For the use of dichlorethylene and alcohol as cellulose acetate solvent, refer to T. Becker (Assignor to F. Bayer & Co.), U. S. P. 988965, 1911; abst. C. A. 1911, **5**, 2176; J. S. C. I. 1911, **30**, 616; Mon. Sci. 1912, **77**, 30; Chem. Ztg. 1911, **35**, 474. E. P. 16932, 1910; abst. J. S. C. I. 1910, **29**, 1299; J. Soc. Dyers Col. 1911, **27**, 10; Mon. Sci. 1915, **82**, 56; Chem. Ztg. 1910, **34**, 889, 1187; Chem. Ztg. Rep. 1911, **35**, 35. F. P. 418309, 1910; J. S. C. I. 1911, **30**, 80; Mon. Sci. 1913, **79**, 86; Chem. Ztg. 1910, **34**, 1162; Kunst. 1911, **1**, 75. Aust. P. Appl. 5592, 1910; abst. Mon. Sci. 1915, **82**, 56; Chem. Ztg. 1911, **35**, 225.

3. E. P. 23995, 1911; abst. C. A. 1913, **7**, 1415; J. S. C. I. 1912, **31**, 279; Chem. Ztg. 1911, **35**, 1422 (no patent granted). F. P. 435742, 1911; abst. J. S. C. I. 1912, **31**, 329; Mon. Sci. 1913, **79**, 133. D. R. P. 241973, 1910; abst. C. A. 1912, **6**, 2170; J. S. C. I. 1912, **31**, 225; Chem. Zentr. 1912, **83**, I, 307; Chem. Ind. 1912, **35**, 57; Chem. Ztg. 1911, **35**, 1359; Chem. Ztg. Rep. 1912, **36**, 49; Chem. Zts. 1912, **11**, No. 2801; Kunst. 1912, **2**, 57; Wag. Jahr. 1911, **57**, II, 422; Zts. ang. Chem. 1912, **26**, 286. Aust. P. Appl. 9227, 1911; abst. Kunst. 1912, **2**, 40. D. R. P. Anm. W-36069, 1910; abst. Chem. Ztg. 1911, **35**, 957. Hung. P. Appl. W-3204, 1911. Belg. P. 241116, 1911; abst. Chem. Ztg. 1912, **36**, 318. L. Lilienfeld, Ital. P. 121072, 1911.

4. J. Koetschet and M. Theumann process; U. S. P. 1030311, 1911; abst. C. A. 1912, **6**, 2528; J. S. C. I. 1912, **31**, 680; Mon. Sci. 1913, **79**, 14; Chem. Ztg. 1912, **36**, 975. E. P. 25893, 1911; abst. C. A. 1913, **7**, 609; J. S. C. I. 1912, **31**, 279; Chem. Ztg. 1912, **36**, 49, 292; Kunst. 1913, **3**, 174. F. P. 437240, 1911; abst. J. S. C. I.

dride in vapor form, but the author is informed that this process has never been used commercially up to the present time. The object of the process is economy of acetic anhydride—the most costly constituent of the esterizing bath. Knoll & Co. issued a series of four separate patents in this art. In the first[1], an uninflammable plastic of cellulose acetate, collodion and zinc chloride is described; in the second[2], the use of sodium ethylsulfate is detailed for altering the solubility (ripening) of cellulose acetate; in the next[3], sulfacetic acid is used as catalyst and the process so adjusted that esters soluble in formic acid, tartaric acid esters, diacetyltartaric acid esters, acetins, chlorhydrins, and nitromethane are formed; while in the last[4], the manufacture of fibrous acetylcellulose is described by a circulatory method in a manner somewhat similar to that used for the continuous flow of centrifugal nitration[5].

1912, **31**, 429; Mon. Sci. 1913, **79**, 134. D. R. P. 258879, 1910; abst. C. A. 1913, **7**, 3227; Chem. Zentr. 1913, **84**, I, 1641; Chem. Ztg. 1913, **37**, 387; Chem. Ztg. Rep. 1913, **37**, 347; Kunst. 1913, **3**, 140; Wag. Jahr. 1913, **59**, II, 16; Zts. ang. Chem. 1913, **26**, 290; Zts. Chem. Ind. Koll. 1914, **14**, 326. D. R. P. Anm. S-32783, 1910; abst. Chem. Zts. 1912, **36**, 318. Can. P. 139046, 1911; abst. C. A. 1912, **6**, 1526. Swiss P. 59412, 1911; abst. Chem. Ztg. 1913, **37**, 567.

1. D. R. P. 255704, 1911; abst. C. A. 1913, **7**, 1807; J. S. C. I. 1913, **32**, 421; Chem. Zentr. 1913, **84**, I, 482; Chem. Ztg. Rep. 1913, **37**, 69; Kunst. 1913, **3**, 40, 95; Wag. Jahr. 1913, **59**, II, 589; Zts. ang. Chem. 1913, **26**, 176. See D. R. P. Anm. K-48490, 48966, 1911; 52789, 1912; abst. Kunst. 1913, **3**, 40, 200; Chem. Ztg. 1912, **36**, 1174.

2. D. R. P. 272121, 1911; abst. C. A. 1914, **8**, 2482; J. S. C. I. 1914, **33**, 640; Chem. Zentr. 1914, **85**, I, 1385; Chem. Ztg. 1914, **38**, 362; Chem. Ztg. Rep. 1914, **38**, 241; Kunst. 1914, **4**, 192; Wag. Jahr. 1914, **60**, I, 13; Zts. ang. Chem. 1914, **27**, 311.

3. F. P. 442512, 1912; abst. C. A. 1913, **7**, 1288; J. S. C. I. 1912, **31**, 917; Chem. Ztg. Rep. 1912, **36**, 693. D. R. P. 273706, 1911; abst. C. A. 1914, **8**, 2948; J. S. C. I. 1914, **33**, 746; Chem. Zentr. 1914, **85**, I, 1863; Chem. Ztg. 1914, **38**, 561; Chem. Ztg. Rep. 1914, **38**, 327; Kunst. 1914, **4**, 179, 234; Wag. Jahr. 1914, **60**, II, 14; Zts. ang. Chem. 1914, **27**, 390.

4. D. R. P. 275962, 1911; abst. J. S. C. I. 1914, **33**, 916; Chem. Zentr. 1914, **85**, II, 367; Chem. Ztg. 1914, **38**, 788; Chem. Ztg. Rep. 1914, **27**, 502; Kunst. 1914, **4**, 317; Wag. Jahr. 1914, **60**, I, 15. It was in 1911 that a process for combining the alkaline compounds of fatty sulfonic acids with cellulose acetate or nitrocellulose was described by L. Lilienfeld, E. P. 14142, 1911; abst. C. A. 1913, **7**, 217; J. S. C. I. 1912, **31**, 680; Chem. Ztg. Rep. 1913, **37**, 54. Aust. P. 55527; abst. Kunst. 1913, **3**, 38.

5. "Technology of Cellulose Esters," 1921, **1**, 1956.

P. Hewitt in his investigations upon methods of producing and utilizing light rays[1], found that retentiveness of the fluorescent quality or durability of the property of transforming light, seems to be seriously modified by the internal structure or physical arrangement of the material in its final state. In order to increase the durability of retentiveness, rhodamine in cellulose acetate with glycerol was found effective[2], especially in the presence of acetic acid[3], the latter being added in sufficient amount to modify the structure of the cellulose acetate upon drying[4], the product[5] having afterwards been claimed.

The acetylcellulose composition as proposed by G. Koller[6] combines phenol with tri- or per-chlorethylene, and that of the Ellis Foster Co.[7] includes castor oil and chloral. Instead of the halogens, chlorine or bromine previously described the Act. Ges. f. Anilinfabr.[8] found iodine mono- or trichloride, iodine monobromide or bromine chloride equally as efficient and less drastic as a catalyst.

1. U. S. P. 907598, 1908.

2. P. Hewitt, U. S. P. 1188655, 1916; abst. C. A. 1916, **10**, 2157; J. S. C. I. 1916, **35**, 898; Kunst. 1916, **6**, 266. E. P. 16271, 1911; abst. Brit. J. Phot. 1911, **58**, 784. D. R. P. 254083, 1911; abst. C. A. 1914, **8**, 1065; Chem. Zentr. 1913, **84**, I, 136.

3. P. Hewitt, U. S. P. 1188775, 1916; abst. C. A. 1916, **10**, 2157; J. S. C. I. 1916, **35**, 898; Mon. Sci. 1917, **84**, 60; Kunst. 1916, **6**, 264.

4. P. Hewitt, U. S. P. 1188776, 1916; abst. C. A. 1916, **10**, 2157; J. S. C. I. 1916, **35**, 898; Mon. Sci. 1917, **84**, 60.

5. P. Hewitt, U. S. P. 1188777, 1916; abst. C. A. 1916, **10**, 257; J. S. C. I. 1916, **35**, 898; Mon. Sci. 1917, **84**, 60.

6. U. S. P. 1079773, 1914; abst. C. A. 1914, **8**, 421; J. S. C. I. 1913, **32**, 1153; Mon. Sci. 1914, **81**, 105; Chem. Ztg. Rep. 1914, **38**, 133. E. P. 4744, 1911; abst. C. A. 1912, **6**, 2315; J. S. C. I. 1912, **31**, 328; Chem. Ztg. 1912, **36**, 395. F. P. 440133, 1912; abst. J. S. C. I. 1912, **31**, 680; J. Soc. Dyers, 1912, **28**, 276; Mon. Sci. 1913, **79**, 138; Kunst. 1912, **2**, 355, 439. D. R. P. 266781, 1912; abst. C. A. 1914, **8**, 573; Chem. Zentr. 1913, **84**, II, 1908; Chem. Ztg. Rep. 1913, **37**, 645; Chem. Zts. 1914, **13**, No. 3421; Kunst. 1914, **4**, 15; 1916, **6**, 114; Wag. Jahr. 1913, **59**, II, 585; Zts. ang. Chem. 1913, **26**, II, 752. Aust. P. 59580, 1913; abst. Chem. Ztg. 1913, **37**, 216, 644; Kunst. 1913, **3**, 376. Belg. P. 243162, 1912.

7. U. S. P. 999490, 1911; 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.

8. F. P. 435507, 1911; abst. J. S. C. I. 1912, **31**, 329; Mon. Sci. 1913, **78**, 390; **79**, 133; Chem. Ztg. 1912, **36**, 382. Belg. P. 239564, 1911; abst. Chem. Ztg. 1912, **36**, 115. E. P. 22237, 1911. F. P. 461058.

A new class of lacquers has been described by the Badisch Anilin & Soda Fabrik[1] in which acetone-soluble cellulose acetate is dissolved in a fully hydrogenized monocyclic ketone as cyclohexanone, methylcyclohexanone or hexanone acetate. Chemische Fabrik von Heyden A.-G. allege the formation of cellulose acetates new to the art result when the fully acetated ester is hydrolyzed to an acetic acid content of 55-59%[2], or 55-62% of combined acetic acid[3]. W. Walker[4] recommended the use of tetrachlorethane and wood alcohol (the latter a non-solvent) as a desirable combination for lacquer formation with acetated cellulose.

1. G. Lutz, assignor to Badische Anilin & Soda Fabrik, U. S. P. 1045895, 1912; abst. C. A. 1912, **6**, 712; J. S. C. I. 1913, **32**, 19; Mon. Sci. 1913, **79**, 110. E. P. 3869, 1912; abst. C. A. 1913, **7**, 2863; J. S. C. I. 1912, **31**, 1176; Kunst .1913, **3**, 94. E. P. 7292, 1912; abst. J. S. C. I. 1912, **31**, 1176. E. P. 14042, 1914; abst. C. A. 1915, **9**, 3359; J. S. C. I. 1915, **34**, 956. E. P. 145511, 1920; abst. Paper, 1921, **28**, No. 3, p. 34; C. A. 1920, **14**. 19, 3154; J. S. C. I. 1921, **40**, 105-A, 144-A; Chem. Met. Eng. 1920, **22**, 989; Faser. 1920, **2**, 185. F. P. 440733, 1912; abst. J. S. C. I. 1912, **31**, 828; Mon. Sci. 1914, **81**, 14; Kunst. 1913, **3**, 17. D. R. P. 251351, 1911; abst. C. A. 1913, **7**, 35, 427, 1426; J. S. C. I. 1912, **31**, 1191; Farben Ztg. 1912, **17**, 2815; Chem. Zentr. 1912, **83**, II, 1246; Chem. Ind. 1912, **35**, 657; Chem. Ztg. Rep. 1912, **36**, 584; Wag. Jahr. 1912, **58**, II, 604; Zts. ang. Chem. 1912, **25**, 2508. D. R. P. 284672, 1914; abst. C. A. 1916, **10**, 117; J. S. C. I. 1915, **34**, 1048; Chem. Zentr. 1915, **86**, 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. D. R. P. Anm. B-64397, 1911; abst. Chem. Ztg. 1912, **36**, 556. D. R. P. Anm. B-75886, 1914 (Addn. to D. R. P. 284672); abst. Chem. Ztg. 1920, **44**, 770. Aust. P. Appl. 1835, 1912; abst. Chem. Ztg. 1914, **38**, 433. Holland P. 103; abst. Chem. Ztg. 1914, **38**, 235.

2. E. P. 3973, 1911; abst. C. A. 1912, **6**, 2172; J. S. C. I. 1911, **30**, 1143, 1156; Chem. Ztg. 1911, **35**, 1042. F. P. 426436, 1911; abst. J. S. C. I. 1911, **30**, 950; Kunst. 1911, **1**, 355. D. R. P. 269193, 1912; abst. C. A. 1914, **8**, 2251; Chem. Zentr. 1914, **85**, I, 506; Chem. Ztg. Rep. 1914, **38**, 111; Kunst. 1914, **4**, 97; Wag. Jahr. 1914, **60**, II, 16; Zts. ang. Chem. 1914, **27**, II, 110. D. R. P. 273029, 1912; abst. C. A. 1914, **8**, 2806; Chem. Zentr. 1914, **85**, I, 1716; Chem. Ztg .Rep. 1914, **38**, 301; Kunst. 1914, **4**, 234; Wag. Jahr. 1914, **60**, II, 16. Aust. P. Appl. 327, 1911. Belg. P. 232475, 1911. Swiss P. 55344, 1911.

3. F. P. 438649, 1912; abst. J. S. C. I. 1912, **31**, 584; Chem. Ztg. 1912, **36**, 618; Kunst. 1912, **2**, 439.

4. U. S. P. 1009116, 1911; abst. C. A. 1912, **6**, 293; J. S. C. I. 1911, **30**, 1447; Mon. Sci. 1912, **77**, 163; Chem. Ztg. 1911, **35**, 1379. F. P. 417319, 1910; abst. J. S. C. I. 1911, **30**, 19.

A. Eichengruen described a phonograph disc record of shellac coated with a thin film of acetylcellulose with alcohol, benzene and dichlorhydrin[1] (see A. Lumiere, J. Aylsworth), and the use of cellulose acetate in medicinal, cosmetic or nourishing preparations, wherein the alcohol-soluble ester is rendered gelatinous and incorporated with solvent medicaments (oil of wintergreen, methyl salicylate) or perfume materials (heliotropine, piperonal)[2]. In the manufacture of artificial filaments according to the disclosures of the Chemische Fabrik. v. Heyden Akt. Ges.[3], cellulose formate in formic acid, or cellulose acetate in acetic acid has water added thereto nearly to the point of precipitation, and is then forced through capillary orifices into water as the coagulant, thus inducing almost immediate setting of the filamentous ester.

The Societe L'Oyonnithe[4] advocate the use of ammonium bisulfate to replace sulfuric acid as catalyst, on the grounds (well known by this time) that the destructive action of the mineral acid on the cellulose is thereby reduced. As possible new solvent combinations[5], tin tetrachloride or antimony trichloride dissolved in alcohol was described. In the formation of acetate plastics, E. Ichenhaeuser[6] detailed methods for causing uniform elimination

1. U. S. P. 1175728, 1916; abst. C. A. 1916, **10**, 1415. E. P. 17574, 1912.

2. E. P. 26987, 1912; abst. C. A. 1914, **8**, 1644. D. R. P. 268489, 1911; abst. C. A. 1914, **8**, 1489; Chem. Zentr. 1914, **85**, I, 319; Chem. Ztg. Rep. 1914, **38**, 20; Zts. ang. Chem. 1914, **27**, II, 36.

3. E. P. 3973, 1911; abst. C. A. 1912, **6**, 2172; J. S. C. I. 1911, **30**, 1156.

4. F. P. 427265, 1911; abst. C. A. 1912, **6**, 1990; J. S. C. I. 1911, **30**, 1051; Mon. Sci. 1913, **78**, 551; **79**, 123; Chem. Ztg. 1911, **35**, 690; Chem. Ztg. Rep. 1911, **35**, 481. Aust. P. Appl. 1787, 1912; abst. Chem. Ztg. 1912, **36**, 1090; Kunst. 1912, **2**, 460. Hung. P. Appl. O-674, 1912; abst. Chem. Ztg. 1912, **36**, 1374.

5. Farbenfabriken vorm. F. Bayer & Co., D. R. P. 268627, 1911 (Addn. to D. R. P. 256922); abst. C. A. 1914, **8**, 2060; Chem. Zentr. 1914, **85**, I, 317; Chem. Ztg. Rep. 1914, **38**, 66; Kunst. 1914, **4**, 96; Wag. Jahr. 1913, **59**, II, 585; Zts. ang. Chem. 1914, **27**, II, 100.

6. F. P. 436538, 1911; abst. J. S. C. I. 1912, **31**, 485; Kunst. 1912, **2**, 272.

of solvent, and L. Nottelle and R. Heraud[1] disclosed new cellulose acetate varnish mixtures, while W. Dixon[2] pointed out technical uses for starch acetates. The use of cellulose formate, acetate, benzoate and sulfacetate for stereotypes[3]; the formation of acetate plastics with chloral, castor oil and amyl lactate[4]; and the manufacture of compound fabrics by evaporating cellulose acetate solutions on a polished surface and then attaching the sheet to the fabric[5], are other proposed fields of application for these products made this year (1911).

H. Peters and H. Collum[6] described a complicated method of preliminary treatment of cotton for esterification, whereby the cellulose is first heated with di-, or epichlorhydrin, palmitic acid, formic acid or glycerol at high temperatures, and is then esterified in the usual manner. It has been stated that the Henckel-Donnersmarck firm purchased all of the Lederer patents in 1911, thus materially strengthening their position in this field. In the manufacture of die and printing plates, cellulose acetate with

1. F. P. 445638, 1911; abst. J. S. C. I. 1913, **32**, 35; Kunst. 1913, **3**, 474.

2. E. P. 27491, 1911; abst. J. S. C. I. 1913, **32**, 214. (Use of starch acetate, feculose, in matches in place of glue.)

3. Compagnie Generale d'Electricite, D. R. P. 272695, 1911; abst. C. A. 1914, **8**, 2786; Chem. Ztg. Rep. 1914, **38**, 276.

4. C. Ellis, U. S. P. 999490, 1911; abst. C. A. 1911, **5**, 3156; J. S. C. I. 1911, **30**, 1051; Mon. Sci. 1912, **77**, 163; Chem. Ztg. 1911, **35**, 965; Kunst. 1911, **1**, 458.

5. Societe Anonyme des Celluloses Planchon, E. P. 7442, 1911; abst. C. A. 1912, **6**, 2356; J. S. C. I. 1912, **31**, 224.

6. U. S. P. 1008489, 1911; abst. C. A. 1912, **6**, 293; J. S. C. I. 1911, **30**, 1447; Mon. Sci. 1912, **77**, 163. U. S. P. 1008557, 1911; abst. C. A. 1912, **6**, 293; J. S. C. I. 1911, **30**, 1447; Mon. Sci. 1912, **77**, 163. E. P. 870, 1910; abst. C. A. 1911, **5**, 2980; J. S. C. I. 1911, **30**, 206. E. P. 14293, 1910; abst. C. A. 1911, **5**, 3347; J. S. C. I. 1911, **30**, 1171. E. P. 16000, 1911; abst. C. A. 1913, **7**, 252; J. S. C. I. 1912, **31**, 637; J. Soc. Dyers, 1912, **28**, 268; Chem. Ztg. 1912, **36**, 948; Kunst. 1913, **3**, 175. E. P. 2859, 1912. E. P. 9867, 1912; abst. J. S. C. I. 1912, **31**, May 15, xiii. E. P. 822, 1912; abst. J. S. C. I. 1912, **31**, 637. F. P. 420127, 1911; abst. J. S. C. I. 1911, **30**, 280; Mon. Sci. 1913, **79**, 21. F. P. 432747, 1911; abst. J. S. C. I. 1912, **31**, 124; Mon. Sci. 1913, **79**, 130; Chem. Ztg. 1912, **36**, 209. See G. Henckel-Donnersmarck, Ital. P. 126270.

small amounts of camphor has been proposed[1]. G. Finck[2] disclosed methods for acetylcellulose manufacture.

In a study upon the colloidal nature of acetylcellulose published by E. Knoevenagel[3] in 1911, it was found that this ester swells in water to an immeasurable extent, but only slightly in absolute alcohol and in many mixtures of organic liquids and aqueous solutions. F. Sander[4] described the hydrolytic and acetolytic breaking up of acetylcellulose under the influence of different contact substances. In a dissertation published in Dresden in 1911, A. Stein[5] has recorded numerous determinations of the mechanics of fatty acid esterification as applied to cellulose and hydrocellulose, while W. Vieweg[6] added critical notes to a general article on the development of the acetated celluloses by L. Clement and C. Riviere[7]. C. Schwalbe[8] continued his experiments of the previous year (see p. 392, n. 4) on the acetylation of cotton cellulose, and deduced conclusions based upon experimentation. In 1911 was published the two volume, 1240 page "Nitrocellulose Industry" by E. Worden, where, in 70 pages, appeared the first attempt to correlate and classify our knowledge of this subject from the commencement up to that time.

1. J. Richter, D. R. P. Anm. R-32631, 1911; D. R. P. 246081, 1911; abst. C. A. 1912, **6**, 2529; Chem. Ztg. 1912, **36**, 62; Chem. Ztg. Rep. 1912, **36**, 323.

2. D. R. P. Anm. F-29131, 1910; F-32321, F-32472, F-32918, 1911; abst. Chem. Ztg. 1911, **35**, 930, 1422; 1912, **36**, 901.

3. Chem. Ztg. 1911, **35**, 248; J. S. C. I. 1911, **30**, 531; Zts. ang. Chem. 1911, **24**, 504.

4. Dissertation, Heidelberg, 1911.

5. Dissertation, Dresden, 1911; Zts. ang. Chem. 1913, **26**, I, 673; abst. C. A. 1914, **8**, 1009; J. C. S. 1913, **104**, i, 1305; J. Ind. Eng. Chem. 1914, **6**, 86; J. S. C. I. 1913, **32**, 673; Chem. Zentr. 1914, **85**, I, 526; Chem. Ztg. Rep. 1914, **38**, 130; Kunst. 1914, **4**, 94; Wag. Jahr. 1913, **59**, II, 543.

6. Kunst. 1914, **4**, 148, 166, 186; abst. C. A. 1914, **8**, 2619.

7. Rev. Chim. Ind. 1911, **22**, 215; Caout. et Gutta. 1911, **8**, 5449; abst. C. A. 1911, **5**, 3908.

8. Zts. ang. Chem. 1911, **24**, 1256; abst. C. A. 1911, **5**, 3154; J. C. S. 1911, **99**, i, 712; J. S. C. I. 1911, **30**, 948; Chem. Zentr. 1911, **82**, II, 670; Chem. Ztg. Rep. 1911, **35**, 367; Kunst. 1911, **1**, 452; Wag. Jahr. 1911, **57**, II, 504.

A. Eichengruen[1] published an historical article on the development of certain phases of cellulose acetate technology and arrived at conclusions as to priority in the discovery of "cellulose triacetate" which were called in question by H. Ost[2], the latter submitting experimental evidence in support of his contentions. This closes the summation of the work for the year 1911.

Renewed activity is evidenced in the next year (1912) in attempts to extend the usefulness of the acetated celluloses by means of increasing the range of applicable solvents. W. Lindsay in a series of patents described the advantages in this connection of acetodichlorhydrin and alcohol[3], ethylenechlorhydrin[4], ethyleneacetochlorhydrin[5], ethylene chloride (b. pt. 83.5°) in methyl or ethyl alcohol[6], ethylenechlorhydrin[7], ethyleneacetochlorhydrin[8], acetone and benzyl benzoate[9], methyl alcohol and pentachlorethane[10],

1. Zts. ang. Chem. 1911, **24**, 1306; abst. C. A. 1912, **6**, 1671; J. C. S. 1911, **100**, i, 712; Chem. Zentr. 1911, **82**, II, 750; Chem. Ztg. Rep. 1911, **35**, 395; Kunst. 1911, **1**, 452. See also Apoth. Ztg. 1911, **26**, 206; abst. Merck's Report, June, 1911, **20**, 170. The article on "Acetylcellulose" in Ullman, "Encylopedie der Technischen Chemie," 1928, Vol. 1, pages 116-141, with 60 bibliographic references, is by A. Eichengruen. A. Martens, Mitt. K. Materialprufungsamt, 1911, **29**, 57.

2. Zts. ang. Chem. 1911, **24**, 1304, 1307; abst. C. A. 1912, **6**, 1671; J. C. S. 1911, **100**, i, 712; Chem. Zentr. 1911, **82**, II, 750; Chem. Ztg. Rep. 1911, **35**, 395; Kunst. 1911, **1**, 452.

3. U. S. P. 1027486, 1912; abst. C. A. 1912, **6**, 1989; J. S. C. I. 1912, **31**, 583; Mon. Sci. 1912, **77**, 164; Chem. Ztg. 1912, **36**, 958.

4. U. S. P. 1027614, 1912; abst. C. A. 1912, **6**, 1989; J. S. C. I. 1912, **31**, 583; Mon. Sci. 1913, **79**, 393; Chem. Ztg. 1912, **36**, 958.

5. U. S. P. 1027615, 1912; abst. C. A. 1912, **6**, 1989; J. S. C. I. 1912, **31**, 583; Mon. Sci. 1913, **79**, 393; Chem. Ztg. 1912, **36**, 958.

6. U. S. P. 1027616, 1912; abst. C. A. 1912, **6**, 1989; J. S. C. I. 1912, **31**, 583; Mon. Sci. 1912, **77**, 163; Chem. Ztg. 1912, **36**, 958.

7. U. S. P. 1027617, 1912; abst. C. A. 1912, **6**, 1989; J. S. C. I. 1912, **31**, 584; Mon. Sci. 1912, **77**, 163; 1913, **79**, 393.

8. U. S. P. 1027618, 1912; abst. C. A. 1912, **6**, 1989; J. S. C. I. 1912, **31**, 584; Mon. Sci. 1912, **77**, 163; 1913, **79**, 393. Observe that whereas U. S. P. 1027615 protects the use of ethyleneacetochlorhydrin with cellulose acetate, U. S. P. 1027618 covers the use of the same with cellulose nitrate.

9. U. S. P. 1027619, 1912; abst. C. A. 1912, **6**, 1989; J. S. C. I. 1912, **31**, 584; Mon. Sci. 1912, **77**, 163; 1913, **79**, 392; Chem. Ztg. 1912, **36**, 958.

10. U. S. P. 1041112, 1912; abst. C. A. 1912, **6**, 3517; J. S. C. I. 1912, **31**, 1075; Mon. Sci. 1913, **79**, 110; Chem. Ztg. 1912, **36**, 1475.

ethyl-*p*-toluenesulfonamide and triphenyl phosphate[1], trichlorhydrin with methyl or ethyl alcohol[2], camphor, triphenyl or tricresyl phosphates with either methyl[3] or ethyl alcohols[4], tetrachlorethyl- or trichlormethyl-acetanilid, triphenyl or tricresyl phosphates and methyl alcohol[5], or ethyl alcohol[6]; and urea[7]. H. Mork[8] detailed the advantages of methyl chloracetate as a direct cellulose acetate solvent.

The utilization of acetylene tetrachloride, especially in conjunction with chloroform, acetone, methyl alcohol and benzene, was advocated by W. Walker as a cellulose ester solvent[9], while L. Desvaux[10] published methods for the manufacture of non-inflammable plastics with cellulose acetate and gelatin, using glacial acetic acid, coal tar creosote, pentachlorethane and alcohol. In another patented method[11], flexible compounds for the manufacture of acetate

1. U. S. P. 1041113, 1912; abst. C. A. 1912, **6**, 3517; J. S. C. I. 1912, **31**, 1075; Mon. Sci. 1913, **79**, 110; Chem. Ztg. 1912, **36**, 1475.
2. U. S. P. 1041114, 1912; abst. C. A. 1912, **6**, 3518; J. S. C. I. 1912, **31**, 1075; Mon. Sci. 1913, **79**, 110; Chem. Ztg. 1912 ,**36**, 1475.
3. U. S. P. 1041115, 1912; abst. C. A. 1912, **6**, 3518; J. S. C. I. 1912, **31**, 1075; Mon. Sci. 1913, **79**, 110; Chem. Ztg. 1912, **36**, 1475.
4. U. S. P. 1041116, 1912; abst. C. A. 1912, **6**, 3518; J. S. C. I. 1912, **31**, 1075; Mon. Sci. 1913, **79**, 110; Chem. Ztg. 1912, **36**, 1475.
5. U. S. P. 1041117, 1912; abst. C. A. 1912, **6**, 3518; J. S. C. I. 1912, **31**, 1075; Mon. Sci. 1913, **79**, 110.
6. U. S. P. 1041118, 1912; abst. C. A. 1912, **6**, 3518; J. S. C. I. 1912, **31**, 1075; Mon. Sci. 1913, **79**, 110.
7. U. S. P. 1045990, 1912; 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. 415518, 1910; 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. The Celluloid Co., D. R. P. 263056, 1910; abst. C. A. 1913, **7**, 3840; Chem. Zentr. 1913, **84**, II, 834; Chem. Ztg. Rep. 1913, **37**, 482; Kunst. 1913, **3**, 300, 375.
8. U. S. P. 1039782, 1912; abst. C. A. 1912, **6**, 3517; J. S. C. I. 1912, **31**, 1027; Mon. Sci. 1913, **79**, 110; Chem. Ztg. 1912, **36**, 1374.
9. U. S. P. 1035108, 1912; abst. J. S. C. I. 1912, **31**, 812; C. A. 1912, **6**, 3333; Mon. Sci. 1913, **78**, 110.
10. F. P. 450746, 1912; abst. J. S. C. I. 1913, **32**, 596; C. A. 1913, **7**, 3227; Kunst. 1913, **3**, 258; Chem. Ztg. Rep. 1913, **37**, 388.
11. H. Danzer, assignor to Cie. Gen. de Phono. Cinemato. et Appareils de Precision, U. S. P. 1089910, 1914; abst. C. A. 1914, **8**, 1551; Mon. Sci. 1914, **81**, 106; Kunst. 1914, **4**, 275; J. S. C. I. 1914, **33**, 375. 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; Chem.

cinematographic films result from the employment as plasticizers, of ether oxides of glycerol as glycerol phenolate or cresolate, diphenylglyceryl ether and phenyl glycide. The Badische Anilin & Soda Fabrik brought forward as desirable solvents in which certain hexahydrophenols (see p. 402, n. 1) are replaced by the esters of cyclopentanols, such as *b*-methylcyclopentanol acetate, cyclohexanol formate and cyclohexanol acetate, which when combined with cellulose acetate or nitrate produce valuable lacquers and varnishes[1]. This firm disclosed also[2], acetyldicyclohexylamine and dicyclohexylsulfonamide as valuable acetate plasticizing agents.

A series of patents was this year (1912) issued to H. Dreyfus in the cellulose acetate art, in which[3] details are given of the classes of esters obtained when increasing and diminishing the amount of acetic anhydride and sulfuric acid in the esterizing bath; and the employment of dilute

Ztg. 1912, **36**, 1412. F. P. 443031, 1911; abst. J. S. C. I. 1912, **31**, 1008. Swiss P. 61929, 1912; abst. C. A. 1914, **8**, 2124; Kunst. 1914, **4**, 98. Swiss P. 63585, 1911; abst. C. A. 1914, **8**, 2252; Kunst .1914, **4**, 216.

1. O. Schmidt, G. Lutz and T. Eichler, assignors to Badische Anilin- und Sodafabrik, U. S. P. 1045895, 1912; 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, 1911; abst. J. S. C. I. 1912, **31**, 1191; Chem. Zentr. 1912, **83**, 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, 1912 (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. 9270, 1914; abst. C. A. 1915, **9**, 2980; J. S. C. I. 1915, **34**, 867. E. P. Appl. 16861, 1920; abst. J. S. C. I. 1920, **39**, 504-A. See also D. R. P. Anm. St-19374, 1914; abst. Chem. Ztg. 1914, **38**, 1235; Kunst. 1914, **4**, 396.

3. E. P. 20978, 1911; abst. Kunst. 1913, **3**, 195; Chem. Ztg. Rep. 1913, **37**, 287. First Addn. 14558 to F. P. 432046, 1911; abst. J. S. C. I. 1912, **31**, 225; Chem. Ztg .1912, **36**, 223. U. S. P. 1217722, 1917; abst. C. A. 1917, **11**, 1545; J. S. C. I. 1917, **36**, 451; Mon. Sci. 1918, **85**, 4. U. S. P. 1286172, 1918; abst. C. A. 1919, **13**, 261; J. S. C. I. 1919, **38**, 358-A. Ital. P. 126542, 1912.

nitric acid[1] as a hydrolyzing agent in the ripening of the ester from the primitive acetylating bath to the desired solubility stage. He uses the products thus produced[2] for the manufacture of artificial silk and celluloid-like masses.

The process disclosed by A. Wohl[3] for cellulose acetation aims at uniformity of penetration and reaction, by first steeping the cellulose in glacial acetic acid or other organic liquid miscible with water as formic acid or acetone, claiming elimination of hygroscopic, moisture by the substitution of a miscible liquid. It is a fact that the previous treatment of cellulose with acetic acid, formic acid or acetic anhydride renders acetylation much more rapid, but it is *also* a fact that the esterizing process is much more difficult to control as the result of the acid pre-treatment. In another process[4], organic esters of cellulose or hydrocel-

1. E. P. 21376, 1912; abst. C. A. 1914, **8**, 1010; J. S. C. I. 1913, **32**, 133; Chem. Ztg. 1912, **36**, 1398. E. P. 22645, 1912; abst. Chem. Ztg. 1912, **36**, 1425; J. S. C. I. 1912, **31**, Oct. 31, xiii. Third Addn. 14783, 1911, to F. P. 432046, 1911; abst. J. S. C. I. 1912, **31**, 329; Chem. Ztg. 1912, **36**, 263. Belg. P. 246250, 246251, 1912.

2. E. P. 20979, 1911; abst. C. A. 1913, **7**, 891; J. S. C. I. 1913, **32**, 133; Chem. Ztg. 1913, **37**, 200; Chem. Ztg. Rep. 1913, **37**, 287; Kunst. 1913, **3**, 95. Second Addn. 14559, 1911, to F. P. 432046 abst. J. S. C. I. 1912, **31**, 225; Chem. Ztg. 1912, **36**, 223. Fourth Addn. 15894, 1912, to F. P. 432046; abst. Chem. Ztg. 1912, **36**, 1229; Kunst. 1913, **3**, 434. Fifth Addn. 15933, 1912, to F. P. 432046; abst. Chem. Ztg. 1912, **36**, 1174; Kunst. 1913, **3**, 435. Swiss P. 63586, 1911; abst. C. A. 1914, **8**, 2252; Chem. Ztg. 1914, **38**, 106.

3. E. P. 12422, 1910; abst. C. A. 1911, **5**, 3156; J. S. C. I. 1911, **30**, 798; J. Soc. Dyers Col. 1911, **27**, 214; Mon. Sci. 1916, **83**, 47; Chem. Ztg. Rep. 1911, **35**, 520; Kunst. 1911, **1**, 295. E. P. 20527, 1912; abst. C. A. 1914, **8**, 1010; J. S. C. I. 1913, **32**, 823; Chem. Ztg. 1912, **36**, 1398; 1913, **37**, 952 (no patent granted). F. P. 448072, 1912; abst. J. S. C. I. 1913, **32**, 420; Mon. Sci. 1914, **81**, 3 ;Kunst. 1913, **3**, 195. D. R. P. 246651, 1910; abst. C. A. 1912, **6**, 2529; Chem. Zentr. 1912, **83**, I, 1742; Chem. Ztg. Rep. 1912, **36**, 332; Kunst. 1912, **2**, 232; Chem. Ztg. 1912, **36**, 1156; Wag. Jahr. 1912, **58**, II, 445; Zts. ang. Chem. 1912, **25**, 1549. D. R. P. Anm. W-30500, 1908 (Addn. to D. R. P. Anm. W-30446); abst. Chem. Ztg. 1911, **35**, 553. D. R. P. Anm. W-34372, 1910; abst. Chem. Ztg. 1911, **35**, 218; Kunst. 1911, **1**, 439. D. R. P. Anm. W-38008, 1911; abst. Chem. Ztg. 1913, **37**, 445; Kunst. 1913, **3**, 180. D. R. P. Anm. W-39709, 1912; abst. Chem. Ztg. 1914, **38**, 11. Aust. P. Appl. 403, 1911; abst. Chem. Ztg. 1912, **36**, 10.

4. A. Wohl, D. R. P. 243581, 1908; abst. C. A. 1912, **6**, 2316; J. S. C. I. 1912, **31**, 381; Chem. Zentr. 1912, **83**, I, 695; Chem. Ztg. 1912, **36**, 141; Chem. Ztg. Rep. 1912, **36**, 196; Wag. Jahr. 1912, **58**, II, 17; Zts. ang. Chem. 1912, **25**, 654; Zts. Chem. Ind. Koll. 1912, **10**, 263.

lulose are formed by acting on the cellulose with acid anhydride with or without the addition of a diluent, at temperatures above 100° and in the presence of less than 0.2% sulfuric acid, the latter being increased as the ash in the cellulose becomes higher. It must be remembered that with even this small amount of mineral acid, subjection of cellulose to temperatures above 100° is a process controllable only with great difficulty.

It was in 1912 that the first of the series of patents appeared on the formation of mixed nitric and acetic esters of the Akt. Ges. fuer Anilin Fabr.—the socalled cellulose acetonitrates (nitroacetates). This firm proposed[1] to conserve the valuable properties of the nitrocelluloses while materially diminishing the inflammability, by subjecting cellulose to the action of nitric and sulfuric acids containing much water so that a low nitrogen ester is formed, and this is then acetylated in the usual manner. In a modification of this process[2], nitroderivatives with at most 5% nitrogen, are esterified in the presence of catalyzers to form mixed esters. In the first process, the nitrogen is intro-

1. E. P. 10706, 1912; abst. C. A. 1913, **7**, 3414; J. S. C. I. 1913, **32**, 597; Chem. Ztg. 1913, **37**, 268; Chem. Ztg. Rep. 1913, **37**, 425. E. P. 21015, 1913; abst. C. A. 1915, **9**, 730; J. S. C. I. 1914, **33**, 350. F. P. 449253, 1912; abst. J. S. C. I. 1913, **32**, 482; Mon. Sci. 1913, **78**, 551; 1914, **81**, 5; Rev. Chim. Ind. 1913, **24**, 180; Kunst. 1913, **3**, 196. D. R. P. Anm. A-19635, 1910; abst. Chem. Ztg. 1912, **36**, 279. D. R. P. 295889, 1911; abst. Chem. Zentr. 1917, **88**, I, 350; Chem. Ztg. 1916, **40**, 1023; Chem. Ztg. Rep. 1917, **41**, 131; Kunst. 1917, **7**, 36; Wag. Jahr. 1917, **63**, II, 13; Zts. ang. Chem. 1917, **30**, II, 40; Zts. Schiess Spreng. 1917, **12**, 138. Aust. P. Appl. 8334, 1911; abst. Kunst. 1912, **2**, 319. Aust. P. Appl. 7132, 1912; abst. Chem. Ztg. 1914, **38**, 902. Belg. P. 248907, 1912; abst. Chem. Ztg. 1912, **36**, 1475. Hung. P. Appl. A-2071, 1914; abst. Chem. Ztg. 1914, **38**, 836. Hung. P .Appl. A-1829, 1911; abst. Chem. Ztg. 1913, **37**, 11. Ital. P. 120751, 1911; abst. Ztg. 1912, **36**, 1332. Ital. P. 127915, 1912; abst. Chem. Ztg. 1913, **37**, 1476. Swiss P. 61424, 1912; abst. Chem. Ztg. 1913, **37**, 1052. In this connection see also Ital. P. 136232, 1913; abst. Chem. Ztg. 1914, **38**, 35.

2. E. P. 1156, 1914 (Addn. to E. P. 10706, 1912); abst. C. A. 1915, **9**, 1843; J. S. C. I. 1914, **33**, 688; Chem. Ztg. 1914, **38**, 182; Kunst. 1914, **4**, 310. Aust. P. Appl. 4671, 1913; abst. Chem. Ztg. 1914, **38**, 486. Aust. P. 67942, 1914; abst. Kunst. 1914, **4**, 94; Chem. Ztg. 1915, **39**, 17. Aust. P. Appl. 183, 1914; abst. Chem. Ztg. 1915, **39**, 380. Aust. P. 70782, 1915 (Addn. to Aust. P. 67942); abst. Chem.

duced by means of a mixture of nitric and sulfuric acids; in the second process, nitric acid alone is used. In a still later method[1], best results are alleged to be obtained when a mixture of nitric acid and nitrobenzene are employed, the product being afterwards acetylated as in the previous processes.

In the acetation of cellulose, L. Lederer[2] claims to depart from the methods brought forward up to this time (1912), by subjecting 5 parts of cotton to a mixture of 20 each of glacial acetic acid and anhydride with 1 of sulfuric acid at a temperature of 20°-25° until solution takes place, when 20 parts of water are added and the mixture allowed to stand for several days, the reaction being terminated by the addition of sodium acetate. This is a method of ripening of the cellulose ester in a gelatinous or precipitated form, and for best results the mass should be frequently agitated in order to ensure uniformity of penetration.

Ztg. 1915, **39**, 954. Holland P. 1476, 1916; abst. C. A. 1916, **10**, 2637. Swiss P. 68002, 1914 (Addn. to Swiss P. 61424); abst. Chem. Ztg. 1915, **39**, 17; Kunst. 1915, **5**, 131. Swiss P. 68921 (Addn. to Swiss P. 61710); abst. Chem. Ztg. 1915, **39**, 279; Kunst. 1915, **5**, 203. See also D. R. P. 299036, 1913 (Addn. to D. R. P. 295889); abst. Chem. Zentr. 1918, **89**, I, 396; Chem. Ztg. Rep. 1918, **42**, 27; Kunst. 1918, **8**, 102; Wag. Jahr. 1918, **64**, II, 7; Zts. ang. Chem. 1918, **31**, II, 28.

1. D. R. P. 301449, 1914 (Addn. to D. R. P. 295889); abst. Chem. Zentr. 1917, **88**, II, 714; Chem. Ztg. Rep. 1918, **42**, 8; Kunst. 1918, **8**, 115; Wag. Jahr. 1917, **63**, II, 13; Zts. ang. Chem. 1917, **30**, II, 373. E. P. 22237, 1911; abst. J. S. C. I. 1912, **31**, 278; C. A. 1913, **7**, 1287; Chem. Ztg. 1912, **36**, 292, specifies the use of about 2% bromine as catalyst. E. P. 145524, 1920, combines bromine with nitric acid and nitrobenzene. E. P. 145525 patents the use of bromine and fused zinc chloride as catalyst.

2. E. P. 7687, 1912; abst. Chem. Ztg. 1913, **37**, 528; C. A. 1913, **7**, 3025; Chem. Ztg. Rep. 1913, **37**, 347; J. S. C. I. 1913, **32**, 483; Kunst. 1913, **3**, 274. F. P. 441864, 1912; abst. Mon. Sci. 1913, **79**, 141; J. S. C. I. 1912, **31**, 916. Aust. P. Appls. 2728, 1907; 6067, 1908; 2503, 1912; abst. Chem. Ztg. 1908, **32**, 651; 1909, **33**, 954; 1914, **38**, 946. Aust. P. 31203, 1907; abst. Chem. Ztg. 1907, **31**, 1234. Aust. P. 67812; abst. Kunst. 1914, **4**, 94; Chem. Ztg. 1915, **39**, 17. Belg. P. 244470, 1912; abst. Chem. Ztg. 1912, **36**, 834; Kunst. 1912, **2**, 399. D. R. P. Anm. L-20597, 1905; L-21824, 1905; L-26357, 1908; L-28615, 1909; L-30568, 1910; abst. Chem. Ztg. 1907, **31**, 415, 92; 1911, **35**, 154, 250; 1912, **36**, 425. Hung. P. Appl. L-2409, 1908; abst. Chem. Ztg. 1908, **32**, 1257. Ital. P. 85490, 1907; 96613, 1908; abst. Chem. Ztg. 1907, **31**, 401; 1909, **33**, 897. Norw. P. 16291, 16292. Swiss P. 61390, 1912; abst. Chem. Ztg. 1913, **37**, 1293; Kunst. 1914, **4**, 378. Ital. P. 128651, 130002, 1912.

In order to conserve the maximum of acetic anhydride, a method has been patented[1] in which the cotton with sulfuric acid is subjected to the vapors of acetic anhydride at reduced pressure, the process being so manipulated that the ester formed has the appearance of the original cotton. The process may be so adjusted that esters soluble or insoluble in acetic acid are obtained. The catalysts protected by Knoll & Co.[2] include anhydrous ferric chloride, stannous chloride, ammonium chloride and cupric chloride, or[3]

1. J. Koetschet and M. Theumann (assignors to Societe Chimique des Usines du Rhone), U. S. P. 1030311, 1912; abst. C. A. 1912, **6**, 2528; J. S. C. I. 1912, **31**, 680; Mon. Sci. 1913, **79**, 14; Chem. Ztg. Rep. 1912, **46**, 485. U. S. P. 1191439, 1916; abst. C. A. 1916, **10**, 2298; J. S. C. I. 1916, **35**, 924; Mon. Sci. 1917, **84**, 29; Chem .Ztg. 1916, **40**, 880; Kunst. 1917, **7**, 9. U. S. P. 1216462, 1917; abst. C. A. 1917, **11**, 1301; J. S. C. I. 1917, **36**, 383; Mon. Sci. 1918, **85**, 4. U. S. P. 1258913, 1918; abst. C. A. 1918, **12**, 1420; J. S. C. I. 1918, **37**, 265-A; Mon. Sci. 1918, **85**, 51. U. S. P. 1286025, 1918; abst. C. A. 1919, **13**, 261; J. S. C. I. 1919, **38**, 102-A; Kunst. 1920, **10**, 101. E. P. 8046, 1915; abst. C. A. 1916, **10**, 3159; J. S. C. I. 1916, **35**, 39; Kunst. 1917, **7**, 84; Zts. ang. Chem. 1917, **30**, II, 309; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 138. Can. P. 139046, 1912; abst. C. A. 1912, **6**, 1526. See also Chem. Fabr. Griesheim Elektron, Ital. P. 123252, 1912.

2. E. P. 4353, 1913; abst. C. A. 1914, **8**, 2804; J. S. C. I. 1914, **33**, 349; Chem. Ztg. 1913, **37**, 348; Kunst. 1914, **4**, 378. See also E. P. 2491, 1913; abst. C. A. 1914, **8**, 2482; J. S. C. I. 1914, **33**, 308; Chem. Ztg. Rep. 1914, **38**, 241; Kunst. 1914, **4**, 359. F. P. 442512, 1912; abst. C. A. 1913, **7**, 1288; J. S. C. I. 1912, **31**, 917; Chem. Ztg. Rep. 1912, **36**, 693. F. P. 453835, 1913; abst. C. A. 1914, **8**, 248; J. S. C. I. 1913, **32**, 785; Mon. Sci. 1914, **81**, 9; Chem. Ztg. Rep. 1913, **37**, 557; Kunst. 1913, **3**, 416. D. R. P. 274260, 1912; abst. J. S. C. I. 1914, **33**, 746; Chem. Zentr. 1914, **85**, I, 2022; Chem. Ztg. 1914, **38**, 592; Kunst. 1914, **4**, 234; Wag. Jahr. 1914, **60**, II, 337; Zts. ang. Chem. 1914, **27**, II, 390. D. R. P. 276013, 1912; abst. C. A. 1915, **9**, 386; J. S. C. I. 1914, **33**, 916; Chem. Zentr. 1914, **85**, II, 370; Chem. Ztg. 1914, **38**, 818; Chem. Ztg. Rep. 1914, **38**, 444; Kunst. 1914, **4**, 271; Wag. Jahr. 1914, **60**, II, 338; Zts. ang. Chem. 1914, **27**, II, 604. D. R. P. 286173, 1912; abst. J. S. C. I. 1915, **34**, 1138; Chem. Zentr. 1915, **86**, II, 450; Chem. Ztg. Rep. 1915, **39**, 328; Kunst. 1915, **5**, 188; Wag. Jahr. 1915, **61**, II, 254; Zts. ang. Chem. 1915, **28**, II, 439. D. R. P. 293261, 1912; abst. C. A. 1917, **11**, 2610; Chem. Zentr. 1916, **87**, II, 361; Chem. Ztg. 1916, **40**, 573; Chem. Ztg. 1916, **40**, 316; Kunst. 1916, **6**, 250. D. R. P. Anm. K-33974, K-33975, 1907 (Addn. to D. R. P. 196730); abst. Chem. Ztg. 1908, **32**, 68, 499. D. R. P. Anm. K-50334, 1912 (Addn. to D. R. P. 203178); abst. Chem. Ztg. 1914, **38**, 454; Kunst. 1914, **4**, 160. Belg. P. 244950; abst. Chem. Ztg. 1912, **36**, 901; Kunst. 1912, **2**, 399.

3. E. P. 8990, 1912; abst. C. A. 1913, **7**, 3113; J. S. C. I. 1913, **32**, 823; Chem. Ztg. 1912, **36**, 807; 1913, **37**, 952; Kunst. 1913, **3**, 415. D. R. P. Anm. K-47775, 1911.

methylamine bisulfate, or the sulfates of diethylamine or toluidine[1]. This firm has described the formation of acetone soluble cellulose acetate by treating the acetone-insoluble modification with acetic acid containing 6% of water in the proportion of one of cellulose acetate to nine of acid, and at 100° until the desired solubility is obtained[2]. Or[3], they allow the vapors from a water bath to enter the acetating bath after the catalysts have been neutralized. It is obvious that the latter two methods are but modifications of the G. Miles partial hydration process.

Dyed cellulose carboxylates (formates, acetates and propionates) are produced when working by the B. Borzykowski patent[4], by introducing the acid dyes in the acidylizing mixture. As proposed by the Chemische Fabrik auf Aktien[5], cellulose is acidylized in the presence of a small

1. D. R. P. 297504, 1912; abst. Chem. Zentr. 1917, **88**, I, 1038; Chem. Ztg. Rep. 1917, **41**, 228; Kunst. 1917, **7**, 239; Wag. Jahr. 1912, **63**, II, 14; Zts. ang. Chem. 1917, **30**, II, 142. See D. R. P. Anm. V-11079, 1912; abst. Kunst. 1921, **11**, 104. D. R. P. 346672, 347817, 1912; Addn. to D. R. P. 297504.

2. D. R. P. 305348, 1912 (Addn. to D. R. P. 297504); abst. Chem. Zentr. 1918, **89**, I, 977; Chem. Ztg. Rep. 1918, **42**, 108; Kunst. 1918, **8**, 260; Wag. Jahr. 1918, **64**, II, 7; Zts. ang. Chem. 1918, **31**, II, 176. See also D. R. P. 303530, 1912; abst. Chem. Zentr. 1918, **89**, I, 499; Kunst. 1918, **8**, 102; Wag. Jahr. 1918, **64**, II, 7.

3. D. R. P. 305884, 1912 (Addn. to D. R. P. 207504); abst. Chem. Zentr. 1918, **89**, I, 236; Chem. Ztg. Rep. 1918, **42**, 151; Kunst. 1918, **8**, 260; Wag. Jahr. 1918, **64**, II, 8; Zts. ang. Chem. 1918, **31**, II, 226.

4. U. S. P. 1041587, 1912; abst. C. A. 1912, **6**, 3518; J. S. C. I. 1912, **31**, 1075; Mon. Sci. 1913, **79**, 110; Chem. Ztg. 1912, **36**, 1425. E. P. 12995, 1912; abst. C. A. 1913, **7**, 3840; J. S. C. I. 1913, **32**, 19; J. Soc. Dyers Col. 1912, **28**, 247; Chem. Ztg. 1913, **37**, 134. F. P. 444588, 1912; abst. J. S. C. I. 1912, **31**, 1075; J. Soc. Dyers Col. 1912, **28**, 332; Chem. Zts. 1912, **36**, 1197; Kunst. 1913, **3**, 15. Aust. P. 60039; abst. Chem. Ztg. 1913, **37**, 834. Belg. P. 246562; abst. Kunst. 1912, **2**, 399. Ital. P. 125696; abst. Chem. Ztg. 1913, **37**, 272. Swiss P. 60510; abst. Chem. Ztg. 1913, **37**, 953. Hung. P. 58767. Russ. P. 26112. D. R. P. Anm. B-63482, 1911; B-65360, 1911; abst .Chem. Ztg. 1912, **36**, 751; 1914, **38**, 987; Kunst. 1912, **2**, 260. For the production of lusterless filaments of cellulose acetate see D. R. P. 262253, 1912; abst. C. A. 1913, **7**, 3414; J. S. C. I. 1913, **32**, 907; Chem. Zentr. 1913, **84**, II, 466; Chem. Ztg. Rep. 1913, **37**, 425; Wag. Jahr. 1913, **59**, II, 443; Zts. ang. Chem. 1913, **26**, II, 524.

5. A. Loose, assignor to Chemische Fabrik auf Aktien (vorm. F. Schering), U. S. P. 1069445, 1913; abst. C. A. 1913, **7**, 3227; J. S. C. I. 1913, **32**, 865; Mon. Sci. 1914, **81**, 39. E. P. 27227, 1912; abst. C. A. 1914, **8**, 1668; J. S. C. I. 1913, **32**, 696; Chem. Ztg. 1913, **37**,

quantity of a sulfate of hydrazine or of hydroxylamine, although F. Paschke[1] recommends the use of copper sulfate as catalyst.

In possible new technical applications for acetated cellulose which were disclosed in 1912, may be mentioned its use to increase the resistance of fish nets[2]; the coating of driving belts[3]; impregnation of canvas for tire covers[4]; imitation engraved or chased metal plates[5]; photographic films[6]; in chromogelatin and similar photographic processes[7]; as a means of indicating decomposition in smokeless powders[8]; the recovery of acetylcellulose solvents[9];

700; Kunst. 1913, **3**, 395. E. P. 27228, 1912; abst. C. A. 1914, **8**, 1668; J. S. C. I. 1913, **32**, 530; Chem. Ztg. 1913, **37**, 76, 528. F. P. 450890, 1912; abst. C. A. 1913, **7**, 3227; J. S. C. I. 1913, **32**, 531; Mon. Sci. 1914, **81**, 6; Rev. Chim. Ind. 1913, **34**, 210; Chem. Ztg. 1913, **37**, 284; Chem. Ztg. Rep. 1913, **37**, 388; Kunst. 1913, **3**, 195. F. P. 452374, 1912; abst. C. A. 1913, **7**, 3663; J. S. C. I. 1913, **32**, 652; Mon. Sci. 1914, **81**, 8; Chem. Ztg. 1913, **37**, 472; Chem. Ztg. Rep. 1913, **37**, 465; Kunst. 1913, **3**, 274. Addn. 17104 to F. P. 452347; abst. J. S. C. I. 1913, **32**, 784; Kunst. 1913, **3**, 416. D. R .P. Anm. C-21388, 1911; C-21994, 1912; abst. Kunst. 1913, **3**, 300. Belg. P. 251010, 251011, 1912; abst. Chem. Ztg. 1913, **37**, 228; Kunst. 1913, **3**, 235. Belg. P. 252882; abst. Kunst. 1913, **3**, 275.

1. Assignor to Safety Celluloid Co., U. S. P. 1082167, 1913; abst. C. A. 1914, **8**, 821; J. S. C. I. 1914, **33**, 72; Mon. Sci. 1914, **81**, 108; Chem. Ztg. Rep. 1914, **38**, 224. E. P. 15868, 1912; abst. C. A. 1913, **7**, 3025; J. S. C. I. 1913, **32**, 192; Chem. Ztg. Rep. 1913, **37**, 273; Kunst. 1913, **3**, 174. Russ. P. Appl. 58459, 1913; abst. Chem. Ztg. 1914, **38**, 203. F. P. 458263, 1913; abst. C. A. 1914, **8**, 225; J. S. C. I. 1913, **32**, 1064; Mon. Sci. 1914, **81**, 55; Chem. Ztg. 1913, **37**, 1093; Chem. Ztg. Rep. 1913, **37**, 133; Kunst. 1913, **3**, 434. Hung. P. Appl. S-6854, 1913; abst. Chem. Ztg. 1913, **37**, 1584.

2. A. van Vriesland, F. P. 452684, 1912; abst. Kunst. 1913, **3**, 475. D. R. P. Anm. Jan. 2, 1912.

3. Soc. Anon. pour l'Exploitation des Procedes Westinghouse-Leblanc, F. P. 437505, 1911. E. P. 1460, 1912.

4. W. Muntz, U. S. P. 1184257, 1916; abst. C. A. 1916, **10**, 1950. E. P. 613, 1912.

5. G. Moncany, E. P. 14537, 1912.

6. F. Thompson, assignor to National Waterproof Film Co., U. S. P. 987092, 1911; abst. C. A. 1911, **5**, 1878. E. P. 20965, 1909. F. P. 406885, 1909.

7. J. Thornton, E. P. 4044, 1912.

8. E. Bouchaud-Praceiq, F. P. 445770, 1912; abst. C. A. 1913, **7**, 1976; Chem. Ztg. Rep. 1913, **37**, 114; J. S. C. I. 1912, **31**, 1203.

9. J. Duclaux, E. P. 2465, 1913; abst. J. S. C. I. 1913, **32**, 82; C. A. 1914, **8**, 2624. U. S. P. 1127871, 1915; abst. C. A. 1915, **9**, 861; Mon. Sci. 1915, **82**, 44. F. P. 439721, 1912; and Addn. 16214, 1912, thereto; abst. J. S. C. I. 1912, **31**, 714; 1913, **32**, 133; Mon. Sci. 1913, **79**, 181; Kunst. 1912, **2**, 333; 1913, **3**, 53. Belg. P. 245532, 1912.

and for the manufacture of transparent cigarette boxes[1]. Preparations of acetylcellulose have also been recommended as dielectrics for electric condensers or for apparatus with condensing action[2]. The acetylcellulose finishing preparation of the Soc. Industrielle des Telephones[3] for coating airplane fabrics or for electric insulation, and the aeroplane waterproofing solution of Gow and St. Armande[4] were also first published in 1912. W. Dixon[5] described the use of acetated starch as a binding agent.

A new class of compounds resulted from disclosures made this year by L. Lilienfeld, in which the hydroxyls of cellulose instead of being replaced by acid radicals as acetic and nitric acids to form esters, are replaced by alkyl radicals as methyl or ethyl, forming cellulose *ethers*. He[6] detailed methods for their preparation and their solubilities in a large number of solvents. The next year[7] improved methods of formation were published, while the following

1. A. and A. Constantin, E. P. 17338, 1912.
2. Siemens-Schuckert-Werke, D. R. P. 282057, 1912 (Addn. to D. R. P. 177667); abst. C. A. 1915, **9**, 2353; Chem. Ztg. Rep. 1915, **39**, 123.
3. F. P. 460915, 1912; abst. C. A. 1915, **9**, 150; J. S. C. I. 1914, **33**, 73; Chem. Ztg. Rep. 1914, **38**, 423.
4. E. P. Appl. 2141, 4957, 4968, 1918; abst. J. S. C. I. 1918, **37**, 111-A, 194-A.
5. E. P. 27491, 1911; abst. J. S. C. I. 1913, **32**, 214.
6. E. P. 12854, 1912; abst. C. A. 1913, **7**, 3839; J. S. C. I. 1913, **32**, 940; Chem. Ztg. 1913, **37**, 1205. F. P. 447974, 1912; abst. J. S. C. I. 1913, **32**, 420; Mon. Sci. 1914, **81**, 3; Chem. Ztg. 1913, **37**, 122; Kunst. 1913, **3**, 195. Belg. P. 254591; abst. Kunst. 1913, **3**, 355. Aust. P. 47237, 1912; abst. Kunst. 1911, **1**, 235. Aust. P. 54719 (Addn. to Aust. P. 47237); abst. Chem. Ztg. 1912, **31**, 975; Kunst. 1912, **2**, 393. Aust. P. 73001; abst. Kunst. 1917, **7**, 222. Aust. P. Appl. 2337, 1912; abst. Chem. Ztg. 1919, **43**, 137. Aust. P. Appl. 2990, 1912; abst. Chem. Ztg. 1913, **37**, 268.
7. L. Lilienfeld, U. S. P. 1188376, 1916; abst. C. A. 1916, **10**, 2145; J. S. C. I. 1916, **35**, 887; Mon. Sci. 1917, **84**, 28; Chem. Ztg. 1916, **40**, 805; Kunst. 1916, **6**, 282. E. P. 6035, 1913; abst. C. A. 1914, **8**, 2947; J. S. C. I. 1914, **33**, 417; Chem. Ztg. 1913, **37**, 472; 1914, **38**, 419; Chem. Ztg. Rep. 1914, **38**, 490; Kunst. 1914, **4**, 345. Belg. P. 254591; abst. Chem. Ztg. 1913, **37**, 567; Kunst. 1913, **3**, 355. Hung. P. Appl. L-3451, 1913; abst. Chem. Ztg. 1919, **43**, 753. Ital. P. 132825, 1913; abst. Chem. Ztg. 1913, **37**, 1334. Norw. P. 27507, 1917; abst. C. A. 1917, **11**, 1748. Span. P. 55104; abst. Chem. Ztg. 1913, **37**, 728. Swiss P. 66512, 1913; abst. Chem. Ztg. 1914, **38**, 1034; Kunst. 1915, **5**, 70, 82.

year (1914)[1] the subject was further broadened by Lilienfeld by publishing commercial processes for their manufacture. The patentee also showed methods of usefulness for filament formation, films manufacture and plastics production[2]. In the application of the cellulose esters in artificial leather manufacture, he also added to our knowledge[3].

In the manufacture of artificial silk and celluloid substitutes, the coupling of cellulose acetate or nitrocellulose with dioxydiphenyldimethylmethane was described by W. Beatty[4], and P. Cattaert[5] called attention to new uses in photography by the utilization of acetylcellulose. A method

1. L. Lilienfeld, "Manufacture of ethers of carbohydrates other than cellulose, such as ethyl-starch," U. S. P. 1350820, 1920 (assigned to The Chemical Foundation); abst. C. A. 1920, **14**, 3251; J. S. C. I. 1920, **39**, 654-A. E. P. 3370, 1914; abst. J. S. C. I. 1916, **35**, 534; Kunst. 1918, **8**, 42. F. P. 468162, 1914; abst. J. S. C. I. 1914, **33**, 958; Mon. Sci. 1916, **83**, 16; Chem. Ztg. 1914, **38**, 651; Chem. Ztg. Rep. 1915, **39**, 69. Aust. P. Appl. 1274, 1913; abst. Chem. Ztg. 1919, **43**, 649. Aust. P. 82866, 1919; abst. Chem. Ztg. 1920, **44**, 877. Ital. P. 140506, 1914; abst. Chem. Ztg. 1914, **38**, 1027.

2. U. S. P. 1217027; abst. C. A. 1917, **11**, 1545; J. S. C. I. 1917, **36**, 383. U. S. P. 1217028, 1917; 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, 1913; 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. Appl. Mar. 16, 1912. Aust. P. 62809, 1913; abst. Chem. Ztg. 1913, **37**, 1499. Hung. P. Appl. L-3294, 1912; abst. Chem. Ztg. 1913, **37**, 11. See also G. Donnersmarck, Ital. P. 126270, 1912. Snowden & Co., Ltd., Ital. P. 122890, 1912.

3. U. S. P. 1140174, 1912; abst. C. A. 1915, **9**, 1856; Kunst. 1915, **5**, 239. Hung. P. Appl. L-3470, 1913; abst. Chem. Ztg. 1913, **47**, 1433. Ital. P. 133188, 1913; abst. Chem. Ztg. 1913, **37**, 1322.

4. U. S. P. 1156969, 1915 (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, 1915; abst. C. A. 1916, **10**, 275; Mon. Sci. 1917, **84**, 28; Kunst. 1916, **6**, 63. U. S. P. 1158961, 1915; abst. C. A. 1916, **10**, 275. U. S. P. 1188356, 1916; 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**, 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, 1912; 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, 147579, 1913; abst. C. A. 1913, **7**, 2127, 2128. D. R. P. Anm. B-68616, 1912; abst. Chem. Ztg. 1914, **38**, 818; Kunst. 1914, **4**, 280.

5. F. P. 441146, 1911; abst. J. S. C. I. 1912, **31**, 845; Kunst. 1912, **2**, 355.

for the formation of acetate plastics was also communicated by Soc. L'Oyonnaxienne[1], and by the Soc. Anon. Le Camphre[2].

G. Eastman patented a plate or films for color photography in 1912[3] in which either nitric or acetic cellulose ester is employed as the transparent support, and the Internationale Cellulose-ester Ges.[4] described the preparation of neutral cellulose acetate solutions. D. Florentin alleged to materially modify the disadvantages of sulfuric acid as a catalyst, by combining small amounts of nitric acid with it[5]. R. Hoemberg[6] and G. Meyer[7] patented methods of formation of acetate plastics, and F. Sammet published his method of formate film formation in which 98% formic acid constitutes the solvent portion[8].

H. Ost and T. Katayama published a study of the comparative acetylation of cellulose, hydrocellulose and alkalized cellulose in 1912[9] using zinc chloride and sulfuric acid, in order to differentiate between cellulose, hydrocellulose and alkalicellulose, the products obtained being tested as to their

1. F. P. 432751, 1911; abst. J. S. C. I. 1912, **31**, 123; Chem. Ztg. 1912, **36**, 223.

2. F. P. 452432, 1912; abst. C. A. 1913, **7**, 3663; J. S. C. I. 1913, **32**, 652; Mon. Sci. 1914, **81**, 52; Chem. Ztg. Rep. 1913, **37**, 465; Kunst. 1913, **3**, 295.

3. U. S. P. 1028337, 1912; abst. C. A. 1912, **6**, 2582.

4. D. R. P. Anm. I-14379, 1912; abst. Chem. Ztg. 1912, **36**, 877; D. R. P. 260984, 1912; abst. C. A. 1913, **7**, 3228; J. S. C. I. 1913, **32**, 748; Chem. Zentr. 1913, **84**, II, 190; Chem. Ztg. 1913, **37**, 628; Chem. Ztg. Rep. 1913, **37**, 388; Kunst. 1912, **2**, 300; 1913, **3**, 273; Wag. Jahr. 1913, **59**, II, 17; Zts. ang. Chem. 1913, **26**, II, 406.

5. F. P. 445798, 1912; abst. Kunst. 1913, **3**, 274; Mon. Sci. 1913, **79**, 143; Chem. Ztg. 1912, **36**, 1296.

6. D. R. P. Anm. H-57941, 1912; abst. Chem. Ztg. 1914, **38**, 182; Kunst. 1914, **8**, 80.

7. Aust. P. Appl. 1793, 1911; abst. Kunst. 1912, **2**, 320; Chem. Ztg. 1912, **36**, 846. Aust. P. 55654, 1912; abst. Chem. Ztg. 1912, **36**, 1253; Kunst. 1913, **3**, 38.

8. D. R. P. Anm. S-37509, 1912; abst. Zts. ang. Chem. 1913, **26**, II, 700. P. Spence & Sons, Ltd., Ital. P. 128759, 128760, 1912.

9. Zts. ang. Chem. 1912, **25**, 1467; abst. C. A. 1913, **7**, 2303; J. C. S. 1912, **102**, i, 680; J. Ind. Eng. Chem. 1912, **4**, 701; J. S. C. I. 1912, **31**, 713; Chem. Zentr. 1912, **83**, II, 1199; Chem. Ztg. Rep. 1912, **36**, 485; Kunst. 1912, **2**, 311; Wag. Jahr. 1912, **58**, II, 560; Phot. Ind. 1912, 1336. See also polemic between H. Ost and A. Eichengruen, Zts. ang. Chem. 1911, **24**, 1304, 1307; abst. J. C. S. 1911, **100**, i, 712.

solubility in alcohol, acetone and chloroform, and the individual fractions as to their rotatory power and acetyl content. H. Ost[1] published a research on the acetolysis of cellulose to dextrose acetate. This subject also formed the dissertation of W. Schliemann[2], while J. Gutsche obtained his Doctorate on the catalytic action by acetylation of starch and cellulose with acetic anhydride[3]. Some experiments on acetylation in ether solution were published by W. Dehn[4].

F. Klein[5] investigated the products obtained by the acetolysis of cellulose by a modification of the method of L. Maquenne and W. Goodwin[6], a lower temperature and less sulfuric acid being employed. The statement of W. Schliemann (see above) that acetates of other bioses than cellobiose result from this acetolysis was not confirmed, nor was glucose pentacetate as described by A. Franchimont[7] found among the products. On the contrary, the regular increase in specific rotation and acetic acid content of the products of the simultaneous acetolysis and hydrolysis of

1. Chem. Ztg. 1912, **36**, 1099; Zts. ang. Chem. 1912, **25**, 1996; Ann. 1913, **398**, 313; abst. C. A. 1913, **7**, 3836; J. C. S. 1913, **102**, i, 446; J. S. C. I. 1913, **32**, 784; Bull. Soc. Chim. 1913, **14**, 1262; Kunst. 1912, **2**, 412; Meyer Jahr. Chem. 1913, **23**, 182.

2. Dissertation, Hannover. Ann. 1911, **378**, 366; abst. C. A. 1911, **5**, 1276; J. C. S. 1911, **100**, i, 179; J. S. C. I. 1911, **30**, 126; Bull. Soc. Chim. 1911, **10**, 1346; Chem. Zentr. 1911, **82**, I, 807; Chem. Ztg. Rep. 1911, **35**, 94; Meyer Jahr. Chem. 1911, **21**, 194; Zts. ang. Chem. 1912, **25**, 771.

3. Dissertation, Heidelberg; abst. Kunst. 1912, **2**, 371.

4. J. A. C. S. 1912, **34**, 1399; abst. C. A. 1913, **7**, 469; J. C. S. 1912, **102**, i, 833; Bull. Soc. Chim. 1913, **14**, 242; Chem. Zentr. 1912, **83**, II, 2056; Meyer Jahr. Chem. 1912, **22**, 198.

5. Zts. ang. Chem. 1912, **25**, 1409; abst. J. S. C. I. 1912, **31**, 713; Chem. Zentr. 1912, **83**, 1196; Chem. Ztg. Rep. 1912, **36**, 532; Kunst. 1912, **2**, 311; C. A. 1913, **7**, 2303; J. C. S. 1912, **102**, i, 679.

6. Bull. Soc. Chim. 1904, **86**, i, 799; abst. Chem. Centr. 1904, **75**, II, 645; Jahr. Chem. 1904, **57**, 1149.

7. Ber. 1879, **12**, 1941; Compt. rend. 1879, **89**, 711, 713, 755; abst. J. C. S. 1881, **40**, 709; Bull. Soc. Ind. Rouen, 1882, **10**, 448; 1883, **11**, 230; Rec. Trav. Chim. 1883, **2**, 239; Jahr. Chem. 1879; **32**, 832.

cellulose, makes it appear that dextrin acetates lying between cellulose acetate and cellobiose acetate are the only intermediate products. E. Worden[1] records an unsuccessful endeavor to increase the range of solvents applicable to the cellulose formates by a partial hydration treatment with a hydroxyl-containing body in a manner similar to those of the corresponding acetates.

The year's work closed with a general summary of the art up to this time published by H. Chauvet[2] and by E. Fischer[3], and a resume of our knowledge of the formylated celluloses by E. Worden and L. Rutstein[4].

In the year 1913, activities seemed to centralize around the two propositions of investigating the possibilities of partial hydration or ripening of the cellulose after acetylation in order to increase the solubility in various fluids, and in attempts to extend the field of useful application in which the solid and fluid cellulose acetate combinations might enter.

In the method of ripening of acetated cellulose as disclosed by the Verein fuer Chemische Industrie in Mainz, the chloroform-soluble ester is heated with small amounts of water until a product soluble in ethyl acetate[5], or in

1. J. S. C. I. 1912, **31**, 1064; abst. C. A. 1913, **7**, 888, 2304; J. C. S. 1913, **104**, i, 19; Mon. Sci. 1913, **78**, 388; Chem. Zentr. 1913, **84**, I, 1105; Meyer Jahr. Chem. 1913, **23**, 182; Zts. ang. Chem. 1913, **26**, II, 302. See also E. Worden, Starch acetate, Kunst. 1913, **3**, 61; abst. C. A. 1913, **7**, 1633; Zts. ang. Chem. 1913, **26**, II, 302. Acetate collodion, Science, 1911, **34**, 256; abst. Zts. ang. Chem. 1912, **25**, 322.

2. Bull. Technologique, May, 1912, No. 5, p. 679. In this connection see also Anon. Sci. Amer. 1912, **107**, 144.

3. Kunst. 1912, **2**, 21; abst. C. A. 1912, **6**, 2314; Chem. Ztg. Rep. 1912, **36**, 307; Wag. Jahr. 1912, **58**, II, 445.

4. Kunst. 1912, **2**, 325; abst. C. A. 1912, **6**, 3329; Chem. Ztg. Rep. 1912, **36**, 562; Zts. ang. Chem. 1913, **26**, II, 302. See also Caout. et Gutta. 1913, **10**, 6897; abst. Kunst. 1913, **3**, 352.

5. E. P. 3849, 1913; abst. C. A. 1914, **8**, 2620; J. S. C. I. 1913, **32**, 940. F. Collischonn and F. Ruppert, U. S. P. 1109512, 1914 (assigned to Verein fuer Chemische Industrie in Mainz); abst. C. A. 1914, **8**, 3502; J. S. C. I. 1914, **33**, 958; Mon. Sci. 1914, **81**, 191; Chem. Ztg. 1914, **38**, 1218; Kunst. 1915, **5**, 177.

acetone or chloroform-alcohol results[1]. V. Pauthonier[2] hydrolyzes with the addition of an anhydrous agent which forms a solvent for the cellulose acetate dissolved in acetic acid, and in passing into combination with the acetic anhydride furnishes the hydroxyl group for the hydrolysis—a somewhat roundabout method. Knoll & Co.[3] treat acetone-insoluble acetylcelluloses with sulfates or bisulfates in the presence of such quantities of water that saponification and hydrolytic disruption of the acetylcellulose is materially retarded. H. Mork hydrolyzed fibrous cellulose acetate by saponification as with dilute ammonia until the desired solubility was obtained[4], or[5], for film formation, superficially saponifying the finished sheet until a solubility in acetone results. In an improvement upon a pre-

1. E. P. 19008, 1913 (void); abst. C. A. 1915, **9**, 377; Chem. Ztg. 1913, **37**, 1215. F. P. 455117, 1913; abst. C. A. 1914, **8**, 573; J. S. C. I. 1913, **32**, 865; Mon. Sci. 1914, **81**, 11; Chem. Ztg. 1913, **37**, 728; Chem. Ztg. Rep. 1913, **37**, 641, 684; Kunst .1913, **3**, 435. Swiss P. 62359, 1913; 66046, 66047 (Addn. to 62359); abst. Kunst. 1915, **5**, 95.

2. F. P. 466009, 1913; abst. C. A. 1915, **9**, 1391; J. S. C. I. 1914, **33**,589; Chem. Ztg. 1914, **38**, 406; Chem. Ztg. Rep. 1914, **38**, 582; Kunst. 1914, **4**, 235. Ital. P. 144105, 1914; abst. Chem. Ztg. 1914, **38**, 1268.

3. E. Knoevenagel (assignor to Knoll & Co.), U. S. P. 1241995, 1917; abst. C. A. 1918, **12**, 223; J. S. C. I. 1917, **36**, 1174; Zts. ang. Chem. 1918, **31**, II, 363. E. P. 2491, 1913; abst. C. A. 1914, **8**, 2482; J. S. C. I. 1914, **33**, 308; Chem. Ztg. 1913, **37**, 262; 1914, **38**, 267; Chem. Ztg. Rep. 1914, **38**, 241; Kunst. 1914, **4**, 359. F. P. 453835, 1913; abst. C. A. 1914, **8**, 248; J. S. C. I. 1913, **32**, 785; Mon. Sci. 1914, **81**, 9; Rev. Chim. Ind. 1913, **24**, 267; Chem. Ztg. Rep. 1913, **37**, 557; Kunst. 1913, **3**, 416. D. R. P. Anm. K-50333, 1912; abst. Kunst. 1913, **3**, 279. D. R. P. 284726, 1912 (Addn. to D. R. P. 203178); abst. C. A. 1916, **10**, 389; Chem. Zentr. 1915, **86**, II, 250; Chem. Ztg. 1915, **39**, 335; Chem. Ztg. Rep. 1915, **39**, 284; Wag. Jahr. 1915, **53**, II, 15; Zts. ang. Chem. 1915, **28**, II, 350. Aust. P. 64085, 1913; abst. Chem. Ztg. 1914, **38**, 278; Kunst. 1914, **4**, 377. Belg. P. 253353, 1913; abst. Chem. Ztg. 1913, **37**, 397; Kunst. 1913, **3**, 355. Ital. P. 131098, 138699, 1913.

4. U. S. P. 1061771, 1913; abst. C. A. 1913, **7**, 2307; J. S. C. I. 1913, **32**, 597; Mon. Sci. 1914, **81**, 23; Chem. Ztg. 1913, **37**, 670; Chem. Ztg. Rep. 1913, **37**, 482; Kunst. 1913, **3**, 436. E. P. 20672, 1910; abst. C. A. 1911, **5**, 2947; J. S. C. I. 1911, **30**, 354. F. P. 416752, 1910; abst. J. S. C. I. 1910, **29**, 1371; Chem. Ztg. 1910, **34**, 1011. (The U. S. P. assigned to Chemical Products Co.)

5. U. S. P. 1074092, 1913; abst. C. A. 1913, **7**, 3839; J. S. C. I. 1913, **32**, 975; Mon. Sci. 1914, **81**, 39; Kunst .1914, **4**, 157. D. R. P. Anm. M-42410, 1910.

viously described process[1], Chemische Fabrik auf Actien[2] hydrolyze, not with an aromatic amine, but salts which are soluble in aromatic amines, or which are decomposed by such with the formation of a salt, as for example the salts of ammonia, hydrazine, alkylamine, pyridine, quinoline, piperidine, and ethylenediamine, or of the chlorides of magnesium, zinc or zinc ammonium. In examples given, the use of aniline, *o*-toluidine, with or without alcohol and benzene are detailed.

As solvents for cellulose formate, mono- or polyhydric phenols[3], or chloral hydrate or alcoholate were brought forward by the Internationale Celluloseester Ges.[4]. In the further use of sulfuryl chloride as catalyst in cellulose acetation, A. Jaquet[5] described a process whereby as small amounts as 0.5% (based on the cellulose) are employed.

In attempts to utilize new solvents and solvent combinations, W. Lindsay patented the use of triphenyl phosphate, urea, acetylene tetrachloride and acetone[6], alcohol

1. E. P. 27227, 1912; abst. C. A. 1914, **8**, 1668; J. S. C. I. 1913, **32**, 696; Kunst. 1913, **3**, 395. Belg. P. 252882, 1913; abst. Kunst. 1913, **3**, 275; Chem. Ztg. Rep. 1913, **37**, 336. D. R. P. Anm. C-22781, C-23703 (Addns. to D. R. P. Anm. C-21994, 1912); abst. Chem. Ztg. 1913, **37**, 1321; Kunst. 1913, **3**, 420.

2. E. P. 2178, 1913 (Addn. to E. P. 27227, 1912); abst. C. A. 1914, **8**, 2620; J. S. C. I. 1913, **32**, 975; Chem. Ztg. 1913, **37**, 1264; Kunst. 1914, **4**, 15. F. P. Addn. 17104 1913, to F. P. 452374, 1912; abst. J. S. C. I. 1913, **32**, 784; Kunst. 1913, **3**, 416. F. P. 452374, 1912; abst. C. A. 1913, **7**, 3663; J. S. C. I. 1913, **32**, 784; Mon. Sci. 1914, **81**, 8; Chem. Ztg. Rep. 1913, **37**, 523; Kunst. 1913, **3**, 274.

3. D. R. P. 265852, 1913; abst. C. A. 1914, **8**, 573; J. S. C. I. 1913, **32**, 1104; Chem. Zentr. 1913, **84**, II, 1635; Chem. Ztg. 1913, **37**, 1186; Chem. Ztg. Rep. 1913, **37**, 645; Chem. Zts. 1914, **13**, No. 3348; Wag. Jahr. 1913, **59**, II, 447; Zts. ang. Chem. 1913, **26**, II, 700.

4. D. R. P. 265911, 1913; abst. C. A. 1914, **8**, 573; J. S. C. I. 1913, **32**, 1104; Chem. Zentr. 1913, **84**, II, 1635; Chem. Ztg. Rep. 1913, **37**, 645; Chem. Zts. 1914, **13**, No. 3351; Kunst. 1913, **3**, 474; Wag. Jahr. 1913, **59**, II, 447; Zts. ang. Chem. 1913, **26**, II, 700. See also D. R. P. 151918, 189703, 220228.

5. E. P. 29882, 1913 (void); abst. Chem. Ztg. 1914, **38**, 142; Chem. Ztg. Rep. 1915, **39**, 361.

6. U. S. P. 1050065, 1913; 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, p. 25. F. P. 415517, 1910; 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.

being sometimes added[1]; or camphor with either methyl[2] or ethyl alcohols[3]. H. Dreyfus discussed the value of glyceryl benzoate as a plastifying body[4]; F. Lehmann[5] advocated coumarone resin as a plastic, and Chemische Werke vorm. Dr. H. Byk[6] described combinations of nitrocellulose or acetylcellulose with ethyl lactate, toluene or xylene, ethyl lactate and xylene being claimed as a satisfactory substitute for amyl acetate. A. Du Bosc[7] gave a resume of the solvents and plastifiers which had been proposed up to this time (1913) as useful adjuncts to the acetated celluloses.

In the extension of technical applications, several meritorious processes were detailed. An artificial wood was described by McTavish, Ramsay & Co.[8] as resulting when finely ground sawdust is incorporated with cellulose acetate,

1. U. S. P. 1067785, 1913; abst. C. A. 1913, **7**, 3025; J. S. C. I. 1913, **3**, 823; Mon. Sci. 1914, **81**, 38; Chem. Ztg. 1913, **37**, 952; Chem. Ztg. Rep. 1913, **37**, 523; Kunst. 1913, **3**, 455.

2. U. S. P. 1076215, 1913; abst. C. A. 1914, **8**, 246; J. S. C. I. 1913, **32**, 1104; Mon. Sci. 1914, **81**, 105; Chem. Ztg. 1913, **37**, 1405.

3. U. S. P. 1076216, 1913; abst. J. S. C. I. 1913, **32**, 1104; C. A. 1914, **8**, 247; Mon. Sci. 1914, **81**, 105; Chem. Ztg. 1913, **37**, 1405.

4. F. P. 461544, 1913; abst. C. A. 1914, **8**, 3859; J. S. C. I. 1914, **33**, 196; Chem. Ztg. Rep. 1914, **38**, 349; Kunst. 1914, **4**, 137.

5. F. P. 468082; abst. Kunst. 1915, **5**, 56. F. P. 469925, 1914; abst. J. S. C. I. 1915, **34**, 25; Mon. Sci. 1916, **83**, 72; Chem. Ztg. 1914, **38**, 880. F. Lehmann and J. Stocker, D. R. P. Anm. L-36336, 1913; 1915, **34**, 187; Chem. Ztg. 1914, **38**, 1010. Belg. P. 266272, 1914; abst. Chem. Ztg. 1914, **38**, 863. Aust. P. Appl. 3130, 1914; abst. Chem. Ztg. 1915, **39**, 730. Hung. P. Appl. L-3731, 1914; abst. Chem. Ztg. 1915, **39**, 55. D. R. P. Anm. L-40529; abst. Chem. Ztg. 1914, **38**, 880. F. Lehmann and J. Stocker, D. R. P. Anm. L-36336, 1913; abst. Chem. Ztg. 1914, **38**, 651.

6. E. P. 25182, 1913 (void). F. P. 464617, 1913; abst. C. A. 1914, **8**, 3364; J. S. C. I. 1914, **33**, 557; Mon. Sci. 1916, **83**, 71. Belg. P. 261693, 1913; abst. Chem. Ztg. 1914, **38**, 36; Kunst. 1914, **4**, 378. D. R. P. Anm. C-23460, 1912; abst. Chem. Ztg. 1915, **39**, 654. Aust. P. Appl. 9194, 1913 (Addn. to Aust. P. 69785); abst. Chem. Ztg. 1916, **40**, 178. See Aust. P. 69785 (nitrocellulose lacquers); abst. Kunst. 1916, **6**, 281. For the manufacture of methyl ,ethyl etc. lactates see E. P. 11741, 1913; abst. C. A. 1914, **8**, 3618; J. S. C. I. 1914, **33**, 375. Russ. P. Appl. 58096, 1913; abst. Chem. Ztg. 1914, **38**, 182.

7. Caout. et Gutta. 1913, **10**, 7011; abst. Kunst. 1913, **3**, 352.

8. McTavish, Ramsay & Co., and A. Ramsay, E. P. 7038, 1913; abst. C. A. 1914, **8**, 2943; J. S. C. I. 1914, **33**, 356; Kunst. 1914, **4**, 237.

while a process for the stiffening of hats was patented[1] where the crown is impregnated with acetylcellulose. The solvent combination of the Act. Ges. fuer Anilin Fabrikation[2] comprises tetrachlorethane, methyl or ethyl alcohol, and amyl alcohol. In the manufacture of splints and body supports[3], or artificial limbs, ears or noses[4] absorbent material as lint coated or saturated with cellulose acetate and rendered pliable as with castor oil, has been brought forward, while Tondl & Co.[5] waterproof collars, cuffs and shirt fronts by means of acetylcellulose solutions[6].

W. Plinatus prepares solid or viscous solutions of uninflammable cellulose esters by admixture of india rubber or gelatin suitably hardened[7]; Y. Charuel[8] combined paper pulp with acetylcellulose in acetone; the H. Belnisch lacquer[9] involved the use of high boiling solvents with cellulose esters; while the playing ball composition of F. Khittl[10] in one form, requires the use of viscose or acetylcellulose

1. Maysers Hutfabrik, D. R. P. 273979, 1913; abst. C. A. 1914, **8**, 3124; Chem. Ztg. Rep. 1914, **38**, 350. See also D. R. P. 272098, 1912; abst. C. A. 1914, **8**, 2813; Chem. Ztg. Rep. 1914, **38**, 291.

2. E. P. 21015, 1913; abst. C. A. 1915, **9**, 730; J. S. C. I. 1914, **33**, 350. F. P. 461058, 1913; abst. J. S. C. I. 1914, **33**, 20; Mon. Sci. 1914, **81**, 125. Belg. P. 259277, 1913; abst. Kunst. 1914, **4**, 238. Belg. P. 265559, 1914; abst. Chem. Ztg. 1914, **38**, 847. Swiss P. 66488, 1913; abst. Chem. Ztg. 1914, **38**, 1034; Kunst. 1919, **9**, 189.

3. J. Peck, E. P. 23777, 1912; abst. J. S. C. I. 1913, **32**, 1006. E. P. 2425, 1913; abst. C. A. 1914, **8**, 2624.

4. W. Longmate, E. P. 3991, 1913.

5. E. P. 15782, 1913; abst. C. A. 1915, **9**, 156; Kunst. 1915, **5**, 129.

6. For waterproofing collars, etc., by means of nitrocellulose see "Technology of Cellulose Esters," 1921, **1**, 2706-2708.

7. E. P. 25449, 1911; abst. Kunst. 1914, **4**, 286. E. P. 25805, 1911; abst. C. A. 1913, **7**, 1627; J. S. C. I. 1912, **31**, 1139; Chem. Ztg. Rep. 1913, **37**, 51. E. P. 16940, 1913; abst. J. S. C. I. 1915, **34**, 793; Chem. Ztg. 1915, **39**, 532. F. P. 450967, 1912; abst. J. S. C. I. 1913, **32**, 545; Kunst. 1914, **4**, 286. F. P. 476991, 1914; abst. J. S. C. I. 1916, **35**, 597; Mon. Sci. 1916, **83**, 86. Russian P .Appl. 59594, 1913; abst. Chem. Ztg. 1914, **38**, 763.

8. F. P. 463156, 1913; abst. C. A. 1914, **8**, 2817; J. S. C. I. 1914, **33**, 417; Mon. Sci. 1915, **82**, 64; Chem. Ztg. Rep. 1914, **38**, 301.

9. D. R. P. 279638, 1913; abst. C. A. 1915, **9**, 1254; Chem. Ztg. Rep. 1914, **38**, 561; Kunst. 1914, **4**, 369; Wag. Jahr. 1914, **60**, II, 457; Zts. ang. Chem. 1914, **27**, II, 733.

10. E. P. 680, 1913.

as a coating material. The Gubinol Ges.[1] prepare sheet metal foil for imprinting, by forming thereon a thin mirror-like surface film of cellite (acetylcellulose) or cellophane (viscose), and Balland & Co.[2] coats gelatin or viscose film with cellulose acetate solution to diminish the permeability. The Verein fuer Chemische Industrie in Mainz[3] and E. Dammann[4] both independently described new methods for artificial silk formation, in the latter process, the filaments being formed directly from the primary cellulose acetate solutions. In aviation and aeronautics, M. Bouffort[5] renders the airplane wings less visible by a composition having a cellulose acetate base, while S. v. Petroczy[6] has described a similar method.

The interposition of a cellulose ester sheet between two layers of glass to diminish their shattering upon being broken, first attempted with the nitric esters[7], was extended to the use of cellulose acetate for this purpose by

1. D. R. P. 283746, 1913; abst. C. A. 1915, **9**, 2442; Chem. Ztg. Rep. 1915, **39**, 160; Wag. Jahr. 1915, **61**, II, 374; Zts. ang. Chem. 1915, **28**, II, 276.

2. F. P. 457925, 1913; abst. J. S. C. I. 1913, **32**, 1033; Kunst. 1913, **3**, 476.

3. D. R. P. Anm. V-11816, 1913 (Addn. to D. R. P. Anm. V-11802); abst. Chem. Ztg. 1918, **42**, 554.

4. E. P. 13872, 1914; abst. J. S. C. I. 1916, **35**, 734; Kunst. 1916, **6**, 282. F. P. 473126, 1914; abst. J. S. C. I. 1915, **34**, 546; Mon. Sci. 1917, **84**, 23. D. R. P. 287073, 1913; abst. C. A. 1916, **10**, 2047; Chem. Zentr. 1915, **86**, II, 732; Chem. Ztg. 1915, **39**, 638; Chem. Ztg. Rep. 1915, **39**, 407; Kunst. 1915, **5**, 225; Wag. Jahr. 1915, **61**, II, 253; Zts. ang. Chem. 1915, **28**, II, 565. D. R. P. Anm. D-29058, 1913; abst. Chem. Ztg. 1914, **38**, 1219; Kunst. 1914, **4**, 396. J. Duclaux, Ital. P. 132188, 1913.

5. F. P. 470897, 1913; abst. J. S. C. I. 1915, **34**, 173.

6. E. P. 12804, 1913.

7. The interposition of a nitrocellulose film between two sheets of glass has been patented by the following: E. Benedictus, E. P. 1790, 1910; abst. C. A. 1911, **5**, 2315; J. S. C. I. 1910, **29**, 818. E. P. 10293, 1911; abst. C. A. 1912, **6**, 2828; J. S. C. I. 1911, **30**, 1059; Kunst. 1912, **2**, 76. E. P. 10324, 1911; abst. C. A. 1912, **6**, 2828; J. S. C. I. 1911, **30**, 1059; Kunst. 1912, **2**, 76. E. P. 17549, 1912; abst. Kunst. 1913, **3**, 454. F. P. 445135, 1912; abst. Kunst. 1913, **3**, 454. Aust. P. 59986; abst. Kunst. 1913, **3**, 454. S. Goldreich, C. McKerrow and Splinterless Anti-Mist Glass Syndicate, Ltd., E. P. 111539, 1916; abst. C. A. 1918, **12**, 986; J. S. C. I. 1918, **37**, 58A. W. Lyttleton and Triplex Safety Glass Co., E. P. 15366, 15367, 15368, 1913; abst. C. A. 1915, **9**, 137. L. Mascart, U. S. P. 1342267, 1342268, 1912; abst. C. A. 1920, **24**, 2247; J. S. C. I. 1920, **39**, 519A.

F. Paschke[1]. C. Dreyfus showed that by impregnating textile fabrics with cellulose acetate in the stretched condition of the fabric, an exceedingly taut surface is produced when the lacquer is dry, the degree of tautness being modified by the use of softening agents in conjunction with the cellulose ester[2]. The acetylcellulose lacquer of this investigator[3] is produced for the above purpose. P. Röder and B. Raabe[4] and also V. Ottorepetz[5] described the formation of artificial sponge. In the first method, an acetate lacquer with sugar, salt or other water-soluble material is made and the solvent evaporated, when the mass is made porous by soaking in water when the water-soluble filler is removed. The latter method involves the application of the same principle. Whereas the coating of cigar tips with cellulose acetate has been described (see p. 367, n. 2). L. Riley[6] alleges to obtain peculiarly desireable results in preventing the sticking of cigarettes to the lips by coating the edges of the paper with an acetate lacquer. For cleaning and renewing celluloid and acetylcellulose articles, A. Peuschel[7] has described the use of "English sulfuric acid," the

1. E. P. 15880, 1913; abst. Kunst. 1916, **6**, 27.
2. E. P. 100180, 1916; abst. J. S. C. I. 1916, **35**, 887.
3. D. R. P. Anm. D-29692, 1913 (withdrawn); abst. Chem. Ztg. 1914, **38**, 35; Kunst. 1914, **4**, 20; 1921, **11**, 5.
4. D. R. P. 280111, 1913; abst. C. A. 1915, **9**, 1378; Chem. Ztg. Rep. 1914, **38**, 582. F. P. 463498, 1913; abst. C. A. 1914, **8**, 3225; Kunst. 1914, **4**, 174. Aust. P. Appl. 8607, 1913 (Addn. to Aust. P. 63556; abst. C. A. 1914, **8**, 3354; Chem. Ztg. Rep. 1913, **37**, 394. Aust. P. 63556; abst. Kunst. 1914, **4**, 195. Aust. P. 67697, 69736. Belg. P. 261288; abst. Kunst. 1914, **4**, 393. Swiss P. 67258; abst. Kunst. 1915, **5**, 56.
5. E. P. 23196, 1913; abst. C. A. 1915, **9**, 956; J. S. C. I. 1914, **33**, 858.
6. E. P. 28490, 1913; 24777, 1914.
7. E. P. 18105, 1913; abst. C. A. 1915, **9**, 377; J. S. C. I. 1914, **33**, 20; Kunst. 1914, **4**, 194. F. P. 461121, 1913; abst. J. S. C. I. 1914, **33**, 196; Kunst. 1914, **4**, 155. D. R. P. Anm. P-31300, 1913; abst. Chem. Ztg. 1913, **37**, 1384; Kunst. 1913, **3**, 439. D. R. P. 270580, 1913; abst. C. A. 1914, **8**, 2252; Chem. Ztg. Rep. 1914, **38**, 133; Kunst. 1914, **4**, 155; Wag. Jahr. 1914, **60**, II, 466; Zts. ang. Chem. 1914, **27**, II, 376. Aust. P. Appl. 499, 1913; abst. Chem. Ztg. 1914, **38**, 50. Aust. P. 65040, 1914; abst. Chem. Ztg. 1914, **38**, 651; Kunst. 1914, **4**, 274. Belg. P. 259019, 1913; abst. Kunst. 1914, **4**, 238; Chem. Ztg. 1913, **37**, 1265. Swiss P. 65741 ,1913; abst. Chem. Ztg. 1914, **38**, 789.

films or other articles being immersed in the acid for a short time, washed and dried.

In the combination of L. Nottelle and R. Heraud[1] fats and oils are combined with the nitrates or acetates of cellulose and then treated with sulfur chloride to induce partial vulcanization. The iridescent films of A. Stiebel originally produced with gelatin[2] and bismuth oxychloride (BiOCl) was modified so that the gelatin was replaced by acetylcellulose as being less water soluble[3].

H. Dreyfus carried our knowledge of the alkyl celluloses (cellulose ethers) a step further[4] by describing new methods for their preparation in commercial quantities.

In an investigation on the hydrolysis and acetolysis of cellulose by H. Ost, it was found that neutral cellulose hydrates may be heated to 120° without decomposition, and that cellulose is completely dehydrated by heating in a toluene drying oven to a maximum of 125°. Elementary analysis is not sufficiently decisive enough to distinguish between cellulose and hydrocellulose. The products of cellulose acetolysis were studied in detail, from which it is concluded that the cellulose molecule is built up of dextrose radicles[5]. In an inaugural dissertation by H. Muschner[6], new data was communicated on cellulose formate, acetate,

1. F. P. 445638, 1911; abst. J. S. C. I. 1913, **32**, 35; Kunst. 1913, **3**, 474; 1914, **4**, 38.
2. D. R. P. 231030, 1909; abst. C. A. 1912, **6**, 1717; Chem. Ztg. Rep. 1911, **35**, 184; Wag. Jahr. 1911, **57**, II, 561.
3. D. R. P. 267370, 1913 (Addn. to D. R. P. 231030); abst. C. A. 1914, **8**, 1711; Chem. Ztg. Rep. 1914, **38**, 44.
4. F. P. 462274, 1912; abst. C. A. 1914, **8**, 3859; J. S. C. I. 1914, **33**, 248; Chem. Ztg. 1913, **37**, 1601; Chem. Ztg. Rep. 1914, **38**, 349.
5. Chem. Ztg. 1912, **36**, 1099; Zts. ang. Chem. 1912, **25**, 1996; Ann. 1913, **398**, 313; abst. C. A. 1913, **7**, 3836; J. C. S. 1913, **104**, i, 446, 833; Vers. deut. Naturf. u. Aerzte, 1913, 124; J. S. C. I. 1913, **32**, 784; J. Soc. Dyers, 1912, **28**, 369; Bull. Soc. Chim. 1913, **14**, 1262; Chem. Zentr. 1913, **84**, II, 1290; Kunst. 1913, **3**, 352.
6. Dissertation, Berlin, 1913. See also O. Hauser and H. Muschner, Zts. ang. Chem. 1913, **26**, 137; abst. J. S. C. I. 1913, **32**, 357; Chem. Zentr. 1913, **84**, I, 1412; J. Soc. Dyers Col. 1913, **29**, 194; Kunst. 1913, **3**, 330; C. A. 1913, **7**, 2854; J. C. S. 1913, **104**, i, 363.

benzoate, and chlorbenzoate. A general review of the art to date (1913) was published by G. Noyer[1].

The following year (1914) saw a determined effort to minimize the drastic action of sulfuric acid by the use of other catalysts, a further search for suitable solvents and high boiling combinations, and an increase in endeavors to replace the better known cellulose nitrates by cellulose acetate, in those industrial fields where diminished inflammability was of prime importance.

Along lines of refinement in methods of manufacture should be mentioned the partial solution process of the Society of Chemical Industry in Basle[2], in which the cellulose is acetylated below 20° with acetic anhydride until a jelly results, the idea being to obtain an ester of high viscosity, sulfuryl chloride being the catalyst specified. The method as advocated by the Fabriek van Chemischen Producten[3] in which acetylsulfuric acid[4] is employed involves the hydrolysis with 10% sulfuric acid, the product obtained being highly viscous in acetone, and capable of withstanding 200° without decomposition. E. Wagner[5] prefers a two-stage esterification, in which partially acetylated cellulose is treated with somewhat less than double its weight of acetic

1. Caout. et Gutta. 1913, **10**, 6875; abst. Kunst. 1913, **3**, 352; C. A. 1913, **7**, 2303.

2. E. P. 21016, 1914; abst. J. S. C. I. 1916, **35**, 39; Kunst. 1916, **6**, 162, 203. F. P. 476383, 1914; abst. C. A. 1916, **10**, 966; J. S. C. I. 1916, **35**, 41.

3. F. P. 470384, 1914; abst. Rev. gen. mat. col. 1916, 34; Kunst. 1917, **7**, 239. For the manufacture of formic acid, see G. Bredig and S. Carter, D. R. P. 339946, Addn. to D. R. P. 283895.

4. N. V. Fabriek van Chemische Producten, F. P. 461539, 1913; abst. C. A. 1914, **8**, 2604; J. S. C. I. 1914, **34**, 219; Mon. Sci. 1914, **81**, 121; Chem. Ztg. Rep. 1914, **38**, 252. Belg. P. 352413.

5. D. R. P. 299181, 1914; abst. J. S. C. I. 1920, **39**, 400-A; Chem. Zentr. 1920, **91**, II, 536; Kunst. 1920, **10**, 68; Paper, 1921, **27**, No. 20, p. 29. Vereinigte f. Chemische Industrie (Swiss P. 62359, 66046, 66047) prepare a cellulose acetate soluble in ethyl acetate. Badische A. & S. F. (Swiss 69960) a plastic of cellulose acetate and acetyldicyclohexylamine. Societe Chimique des Usines du Rhone (Swiss 68966; F. P. 473399, and Addn. 22587) process for acetyl cellulose production. W. Plinatus (Swiss 95376, 95377) a method of gelatinizing acetylated cellulose. E. Heusch and J. Paisseau (F. P. 471581) details of mother-of-pearl manufacture from cellulose acetate.

anhydride, whereby the insoluble acetyl compounds are converted into higher acetylated products, directly soluble in acetone, the final ester containing about 61% of combined acetic acid.

The Societe Chimique des Usines du Rhone had previously described the acetylation of cellulose using 5% sulfuric acid as catalyst (see p. 412, n. 1), or acetic anhydride vapors (see p. 399, n. 4). Additional processes were shown in 1914, involving the use of trioxymethylene[1], or methylene sulfate[2], as catalysts; the preliminary dehydration of the cellulose by soaking in acetic acid and anhydride[3]; nitric acid in small amounts being added to the reaction mixture[4].

The Verein fuer Chemische Industrie in Mainz[5] claim that a particularly good acetate can be obtained by acetylating *dry* cellulose, care being taken that a considerable ex-

1. J. Koetschet and M. Theumann (assignors); U. S. P. 1216462, 1917; abst. C. A. 1916, **10**, 1301; J. S. C. I. 1917, **36**, 383; Mon. Sci. 1918, **85**, 4. E. P. 7773, 1915; abst. C. A. 1916, **10**, 3160; J. S. C. I. 1916, **35**, 302; Kunst. 1916, **6**, 162; 1917, **7**, 283; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 138. F. P. 477620, 1914; abst. J. S. C. I. 1916, **35**, 357; Mon. Sci. 1916, **83**, 87. Swiss P. 71695, 1915; abst. C. A. 1916, **10**, 2637. See H. Dreyfus, India P. 1601, 1914.

2. U. S. P. 1191439, 1916; abst. C. A. 1916, **10**, 2298; J. S. C. I. 1916, **35**, 924; Mon. Sci. 1917, **84**, 29; Kunst. 1917, **7**, 9. E. P. 10822, 1915; abst. C. A. 1917, **11**, 209; J. S. C. I. 1915, **34**, 1086; Kunst. 1916, **6**, 73. F. P. 478436, 1914; abst. C. A. 1916, **10**, 2299; J. S. C. I. 1916, **35**, 1009; Mon. Sci. 1916, **83**, 88; Kunst. 1918, **8**, 46; Zts. Farbenind. 1918, **16**, No. 11/12, p. 48. Swiss P. 77663, 1915; abst. Kunst. 1919, **9**, 9.

3. U. S. P. 1258913, 1918; abst. C. A. 1918, **12**, 1420; J. S. C. I. 1918, **37**, 265-A; Mon. Sci. 1918, **85**, 51. E. P. 13696, 1914; abst. C. A. 1915, **9**, 3358; J. S. C. I. 1915, **34**, 606; Chem. Ztg. 1914, **38**, 959. F. P. 473399, 1914; abst. J. S. C. I. 1915, **34**, 488; Mon. Sci. 1916, **83**, 81; Chem. Ztg. 1915, **39**, 380; 1916, **40**, 95; Kunst. 1918, **8**, 44; Zts. Farben-Ind. 1918, **16**, No. 11/12, p. 47. D. R. P. Anm. S-39408, 1913; abst. Chem. Ztg. 1916, **40**, 463. Swiss P. 68996, 1914; abst. Kunst. 1915, **5**, 177.

4. U. S. P. 1286025, 1918; abst. C. A. 1919, **13**, 261; J. S. C. I. 1919, **38**, 102-A. E. P. 8046, 1915; abst. C. A. 1916, **10**, 3159; J. S. C. I. 1916, **35**, 39; Kunst. 1917, **7**, 84; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 138. Addn. 20072, 1915, to F. P. 473399; abst. C. A. 1916, **10**, 2299; J. S. C. I. 1916, **35**, 1106. Swiss P. 71991, 1915; abst. Kunst. 1916, **6**, 173. D. R. P. Anm. S-42494; abst. Chem. Ztg. 1916, **40**, 554; Kunst. 1916, **6**, 164.

5. E. P. 9266, 1914; abst. C. A. 1915, **9**, 2980; J. S. C. I. 1915, **34**, 868; Chem. Ztg. Rep. 1914, **38**, 608. D. R. P. 303018; abst. Chem. Ztg. 1917, **41**, 874.

cess of acetic anhydride is present to overcome the small amounts of water normally present in glacial acetic acid. R. Adler[1], E. de Haen[2] and W. Ramsay and S. Lewis[3] also disclosed new variations in the esterification of cellulose.

In the field of cellulose acetate solvents and plastifying bodies are to be included the ethylidene and methylene chlorhydrins as examples of suitable alkyl and alkylidene esters of chlorhydrins[4]; and cyclohexanone or methylcyclohexanone in conjunction with ethyl acetate[5]. As combinations for the formate, acetate, butyrate and benzoate of cellulose, polymers of isoprene are specified[6], which are formed in a certain stage in the manufacture of synthetic rubber, and which are soluble in acetone and in methyl acetate. J. Hardcastle and A. Taylor[7] have described a varnish for the treatment of fabrics composed of cellulose acetate, benzene, trichlorethylene and chloroform, to which resorcinol diacetate (see p. 374, n. 3) is added for increased flexibility.

The cellulose acetates and their solvents for the production of lacquers and varnish coatings have been reviewed by L. Clement and C. Riviere[8]. It has been found necessary to restrict the use of tetrachlorethane on account of its toxic

1. D. R. P. Anm. A-25155, 1913; abst. Chem. Ztg. 1914, **38**, 1198.
2. D. R. P. Anm. H-67436, 1914; abst. Chem. Ztg. 1916, **40**, 152.
3. E. P. 22718, 1914. For the manufacture of acetylacetic ether from acetaldehyde, see Consortium fuer Elektrochemische Industrie, D. R. P. 318898.
4. Chem. Fabrik von Heyden A.-G., D. R. P. 288267, 1914; abst. C. A. 1916, **10**, 2299; J. S. C. I. 1916, **35**, 356; Chem. Zentr. 1915, **86**, II, 1037; Chem. Ztg. 1915, **39**, 746; Chem. Ztg. Rep. 1915, **39**, 467; Wag. Jahr. 1915, **61**, II, 368; Zts. ang. Chem. 1915, **28**, II, 646; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 139.
5. Badische Anilin & Soda Fabrik, E. P. 14042, 1914; abst. C. A. 1915, **9**, 3359; J. S. C. I. 1915, **34**, 956.
6. Compagnie Generale des Etablissements Pathe Freres, F. P. 475351, 1914; abst. J. S. C. I. 1916, **35**, 73; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 308.
7. E. P. 13100, 1914; abst. C. A. 1915, **9**, 3136; J. S. C. I. 1915, **34**, 146.
8. Bull. Soc. Encour. 1914, **121**, 187; abst. C. A. 1915, **9**, 1253; J. S. C. I. 1915, **34**, 75; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 193. Bull. soc. d'encour. ind. nat. 1914, **121**, 187.

properties[1], and with a realization of this fact, there is evident increased stimulation in endeavors to find suitable solvents of wide applicability. A fabric for aviation purposes of indistinct visibility is said to result by applying cellulose acetate solution in which is incorporated *b*-naphthol, *b*-naphthol ethyl ether and benzenesulfonamide[2]. The use of amyl alcohol in conjunction with acetone has been proposed as an efficient substitute for tetrachlorethane[3]. The "La Solvea"[4] describe acetylcellulose solution applicable for lacquering.

In new technical applications described and patented as having been brought forth this (1914) year, are to be included the cement for joining portions of moving picture films formed of celluloid, acetylcellulose, acetone, chloroform, glacial acetic acid and amyl acetate[5]; the cellulose acetate coated viscose sheets of P. Lagrange[6]; the acetylcellulose varnish composition of J. Aylsworth[7] containing a dehydrated phenol resin in acetylene tetrachloride; and the coating of leather and skins with celluloid or amyl acetate as brought forth by D. MacDonald[8]. A mixture of pentachlorethane and acetone with acetylcellulose for the manufacture of relatively thin sheets and films is the novelty in the D. Reid process[9], while a process for producing woven

1. Lancet, 1915, **188**, 544; abst. J. S. C. I. 1915, **34**, 508. For cellon varnish see Elektrotechn. Zts. 1916, **37**, 109.

2. Leduc, Heitz & Co., and The British Emaillite Co., E. P. 1049, 1914; abst. J. S. C. I. 1915, **34**, 867.

3. A.-G. fuer Anilinfabrikation, F. P. 461058, 1913; abst. J. S. C. I. 1914, **33**, 20; 1915, **34**, 75; Mon. Sci. 1914, **81**, 125.

4. Societe Anonyme par Actions "La Solvea," D. R. P. Anm. S-42073, 1914; abst. Kunst. 1914, **4**, 384.

5. A. Tessler, assignor to New Jersey Patent Co., U. S. P. 1122554, 1914; abst. C. A. 1915, **9**, 516; Mon. Sci. 1915, **82**, 45; Kunst. 1915, **5**, 176.

6. F. P. 463613, 1912; abst. C. A. 1914, **8**, 2805; Chem. Ztg. Rep. 1914, **38**, 302; Kunst. 1914, **4**, 294.

7. U. S. P. 1094830, 1914; abst. C. A. 1914, **8**, 2268; J. S. C. I. 1914, **33**, 604; Mon. Sci. 1914, **81**, 146.

8. E. P. 714, 1914; abst. C. A. 1915, **9**, 1856; J. S. C. I. 1915, **34**, 239. L. Lilienfeld, D. R. P. 246443, combines cellulose acetate, rubber and wool oil.

9. U. S. P. 1095999, 1914 (assigned to Eastman Kodak Co.); abst. C. A. 1914, **8**, 2124; J. S. C. I. 1914, **33**, 640; Mon. Sci. 1914, **81**, 146.

effects in printing was disclosed in this year (1914) in which cellulose derivatives as the acetate dissolved in suitable solvents, are printed on the tissue by means of an engraved roller[1].

M. Dickert[2] described a process for waterproofing by means of balata or caoutchouc followed by cellulose acetate; while F. Laarmann[3] makes a vulcanized, highly porous or foam-like mass of rubber, cellulose acetate or nitrocellulose by forming a foam with a solution of the material with a compressed gas as nitrogen in a closed receptacle, then evaporating the solvent and liberating the gas.

The H. Chalmers waterproof cement first described this (1914) year, is formed of cellulose acetate dissolved in acetone and chloroform and then mixed with a small amount of phenol and castor oil, and is claimed to be especially useful also for leather belting[4]. W. Vieweg[5] described new methods of artificial silk manufacture from cellulose acetate, while J. Bock[6] and J. Paisseau[7] detailed the application of acetylcellulose or nitrocellulose in the formation of artificial pearls. G. Heyl[8] forms a tire fabric wholly or partially from acetylcellulose yarns which may be spun from threads or filaments of the material, and covered with a winding of cotton.

The principle of the process of the Anhydat-Leder-Werke Akt.-Ges. and K. Haring for introducing molten material of considerable viscosity into prepared skin and

1. Societe des Manufactures N. N. Konchine, F. P. 469371, 1914; abst. J. S. C. I. 1915, **34**, 26.
2. D. R. P. 302542, 1914; abst. Chim. et Ind. 1920, **3**, 488; Chem. Zentr. 1920, **91**, II, 39; Kunst. 1919, **9**, 248.
3. U. S. P. 1089482, 1914; abst. C. A. 1914, **8**, 1679; J. S. C. I. 1914, **33**, 365. See also E. P. 13390, 1909; abst J. S. C. I. 1910, **29**, 503. F. P. 402996, 1909; abst. J. S. C. I. 1910, **29**, 35.
4. U. S. P. 1112890, 1914; abst. C. A. 1914, **8**, 3841; Mon. Sci. 1915, **82**, 46.
5. E. P. 15544, 1914 (void); abst. Chem. Ztg. 1914, **38**, 1010. F. P. 474163, 1914; abst. Mon. Sci. 1917, **84**, 24; Kunst. 1916, **6**, 63.
6. F. P. 469017; abst. Kunst. 1914, **4**, 370.
7. E. P. 23137, 1914.
8. E. P. 7880, 8154, 1914.

finished leather[1], or to other fibrous material[2] is by impregnation with a heavy cellulose acetate solution. In preparing washable fireproof material, fabric or paper is impregnated with borates or molybdates dissolved with acetylcellulose in a common solvent combination[3].

In the field of cellulose ethers, W. Denham and H. Woodhouse in extending their previous work on the methylation of cellulose[4], studied the hydrolysis of methylated cellulose, and determined that the highest product formed is represented by trimethyl glucose after hydrolysis, which confirms the existence of three hydroxyl groups in the C_6 unit[5].

With the nitroacetylcelluloses (cellulose acetonitrates), H. Nishida detailed the three methods for their preparation[6], and a process was patented for the manufacture of a material resembling caoutchouc in which nitroacetylcellulose is combined with triacetin, amyl alcohol and cork meal[7]. A peculiar method has been described by L. Grote[8] for preparing a binding medium for use in making plastic materials, which upon close inspection appears to be a process for hydrocellulose acetation.

1. W. Spalteholz and K. Haring, E. P. 28392, 1912; abst. C. A. 1914, **8**, 1886; J. S. C. I. 1914, **33**, 95.

2. E. P. 14868, 1914; abst. J. S. C. I. 1915; **34**, 972; Kunst. 1916, **6**, 162.

3. A. Eichengruen, E. P. 7418, 1913; abst. C. A. 1914, **8**, 3124; J. S. C. I. 1914, **33**, 478. E. P. 7899, 1914; abst. C. A. 1915, **9**, 2597; J. S. C. I. 1914, **33**, 478. F. P. 455811, 1913; abst. C. A. 1914, **8**, 2490; J. S. C. I. 1913, **32**, 939; Chem. Ztg. Rep. 1913, **37**, 244.

4. J. C. S. 1913, **103**, 1735; abst. C. A. 1914, **8**, 243; J. S. C. I. 1913, **32**, 974; Bull. Soc. Chim. 1913, **14**, 1495; Chem. Zentr. 1913, **84**, II, 1857; Chem. Ztg. Rep. 1914, **38**, 241; Meyer Jahr. Chem. 1913, **23**, 536; Chem. Soc. Ann. Rep. 1913, **10**, 88.

5. J. C. S. 1914, **105**, 2357; abst. C. A. 1915, **9**, 203; J. S. C. I. 1914, **33**, 1084; Bull. Soc. Chim. 1915, **18**, 199; Chem. Zentr. 1915, **86**, I, 81; Chem. Soc. Ann. Rep. 1914, **11**, 93.

6. Kunst. 1914, **4**, 141; abst. J. S. C. I. 1914, **33**, 476; Chem. Ztg. Rep. 1915, **39**, 195; Wag. Jahr. 1914, **60**, II, 466; Zts. ang. Chem. 1914, **27**, II, 503.

7. Aktien-Ges. f. Anilinfabrikation, E. P. 5633, 1914 (void); abst. Chem. Ztg. 1914, **38**, 532. F. P. 461058, 1913; abst. J. S. C. I. 1914, **33**, 20; Mon. Sci. 1914, **81**, 125; Chem. Ztg. 1913, **37**, 1405. F. P. 463622, 1913; abst. C. A. 1914, **8**, 3245; J. S. C. I. 1914, **33**, 431.

8. E. P. 23728, 1912; abst. C. A. 1914, **8**, 1346; J. S. C. I. 1913, **32**, 1104; Chem. Ztg. Rep. 1913, **37**, 224.

C. Schwabe (not Schwalbe) gave a resume of the commercial uses of the acetated celluloses[1], and pointed out the use of such plasticizers as naphthol benzoate, thymol and salol, either alone or as adjuncts to camphor. Hollow bodies from cellulose acetate were described by J. Faber[2].

In the acetylation of organic compounds[3], E. Knoevenagel studied the influence of the following catalyzers upon the acetation of the C:O group by acetic anhydride:—chlorides of ferric iron, zinc, tin, and phosphorous; sulfuric acid, ferrous sulfate, sulfates of copper, zinc, ammonia, and methylamine. He has pointed out[4] that acetylcelluloses are made exclusively by the action of acetic anhydride on cellulose in the presence of a catalyst, the use of acetyl chloride having been abandoned. Many catalysts, especially sulfuric acid, induce acetolysis of the cellulose molecule, a process quite distinct from hydrolysis and leading ultimately to the transformation of the cellulose into cellobiose octoacetate and dextrose pentacetate. The process of H. Mork[5] for preparing filaments and films closes the work of 1914, his method being to dissolve the cellulose ester in a solvent composed largely of acetylene tetrachloride, the filaments being afterwards coagulated by a mixture of the former with a petroleum hydrocarbon, the average boiling point of which is higher than that of the solvent.

Cellulose Ester Progress 1915-1919. This semi-decade covered the war period when men of reflection in science were occupied primarily in advancement of the warlike arts. In addition, those discoveries which were perfected, patented and published were often held quiescent in the Patent

1. J. Soc. Dyers Col. 1914, **30**, 13; abst. C. A. 1914, **8**, 1344; J. S. C. I. 1914, **33**, 131.
2. D. R. P. 306318, 1914; abst. Chem. Ztg. 1919, **43**, 269.
3. Ann. 1914, **402**, 111; abst. C. A. 1914, **8**, 913; J. C. S. 1914, **106**, i, 163; J. S. C. I. 1914, **33**, 102; Bull. Soc. Chim. 1914, **16**, 374; Chem. Zentr. 1914, **85**, I, 749; Chem. Ztg. Rep. 1914, **38**, 187.
4. Zts. ang. Chem. 1914, **27**, 505; Chem. Ztg. 1914, **38**, 757; abst. C. A. 1915, **9**, 524; J. C. S. 1915, **108**, i, 383; J. S. C. I. 1915, **34**, 134; Kunst. 1914, **4**, 232.
5. U. S. P. 1107222, 1914; abst. C. A. 1914, **8**, 3371; J. S. C. I. 1914, **33**, 958; Mon. Sci. 1914, **81**, 191; Chem. Ztg. 1914, **38**, 1188; Kunst. 1915, **5**, 240; Zts. ang. Chem. 1916, **29**, I, 51.

Office archives on the ground that their disclosure might be valuably suggestive to the enemy. However, in the aircraft industry which was given such an impetus in the latter portion of the War, investigation was widespread in all the countries, especially in devising formulas and methods of application of varnishes, lacquers, dopes and other protective coatings for covering the canvas of the wings, and inasmuch as this involved the discovery and economical utilization of vast amounts of solvents, coupled with the fact that the acetated celluloses are relatively much less flammable than are the corresponding nitrates, greatly advanced the cellulose ester art from the two-fold viewpoint of cellulose acetate mass production and the selection and manipulation of solvents and solvent combinations to bring out the maximum of efficiency at the minimum of cost. During this five year period, there is touched upon herein over five hundred literary contributions brought forth and patented processes evolved, as indicating the scope and trend of this industry under what must be admitted as difficult conditions.

W. Abbott described his waterproof fiber sheet and sole made therefrom[1], in which a pluralilty of plies of chemically treated fiber is coalesced by means of a nitro- or acetylcellulose solution, in which is dissolved resins and thickened oils. He also devised an insole[2] of high flexibility prepared by introducing between layers of hardened paper, a linseed oil coating and superposing on the outside layers a film of cellulose acetate or pyroxylin. R. Adler brought forth his scheme for fabricating plastic compositions[3], by mixing ammonia with an albuminous compound and oxycellulose, to which fatty acid esters of cellulose were added as final coatings. Cellulose acetonitrates were put forward as combining most of the advantages and few of the disadvantages arising from admixtures of the nitric and acetic acid

1. U. S. P. 1263186.
2. W. Abbott, U. S. P. 1263187.
3. R. Adler (Naamlooze Vennootschap "Hollandsche Proteine

esters[1], by nitrating cotton to a 5% nitrogen content, then acetating this low-nitrogen ester. The mixed ester so obtained when incorporated with glyceryl lactate or butyrate, no volatile solvents being employed, is said to produce an excellent plastic. The truth is, it is almost impossible to make a permanently hard plastic with the two above high-boilers on account of their hygroscopicity[2]. In preparing mixed acetic-nitric cellulose esters, an alleged improvement was patented in that the esterification is to be conducted in the presence of benzene[3], thus forming a fibrous product.

A successful paint remover composition must have dissolved in the volatile solvent portion, sufficient of a solid so that at some stage of the evaporative process a skin is formed and thus protects further evaporation until the solvent can properly act upon the paint layer to be removed. Cellulose acetate and wax in solution have been brought forward for this purpose[4], especially effective being cellulose acetate dissolved in methylacetone[5].

Andes contributed an article on nitro- and acetyl-cellulose lacquers for airplane wing fabrics[6], and A. Arent[7] a method for waterproofing fibrous materials combined with a fire-proofing treatment by coating or impregnating with cellulose acetate in solution containing antimony trichloride as fire-retardant. In the coating of hygroscopic materials as wood, paper, vulcanized fiber and parchment paper, acetylcellulose in "extremely fluid solution" is recommended[8].

1. Aktien-Ges. fur Anilin Fabrikation, D. R. P. 295889, and Addn. D. R. P. 299036. Aust. P. 70782 Addn. to 67942; abst. Kunst. 1916, **6**, 50; Chem. Ztg. 1915, **39**, 954. Holl. P. 1476; abst. C. A. 1916, **10**, 2637.
2. Aktien-Ges. vorm. Haaf & Co., F. P. 493893; abst. Chim. et Ind. 1920, **3**, 353.
3. Akt. Ges. für Anilin Fabrikation, D. R. P. 301449. E. P. 145524 Addn. to E. P. 10706, 1912; abst. Chem. Met. Eng. 1920, **23**, 1036; Paper, 1921, **28**, No. 3, 35.
4. W. Alexander, U. S. P. 1143877.
5. W. Alexander, U. S. P. 1143878.
6. Farb. Ztg. 1918, **24**, 128; abst. Kunst. 1919, **9**, 123.
7. E. P. 138641. See E. P. 2311, 1871; 123813.
8. M. Arosio, E. P. 131911; abst. Chim. et Ind. 1920, **4**, 798; Kunst. 1920, **10**, 69. See E. P. 267, 1884; 12693, 1896; 7134, 1903;

In protecting and strengthening articles of wood (as wooden screw propellers), the article is first fitted with a covering of vulcanized fiber upon which is placed a solution of acetylcellulose[1], this combination acting also as an excellent insulating material[2].

F. Aston[3] in his (then) confidential Report T-1019 to the Superintendent, Royal Aircraft Factory, England, on the action of sunlight on airplane fabric, detailed the various protective lacquers of cellulose acetate which had been proposed for this purpose up to that time (Oct., 1917). In making projection screens in the moving picture industry[4], a surface adapted to produce a more complete refraction or absorption results, if the light from the side of the screen toward the spectator is coated with a transparent cellulose acetate solution. The advantages of ethyl glycollate and acetoglycollate as a cellulose acetate plasticizer were brought out by G. Austerweil in 1919[5], as well as chlorine-free polymerized vinyl esters[6].

In 1919 appeared Report 13,228, submitted to the Bureau of Aircraft Production, Washington, D. C., by E. Worden, L. Rutstein, P. Drinker, J. Buford, R. Dort, 8 vols., 5300 pages, on the chemical activities in connection with aviation warfare during th World War.

In a series of patents issued to J. Aylsworth in connection with the phonograph record industry, are described methods for formation of record blanks comprising a thin, flexible sheet of cellular texture[7] impregnated with cellulose acetate in solution and containing thermoplasticizers,

1. M. Arosio, E. P. 131916; abst. Chim. et Ind. 1920, **4**, 798; Kunst. 1920, **10**, 69; C. A. 1920, **14**, 359.
2. M. Arosio, E. P. 131907; abst. J. S. C. I. 1921, **40**, 143-A. D. R. P. 331024; abst. Chem. Tech. Ueber. 1922, **46**, 98.
3. "Report on the Action of Sunlight on Aeroplane Fabric," R. A. F. T. 1919, Oct. 1917.
4. L. Auerbacher, U. S. P. 1206287.
5. G. Austerweil, Aust. P. 78982; abst. Chem. Ztg. 1919, **43**, 733; Kunst. 1920, **10**, 214.
6. G. Austerweil, Aust. P. 78983; abst. Chem. Ztg. 1919, **43**, 733; Kunst. 1920, **10**, 215.
7. J. Aylsworth, U. S. P. 1146387. See U. S. P. 962877, 1062579, 1102630.

afterwards impressed by means of heat and high pressure[1]. A phenolic condensation product may constitute the inner portion of the record mass, superposed upon which is a more resistant but relatively thinner layer of acetylcellulose film or solution with volatile solvents[2]. The sonority and other acoustic properties are said to be improved by the addition to the matrix substance in conjunction with cellulose acetate, insoluble fibrous materials such as cotton flock or wood flour[3]. The plasticity may be only in the central layer of the record substance, the outer portion consisting of a cellulose acetate veneer which gives additional tensile strength and minimizes abrasion of the sound undulations upon the passage of the needle thereupon[4].

A. Baboin & Co.[5] produce metallic effects by dissolving acetylcellulose 10, in tetrachlorethane 130, to which is added bronze powder 100, and the Badische Co.[6], cellulose acetate lacquers by the use of such high-boilers as the formate and acetate of cyclohexanol and *b*-methylcyclopentanol; or[7] cyclohexanone diluted with acetone and benzene. Advan-

1. J. Aylsworth, U. S. P. 1146391. See U. S. P. 855556, 1046137, 1094830.

2. J. Aylsworth, U. S. P. 1167468. See U. S. P. 1096608.

3. J. Aylsworth, U. S. P. 1230816. See U. S. P. 1020593, 1146388.

4. J. Aylsworth, U. S. P. 1283450.

5. F. P. 475338; abst. J. S. C. I. 1916, **35**, 42; Kunst. 1916, **6**, 150.

6. Badische Anilin und Soda-Fabrik, F. P. 440733, 1912; abst. J. S. C. I. 1912, **31**, 828; Kunst. 1913, **3**, 17; 1920, **10**, 118; J. Soc. Dyers Col. 1912, **28**, 309; Mon. Sci. 1914, **81**, 14; Rev. Chim. Ind. 1912, **23**, 282. See also D. R. P. 295075, 1914; abst. Chem. Tech. Uber. 1921, **45**, 47. D. R. P. 301751, 1916; abst. Chem. Tech. Uber. 1921, **45**, 11; C. A. 1921, **15**, 1030. D. R. P. 332679, 332680, 1915; abst. Chem. Tech. Uber. 1921, **45**, 76; J. S. C. I. 1921, **40**, 370-A; Ann. Rep. Soc. Chem. Ind. 1922, **7**, 1161. D. R. P. 334871, 1914 (Addn. to D. R. P. 284672, 1914); abst. Chem. Ztg. 1921, **45**, 249; Kunst. 1921, **11**, 95; J. S. C. I. 1921, **40**, 505-A. E. P. 145511, 1920; abst. J. S. C. I. 1921, **40**, 144-A. See D. R. P. 272391.

7. *Ibid.* D. R. P. 284672; abst. J. S. C. I. 1915, **34**, 1048; Chem. Zentr. 1915, II, 111; Chem. Ztg. 1915, **39**, 322. E. P. 14042, 1914; abst. J. S. C. I. 1915, **34**, 956.

tages of Cellit (Cellone) acetylcellulose plastic[1] as substitute for celluloid have been pointed out. A balloon varnish has been patented[2] in which amyl formate is the preferred solvent, and this has also been advocated together with ethyl formate[3], as a lacquer for reinforced glass production[4].

J. Barfuss[5] has described certain advantages in using stinging nettle filaments cellulose acetate coated, for artificial filament formation. In the preparation of airplane dopes[6], metallic powder and mineral or inorganic pigments are added to a cellulose acetate solution to coat airship envelopes. Cellulose acetate solutions may be purified from some of their objectionable components by submitting them to dialysis, if there are dissolved crystalloids therein. For instance, a solution of cellulose acetate in tetrachlorethane and containing hexachlorethane[7], may be freed from the latter by using caoutchouc membranes. The cellulose ester lacquer of B. Baumeister[8] appeared in 1921.

The Farbenfabriken in 1915 described carbohydrate phosphoric esters[9], obtained from fermentable carbohydrates

1. Phot. J. 1913, 10; abst. Ann. Rep. S. C. I. 1916, **1**, 307. Balland & Co., F. P. 473189; abst. J. S. C. I. 1915, **34**, 513; Ann. Rep. S. C. I. 1916, **1**, 307.
2. Ballonhüllen-Ges., D. R. P. 321264; abst. J. S. C. I. 1920, **39**, 698-A.
3. A. Bardin, U. S. P. 1228165; abst. C. A. 1917, **12**, 2268. E. P. 9666, 1913. Can. P. 169507.
4. B., Diamant, 1915, **37**, 485; abst. C. A. 1915, **9**, 2973.
5. Faser. 1919, **1**, 181; abst. Chem. Zentr. 1919, **90**, IV, 930.
6. A. Barr and H. Lazell, E. P. 131641; abst. C. A. 1920, **14**, 359; J. S. C. I. 1919, **38**, 834-A; Ann. Rep. S. C. I. 1920, **5**, 324; Chim. et Ind. 1922, **7**, 342; Kunst. 1920, **10**, 134; 1922, **12**, 6.
7. C. Bary, U. S. P. 1136462; abst. C. A. 1915, **9**, 1556; Mon. Sci. 1916, **82**, 56; Zts. ang. Chem. 1916, **29**, I, 243.
8. B. Baumeister, D. R. P. Anm. B-90474; abst. Kunst. 1921, **11**, 48; Chem. Ztg. 1921, **45**, 137.
9. Farbenfabr. vorm. F. Bayer & Co., D. R. P. 292817, 1915; abst. C. A. 1917, **11**, 1519; J. S. C. I. 1916, **87**, 1082; Chem. Zentr. 1916, **87**, II, 244; Chem. Ind. 1916, **39**, 300; Chem. Ztg. Rep. 1916, **40**, 271; Wag. Jahr. 1916, **62**, II, 12; Zts. ang. Chem. 1916, **39**, 338. In this connection see Belg. P. 226582, 1910. Ital. P. 85347, 1907; abst. Chem. Ztg. 1907, **31**, 401. Aust. P. Anm. 2376, 1911; abst. Chem. Ztg. 1912, **36**, 252. Aust. P. Anm. 5148, 1910; abst. Chem. Ztg. 1911, **35**, 262. Aust. P. Anm. 5896, 1910; abst. Chem. Ztg. 1911, **35**, 518. Aust. P. Anm. 8776, 1910; abst. Chem. Ztg. 1911, **35**, 1162. Aust. P.

and inorganic phosphates. Plastics are formed[1] by admixing cellulose acetate with condensates of acetone and phenol, dioxydiphenyldimethylmethane being an example, dissolved in alcohol or chloroform, pointing out[2] that such solutions produce excellent moving picture films and are suitable for phonograph record manufacture[3], as well as artificial filament formation[4]. A pigmented airplane dope has been described[5], formed by mixing a pigment, as a mixture of yellow ochre, vegetable black and prussian blue with Chinese wood oil, with benzene as diluent, and adding this to dissolved cellulose acetate. H. Berg[6] enhances the keeping qualities of medicinal candles and suppositories by coating them with a cellulose acetate solution, and E. Berger[7] prepares a disinfecting gas by igniting tetrachlorethane solidified in zinc oxide, calcium silicate and sodium chlorate. As a substitute for collodion sacs in dialysis experiments and pharmaceutical technique[8], a 15% solution of acetated cellulose evaporated to dryness over a test tube and then removed was brought forward in 1915. Such tubes[9] are said to be substantially impervious to gases. A method for polishing cellulose acetate surfaces was patented[10] in 1917.

52289, 1911; abst. Chem. Ztg. 1912, **36**, 279. D. R. P. Anm. F-15278, 1901; abst. Chem. Ztg. 1902, **26**, 712. D. R. P. Anm. F-28233, 1909; abst. Chem. Ztg. 1910, **34**, 763. D. R. P. Anm. 28933, 28934, 1909; abst. Chem. Ztg. 1910, **34**, 1362; D. R. P. Anm. F-29005, 1909; abst. Chem. Ztg. 1910, **34**, 826. D. R. P. Anm. F-32828, 1911; abst. Chem. Ztg. 1912, **36**, 556. D. R. P. Anm. 34110, 1912; abst. Kunst. 1912, **2**, 359.

1. W. Beatty, U. S. P. 1158960; abst. J. S. C. I. 1915, **34**, 1205; Kunst. 1916, **6**, 63. F. P. 447645; abst. J. S. C. I. 1913, **32**, 283.
2. *Ibid.* U. S. P. 1158963; abst. C. A. 1916, **10**, 158.
3. *Ibid.* U. S. P. 1158964; abst. C. A. 1916, **10**, 257.
4. *Ibid.* U. S. P. 1156969.
5. A. Beck and J. Nicholson & Sons, Ltd., E. P. 134899; abst. Chim. et Ind. 1921, **6**, 816.
6. U. S. P. 1289093.
7. E. Berger, F. P. 501836; abst. Chim. et Ind. 1921, **5**, 444.
8. E. Bertarelli, Cent. Bak. Parasitenk. Abt. 1915, I, **76**, 463; abst. Chem. Zentr. 1915, **86**, II, 865; C. A. 1916, **10**, 3088.
9. H. Bier, D. R. P. 309939; abst. Chim. et Ind. 1920, **4**, 385.
10. G. Blatt, D. R. P. 297030; abst. Chem. Zentr .1917, I, 940.

In preparing a gas impermeable material[1], the fabric is impregnated with cellulose acetate dissolved in a combination of low boiling solvent with a high boiling plastifier which remains, but imparts softness. A study has been made of the acetylation of cellulose and starch by means of acetic anhydride in the presence of various catalysts[2], hydriodic acid and acetyl iodide being more satisfactory than hydrobromic acid, and this in turn than hydrochloric acid, sulfuric acid being the best. Plastics of cellulose acetate, benzoate or palmitate result[3] by combining them with bodies yielding negative radicals as carbon bisulfide, being producable of especial value when added to the product obtained by condensation of phenol and formaldehyde[4].

The G. Bonwitt lacquer[5] intended for the impregnation of balloon fabrics comprises acetylcellulose, tetrachlorethane and ethyl lactate. In old balloon cloth[6] the solvents may be recovered by extraction with furfural and ethyl acetate, or cyclohexanone and ethyl acetate, which also removes the acetated cellulose. Furfural alone has been patented for this purpose[7]. A general historical review of the cellulose acetate industry appeared under the authorship of G. Bonwitt[8] in 1920. As a leather substitute[9], a com-

1. R. Blochmann, D. R. P. 309171; abst. Kunst. 1921, **11**, 21.
2. J. Boeseken, J. Berg and A. Kerstjens, Rec. trav. chim. Pays-Bas. 1916, **35**, 320; abst. Kolloid Zts. 1917, **21**, 160; Kunst. 1918, **8**, 102; J. C. S. 1916, **110**, i, 308; Chem. Zentr. 1916, II, 173. See J. Boeseken, Rec. trav. chim. Pays-Bas. 1912, **31**, 350; 1914, **33**, 202; abst. Chem. Zentr. 1913, I, 400; 1914, II, 322.
3. W. Bonner, U. S. P. 1173336; abst. C. A. 1916, **10**, 1269; J. S. C. I. 1916, **35**, 465. U. S. P. 1180902; abst. C. A. 1916, **10**, 1699; J. S. C. I. 1916, **35**, 629.
4. *Ibid.* U. S. P. 1173337; abst. C. A. 1916, **10**, 1084; Kunst. 1916, **6**, 196; J. S. C. I. 1916, **35**, 965; Chem. Ind. 1916, **39**, 465.
5. D. R. P. 365283; abst. Chem. Ztg. 1922, **46**, 1029; Kunst. 1923, **13**, 22; Textil Ber. 1922, **3**, 477.
6. G. Bonwitt, D. R. P. 331285; abst. J. S. C. I. 1921, **40**, 344-A.
7. *Ibid.* Aust. Anm. A-2611, 1918; abst. Kunst. 1922, **12**, 16. Hung. Appl. B-8132; abst. Chem. Ztg. 1919, **43**, 429.
8. *Ibid.* Chem. Ztg. 1920, **44**, 973; abst. C. A. 1921, **15**, 1396; Mon. Sci. 1921, **88**, 65; Chem. Tech. Uebers. 1922, **46**, 9; Chem. Ztg. 1921, **45**, 194.
9. V. Bordigone and D. Maier, Swiss P. 81135; abst. Kunst. 1920, **10**, 124.

bination of cellulose acetate, thickened vegetable oils, plastifiers with pronounced softening action, and the requisite amount of volatile solvents has been published.

S. Born and J. Nelson[1] have described improved methods for carbohydrate acetylation, sucrose treated with acetyl chloride or bromide yielding acetochlorglucose or acetobromglucose, while maltose gave acetochlormaltose or acetobrommaltose[2]. Inulin with ice-cold acetyl bromide gave an acetobrominulin, unidentified. The use of the acetylcellulose plastic "Cellon"[3] was reviewed by M. Bottler in 1916. For fireproofing aircraft cloth and wooden parts, P. Bradley[4] coats first with cellulose acetate, then with alginic acid or alginates. Or[5] the aircraft parts may be covered with a thin metal foil, cellulose acetate coated. He has devised a mechanical apparatus for applying the acetate dope[6]. J. Bregeat[7] recovers cellulose acetate from used film or coated fabric by dissolving off in a volatile solvent, then precipitating the cellulose derivative by means of a non-solvent as benzene or benzine. In order to lessen the normal rapidity of evaporation in airplane dopes of cellulose acetate after application[8], beeswax 5-8%, or paraffin 4-5% based on the acetylcellulose is added.

Cellulose ester solutions on standing are apt to become less viscous[9]. This may be obviated by rendering the so-

1. J. A. C. S. 1915, **37**, 1763; abst. C. A. 1915, **9**, 2249; J. S. C. I. 1915, **34**, 1769. See J. Nelson and S. Born, J. A. C. S. 1914, **36**, 393; abst. C. A. 1914, **8**, 1435.
2. Bosnische Electricitäts A. G., Nor. P. 26527. See B. Borzykowski, Ital. P. 167117. Acetic anhydride mfr. from ethylidene diacetate.
3. M. Bottler, Kunst. 1916, **6**, 56.
4. P. Bradley, U. S. P. 1321708; abst. J. S. C. I. 1920, **39**, 13-A. E. P. 151396; abst. J. S. C. I. 1920, **39**, 757-A. Can. P. 197134.
5. *Ibid.* U. S. P. 1309453. E. P. 130351, 201665.
6. *Ibid.* E. P. 201664.
7. F. P. 493211; abst. Chim. et Ind. 1920, **3**, 353; Chem. Ztg. 1920, **44**, 29. D. R. P. Anm. B-88993; abst. Faser. 1921, **3**, 59.
8. British Aeroplane Varnish Co., Ltd., and S. Groves, E. P. 128974; abst. C. A. 1919, **13**, 3028; J. S. C. I. 1919, **38**, 518-A.
9. British Aeroplane Varnish Co., Ltd., and J. Ward, E. P. 129033; abst. J. S. C. I. 1919, **38**, 678-A; Chem. Ztg. 1919, **43**, 629. J. Ward, F. P. 499703; abst. Chem. Ztg. 1920, **44**, 209; Mon. Sci. 1921, **88**, 29.

lutions immediately after manufacture slightly acid with citric or tartaric acid (0.01%). In a process by C. Cross[1] for the hydrolysis or saponification of esters granted in Canada in 1918, the "claims are withheld from public inspection." In 1920 the British Cellulose & Chemical Manufacturing Co.[2] were granted protection on an apparatus for producing cellulose acetate filaments which is detailed under "Artificial Filaments" topic.

An airplane dope with increased strength and in which the toxic properties are substantially eliminated[3], is said to be producible using cellulose acetate with triacetin, triphenyl phosphate, methyl acetone, methylethyl ketone and acetanilid. Cellulose formates are precipitated as a slimy mass from solutions in formic acid by treatment with amyl acetate, methyl alcohol or toluene[4], and after separating the liquid portion, the solid mass may be kneaded into highly plastic celluloid substitutes. Lactic acid is an excellent direct solvent for formylated cellulose[5]. When acetyl- and nitro-cellulose are combined with readily dissolvable resins (copal, elemi, dammar) highly plastic solid masses result of good moldability[6].

1. British Cellulose & Chem. Manufacturing Co. and C. Cross, Can. P. 183250. See Belg. P. 311568.

2. E. P. Appl. 13796, 13926, 1920; abst. J. S. C. I. 1920, **39**, 432-A.

3. British Emaillite Co., Ltd., and J. Goldsmith, E. P. 124515; abst. C. A. 1919, **13**, 1771; J. S. C. I. 1919, **38**, 378-A; Chim. et Ind. 1921, **5**, 572; Caout. et Gutta. 1919, 10075; Kunst. 1920, **10**, 90. U. S. P. 1298199.

4. E. Bronnert, U. S. P. 1153596, 1915; abst .C. A. 1915, **9**, 3129; J. S. C. I. 1915, **34**, 1049; Mon. Sci. 1917, **84**, 28; Kunst. 1918, **8**, 308; 1919, **9**, 137.

5. U. S. P. 1029341, 1912; abst. C. A. 1912, **6**, 2528; J. S. C. I. 1912, **31**, 637; Mon. Sci. 1912, **77**, 164; 1913, **78**, 393. F. P. 423774, 1910; abst. C. A. 1911, **5**, 3340; J. S. C. I. 1911, **30**, 615; Mon. Sci. 1913, **78**, 393; 1913, **79**, 31; Kunst. 1911, **1**, 235.

6. Byk-Guldenwerke Chem. Fabrik A. G., D. R. P. Anm. B-87081, 1918; abst. Chem. Ztg. 1921, **45**, 1007; Kunst. 1921, **11**, 191. For development in Austria in cellulose esters up to 1915, see Aust. P. 8165, 17456, 21213, 29219, 31203, 31391, 32637, 33472, 33508, 34272, 34908, 35015, 41461, 41811, 41831, 46991, 47244, 47679, 47899, 49177, 50331, 52289, 53099, 53738, 54512, 54574, 54819, 57421, 60447, 64065, 65834, 67676, 67812, 67814, 67942.

O. Carlsson and E. Thall[1] reduce the viscosity of cellulose esters, especially nitrocellulose, by heating the solutions above 60° but under the point of incipient decomposition of the ester. Soft and pliable threads are said to be produced by treating the cellulose fiber with vapors of acetic anhydride in the presence of condensing agents at 40-50° for 50 hours until the increase in weight of the fiber does not exceed 45-50%. The incompletely acetylated threads cannot be dyed with direct dyestuffs[2]. In preparing "soilproof" fabric, a coating of dissolved cellulose acetate in volatile solvents, a softener (castor oil, linseed oil, glycerol) being added[3].

A method was illustrated in 1917 for coating airplane fabric with cellulose ester dope[4], the preparation of a dope especially suited for this purpose[5], involving the use of *iso*butyl *iso*butyrate, cyclohexanone or methylcyclohexanone[6], in cellulose acetate mixtures as substitutes for benzyl alcohol or tolyl alcohol. Photographic films are made by combining acetylcellulose with triphenyl phosphate, *p*-toluenesulfonamide and a monohydroxyaliphatic alcohol (such as the alcohols in fusel oil)[7]. The dyed fibers of cellulose acetate have been recommended for use in connection with microscopic chemical analysis[8].

1. U. S. P. 1375208. E. P. 136141; abst. C. A. 1920, **14**, 1219; J. S. C. I. 1921, **40**, 296-A; Paper, 1921, **28**, No .4, 35; Kunst. 1920, **10**, 158; 1922, **12**, 7. F. P. 505438; abst. Caout. et Gutta. 1921, **18**, 10893. D. R. P. 359311; abst. Chem. Ztg. 1922, **46**, 688.

2. L. Cassella & Co., D. R. P. 347130; abst. J. S. C. I. 1922, **41**, 249-A; Chem. Tech. Uebers, 1922, **46**, 97.

3. L. Cavanaugh, U. S. P. 1277695. E. P. 133180; abst. J. Soc. Dyers, 1920, **36**, 27; Kunst. 1920, **10**, 69, 149.

4. Cellon, Ltd., and A. Barr, E. P. 129698; abst. J. S. C. I. 1919, **38**, 558-A.

5. Cellon, Ltd., T. Tyrer & Co., Ltd., and T. Tucker, E. P. 123628; abst. J. S. C. I. 1919, **38**, 207-A. Ital. P. 177682.

6. Cellon, Ltd., T. Tyrer & Co., P. Chambers and G. Feasey, E. P. 130402; abst. J. S. C. I. 1919, **38**, 714-A; Chem. Ztg. 1919, **43**, 649; Kunst. 1920, **10**, 92; 1922, **12**, 5; Chim. et Ind. 1921, **5**, 577. F. P. 510356; abst. Chem. Ztg. 1921, **45**, 377.

7. Celluloid Co., F. P. 482239; abst. C. A. 1917, **11**, 3182.

8. E. Chamot and H. Cole, J. I. E. C. 1918, **10**, 48; abst. C. A. 1918, **12**, 48. See J. I. E. C. 1917, **9**, 906; abst. C. A. 1917, **11**, 3194.

Highly purified acetic acid may be prepared from the commercial variety[1] by distillation in the presence of mercury. As solvent for cellulose acetate, has been patented ethylidene diacetate[2], chlorethyl benzoate, ethylidene acetobenzoate, chlorethyl acetate and similar compounds[3]. *b*-Chlorethyl acetate may be produced by the method of the Chemische Fabrik Kalk[4], and formic acid[5] by the distillation of formates with sulfuric acid in fine films on a heated rotary evaporator. *b*-Chlorethyl acetate[6] has been patented as a direct cellulose acetate solvent.

Ethyl acetylhydroxyacetate and amyl acetylglycollate[7] have received patent protection, the first for acetylcellulose, the latter for nitrocellulose. As plasticizing agents for the cellulose acetates have been recommended methyl- and ethylglycerol chlorhydrin and methylene- and ethylidene-chlorhydrin[8]. It has been claimed[9] that acetate films may be

1. Chem. Fabr. Griesheim Elektron, E. P. 143891; abst. Chem. Met. Eng. 1920, **23**, 752. Chem. Fabr. Griesheim Elektron and N. Gruenstein, D. R. P. 347190; abst. Chem. Tech. Uebers. 1922, **46**, 96.

2. Chem. Fabr. Griesheim Elektron, D. R. P. 281373, 1915; abst. C. A. 1915, **9**, 1850; Chem. Centr. 1915, **86**, I, 235; Chem. Ind. 1915, **38**, 87; Chem. Ztg. Rep. 1915, **39**, 23; Meyer Jahr. Chem. 1914, **24**, 304; Zts. ang. Chem. 1915, **28**, 83; Kunst. 1916, **6**, 115. D. R. P. Anm. C-22873, 1912; abst. Kunst. 1913, **3**, 479. D. R. P. Anm. C-23612, 1913; abst. Chem. Ztg. 1914, **38**, 1134.

3. *Ibid.* D. R. P. 313696, 1915; abst. J. S. C. I. 1920, **39**, 44-A; Chimie et Ind. 1920, **4**, 89; Chem. Zentr. 1919, **90**, II, 664; Kunst. 1920, **10**, 34; Wag. Jahr. 1919, **65**, II, 20.

4. D. R. Anmel. C-27590.

5. Chem. Fabrik Gruenau, Landshoff & Meyer A. G., E. P. 16215, 1915; U. S. P. 1174663; D. R. P. 305429; Swiss P. 72378; Aust. P. 35448; abst. C. A. 1916, **10**, 2387; 1917, **11**, 1519; J. S. C. I. 1916, **35**, 468, 635.

6. Chem. Fabr. Kalk, G. m. b. H., Swiss P. 85868; abst. Kunst. 1920, **10**, 47; 1921, **11**, 39. D. R. P. Anm. C-26786, 1917; abst. Chem. Ztg. 1921, **45**, 89; Kunst. 1921, **11**, 39.

7. Chem. Fabr. von Heyden, D. R. P. 324786; abst. J. S. C. I. 1920, **39**, 779-A; Chim. et Ind. 1922, **7**, 763; Chem. Zentr. 1920, IV, 507; Chem. Tech. Uebers. 1921, **45**, 215; Kunst. 1920, **10**, 143. Aust. P. 79427; abst. Chem. Ztg. 1919, **43**, 901; Caout. et Gutta. 1921, **18**, 11157. Hung. Anm. H-5930.

8. *Ibid.* D. R. P. Anm. C-26778, abst. Chem. Ztg. 1919, **43**, 345; Kunst. 1919, **9**, 182. D. R. P. Anm. C-26780; abst. Chem. Ztg. 1919, **43**, 309. D. R. P. 288267; abst. Kunst. 1916, **6**, 115.

9. *Ibid.* D. R. P. Anm. C-26939; abst. Chem. Ztg. 1919, **43**, 113; Chem. Zentr. 1919, II, 386. D. R. P. 365351; abst. Kunst. 1923, **13**, 22.

increased in strength by the addition thereto of relatively small amounts of bronze or colors, and that augmented strength also is attained by admixture of dissolved nitro- and acetyl-cellulose, over either ester separately[1], or extended by the addition thereto of high boiling solvents which volatilize slowly but completely[2]. The cellulose acetate solvent of H. Clarke[3] involves the use of but slightly volatile oxalic esters (dibutyl or diamyl oxalate).

It is recommended in the manufacture of cellulose acetonitrates[4], to first partially nitrate in a bath containing HNO_3 43%, then acetylate in the presence of bromine. As a superior coating composition[5], the solution of acetylcellulose in tetrachlorethane and amyl alcohol has been put forward, especially valuable for coating the cloth of aeroplane wings, solvent proportions being 9:1. In 1919 L. Clement and C. Riviere[6] reviewed our knowledge of cellulose acetate solvents, and discussed the relative merits of benzyl alcohol, triacetin, eugenol and furfural, and the role of the more volatile solvents in connection with acetate plastifying bodies, including a resume of the patent and journal literature[7]. They found[8] a mixture of acetone and methyl acetate as the most satisfactory general solvent from

1. Chem. Fabr. von Heyden, D. R. P. Anm. C-27198; abst. Kunst. 1919, **9**, 222.

2. Chem. Werke H. Byk, Swiss P. 66510; abst. Kunst. 1916, **6**, 115.

3. U. S. P. 1309980; abst. C. A. 1919, **13**, 2443; Chim. et Ind. 1921, **6**, 512.

4. L. Clement and C. Riviere, U. S. P. 1168164; abst. J. S. C. I. 1916, **35**, 251. See E. P. 19107, 1906.

5. *Ibid.* U. S. P. 1173931; abst. C. A. 1916, **10**, 1104; J. S. C. I. 1916, **35**, 465; Chem. Ztg. 1916, **40**, 332. F. P. 461058; abst. J. S. C. I. 1914, **33**, 20. See F. P. 479387; abst. C. A. 1916, **10**, 2308. F. P. 505073; abst. Chim. et Ind. 1921, **6**, 88; Caout. et Gutta. 1921, **18**, 10893, discloses the use of methyl and ethyl acetoacetate as cellulose acetate solvents.

6. Bull. soc. encour. Ind. Nat. 1918, **117**, 238; abst. J. S. C. I. 1915, **34**, 75; Chem. Zentr. 1919, II, 511. L'Industrie Chim. 1919, **6**, 107. In this connection see J. Hardcastle and A. Taylor, E. P. 13100, 1914; abst. J. S. C. I. 1915, **34**, 146. W. Wilcox, Lancet, 1915, **188**, 544; abst. J. S. C. I. 1915, **34**, 508. Elektrochem. Ztg. 1916, **37**, 109.

7. *Ibid.* Kunst. 1914, **4**, 148, 186; abst. C. A. 1914, **8**, 2619. See Kunst. 1912, **2**, 436.

8. *Ibid.* Kunst. 1919, **9**, 204. Ind. Chimique, 1919, **6**, 107; abst. Chem. Zentr. 1919, IV, 542.

a price consideration point of view in 1919. Their joint authorship contributed two additional articles during this period, one on acetate plastics[1], and the other on the relative saponification values of different acetates, including a stretch curve of a semi-elastic, plastic cellulose acetate compound[2].

F. Clouth claims[3] that anthracene oil when added to cellulose acetate, increases the elasticity and waterproof qualities. High boiling tar oil and creosote oil perform a similar function[4]. Cellulose acetate insoluble in acetone is rendered soluble[5], by heating in a solution containing water or other substance having a hydrolytic action to 90-110°, the reaction being discontinued before the ester becomes soluble to a clear solution in ethyl acetate. The solvent portion of the preferred acetated cellulose lacquer of L. Collongy[6] comprises substantially a mixture of methyl acetate, dimethyl acetate and diphenyl acetate. A method for chlorhydrin manufacture was published in 1919 by the Commercial Research Co.[7]. Processes for the manufacture of trichlorethylene[8], tetrachlorethane[9] and acetaldehyde[10] were published in 1919.

1. L. Clement and C. Riviere, 8th Inter. Cong. Appl. Chem. 1912, **9**, 59; abst. C. A. 1912, **6**, 3182; J. S. C. I. 1912, **31**, 869.
2. *Ibid.* Rev. Chim. Ind. 1911, **22**, 215; abst. C. A. 1911, **5**, 3907.
3. F. Clouth, D. R. P. 319723; abst. J. S. C. I. 1920, **39**, 568-A; Ann. Rep. S. C. I. 1920, **5**, 324; Kunst. 1920, **10**, 149; Chem. Tech. Uebers. 1920, **44**, 296; 1921, **45**, 215; Chem. Ztg. 1920, **44**, 133; Chem. Zentr. 1920, IV, 19.
4. *Ibid.* D. R. P. 324944, Addn. to D. R. P. 319723; abst. Chim. et Ind. 1922, **7**, 763; Kunst. 1920, **10**, 222. For manufacture of cellulose isocyanates, see P. Goissedet, F. P. 496526.
5. F. Collischonn and F. Ruppert, U. S. P. 1201260; abst. C. A. 1916, **10**, 3159; J. S. C. I. 1916, **35**, 1256. See U. S. P. 1109512. D. R. P. 159524.
6. F. P. 502538; abst. Chim. et Ind. 1921, **5**, 571.
7. F. P. 496194, 498643; abst. Mon. Sci. 1921, **88**, 25, 28.
8. Compagnie des Produits Chimiques d'Alais et de la Camargue, E. P. 132755; abst. Kunst. 1920, **10**, 68; Rev. Prod. Chim. 1920, **23**, 197.
9. *Ibid.* E. P. 132757; abst. Kunst. 1920, **10**, 69; Rev. Prod. Chim. 1920, **23**, 197.

The manufacture of acetaldehyde from acetylene[1], or acetic acid from acetaldehyde[2] and crotonaldehyde were published in 1915-16 by Consortium fuer Elektrochemische Ind. A symposium on the chemical changes undergone by cellulose during the beetling process was contributed by C. Cross[3] in 1919, who reviewed our knowledge of the hydrolysis of the chloroform-soluble to the acetone-soluble cellulose acetate[4], the ideas being embodied in a patent[5]. Incipient hydrolysis and saponification are performed by the joint action of methyl or ethyl alcohol and an amount of alkali or base in amount less than the equivalent of the acetic acid in combination with the cellulose.

In producing tautness in fabrics, especially applicable to aeroplane wings[6], stretched fabric is coated with a cellulose acetate solution containing high and low-boiling solvents, and while the fabric is still wet, a sheet of cellulose acetate is applied. In obtaining ethylene dichloride from ethylene[7], the latter is brought in contact with chlorine in stoichiometrical proportions by combined pressure and heat.

Artificial threads or ribbons may be prepared by the E. Dammann process[8], by squirting an original solution of the crude products of the acetylation of cellulose (without previous isolation of the ester) into a coagulating bath composed of 5% sodium hydroxide saturated with sodium chloride or sulfate. In preparing porous membranes by evaporating solvent from a film of a solution of cellulose

1. D. R. P. 304104, 309103; abst. Chim. et Ind. 1922, **7**, 331, 332. Nor. P. 27166. D. R. P. 383528; abst. J. S. C. I. 1924, **43**, 449-B.
2. D. R. P. 305125, 305550; abst. Chim. et Ind. 1922, **7**, 331, 332.
3. J. Soc. Dyers Col. 1919, **35**, 270; abst. C. A. 1920, **14**, 3324; J. S. C. I. 1920, **39**, 58-A.
4. C. Cross and E. Bevan, J. Soc. Dyers Col. 1920, **36**, 19; abst. Chem. Zentr. 1920, II, 542.
5. C. Cross and C. Dreyfus, E. P. 125153; abst. J. S. C. I. 1919, **38**, 427-A.
6. F. Cumbers and British Cellulose & Chem. Mfr. Co., E. P. 131384; abst. J. S. C. I. 1919, **38**, 759-A.
7. G. Curme, U. S. P. 1315545; abst. C. A. 1919, **13**, 2883; Chim. et Ind. 1920, **4**, 659.
8. D. R. P. 287073; E. P. 13872, 1914; F. P. 473126; abst. C. A.

acetate[1], the evaporation is conducted in a moist atmosphere so that an opaque film is produced of varying impermeability and high filtering capacity. Report 230 by M. Deschiens to the French Section Technique[2], in 1919, involved an intensive study of the effect of sunlight upon doped fabrics, especially those containing cellulose acetate, both clear and pigmented.

A flexible fabric composed of textiles or wire[3] is attached to an airplane and coated with a sufficient number of cellulose acetate applications to render the fabric impervious to water. W. Deutsch claims[4] that cellulose acetate plastic (Cellon) may be kept impervious to moisture by soaking the film in a solution or suspension of soap, fats or fatty acids. The Deutsche Gasglühlicht A. G.[5] allege that merchantable cellulose acetate is producable containing more than 20% of fixed acetic acid therein, using hydracellulose as the initial cellulosic material. They claim[6] that glass coated with acetylcellulose, by a short immersion in feebly alkaline or aqueous methyl alcohol solution, is not obscured by condensed moisture.

In 1917 appeared the acetaldehyde manufacturing process of the Deutsche Gold- u. Silber-Scheideanstalt[7] in Switzerland. When mercerized cellulose is treated with

1. Haen Chemische Fabrik Ges, E. de E. P. 134228.
2. Report "AT-230" French Section Technique, Paris.
3. E. Descamps, U. S. P. 1156894; abst. J. S. C. I. 1915, **34**, 1139; Kunst. 1916, **6**, 38. See Leduc, Heitz et Cie, E. P. 6798, 1912; F. P. 451420.
4. D. R. P. 309201; abst. Chem. Zentr. 1920, II, 612; Kunst. 1920, **10**, 78.
5. E. P. 75, 1915; abst. C. A. 1916, **11**, 1789; J. S. C. I. 1916, **35**, 39; 1917, **36**, 138; 1919, **38**, 358-A; J. Soc. Dyers, 1916, **32**, 121; Kunst. 1916, **6**, 162, 250; Zts. ang. Chem. 1917, **30**, I, 74; E. Wagner, D. R. P. 299181, 1914; abst. Ann. Rep. Sci. 1920, **5**, 136; J. S. C. I. 1920, **39**, 400-A; Chem. Zentr. 1920, **91**, II, 536; Chem. Ztg. 1920, **44**, 5, 91; Kunst. 1920, **10**, 68. A. Polotsky, U. S. P. 1296847, 1919; abst. C. A. 1919, **13**, 1637; J. S. C. I. 1919, **38**, 358-A. Ital. P. 146751; Caout. et Gutta. 1919, 10074.
6. Deutsche Gasglühlicht, A. G., D. R. P. 297955; abst. J. S. C. I. 1920, **39**, 519-A; Kunst. 1920, **10**, 69; Chim. et Ind. 1921, **5**, 578; Chem. Zentr. 1920, II, 651.
7. Swiss P. 93272, 93273; abst. Chem. Ztg. 1922, **46**, 59.

chloracetic acid[1] or its homologues in the presence of alkali hydroxides, the cellulose finally dissolves to form clear, viscous solutions in hot or cold water, which upon evaporation, yield useful films. The alkali salts of cellulose-acetic acid and cellulose-propionic acid may be used as substitutes for gelatin. In waterproofing cardboard gun-cartridges[2], the material is successively coated with balata and cellulose acetate and then heated to soften the balata and cause it better to fill the pores of the material. A. Djeinheim[3] reviewed in 1919 the literature and published patents on cellulose acetate.

The W. Doerflinger aeroplane wing dope or lacquer[4] comprises a cellulose ester with high boiling plasticizing agents in the presence of a non-inflammable element (tricresyl phosphate, boric acid). In 1917, Dover Co., Ltd.[5], submitted their cellulose acetate plastic, Doverite, to the British Government as being especially useful in the formation of tubes. Product not patented. In order to produce an exceedingly taut surface[6], textiles impregnated with cellulose acetate are stretched on aeroplane wing frames whilst still not dry after coating, and are then further moistened with solvent containing little or no plasticizer. As a softener and emollient for use with cellulose acetate[7], anhydrous lanolin dissolved in acetone was patented in

1. Deutsche Celluloid Fabrik, E. P. 138116. D. R. P. 332203; abst. J. S. C. I. 1921, **40**, 344-A; Kunst. 1921, **11**, 94; Chim. et Ind. 1922, **8**, 426; Chem. Tech. Uebers. 1921, **45**, 59; C. A. 1921, **15**, 2184. F. P. 517815; abst. Caout. et Gutta. 1921, **18**, 11148. Nor. P. 31018; abst. Chem. Tech. Uebers. 1921, **45**, 13. Swiss P. 85075; abst. Kunst. 1921, **11**, 39.

2. M. Dickert, U. S. P. 1180704; abst. C. A. 1916, **10**, 1710; J. S. C. I. 1916, **35**, 643.

3. Caout. et Gutta. 1919, **16**, 9890; abst. C. A. 1919, **13**, 3314; Kunst. 1920, **10**, 19.

4. W. Doerflinger, U. S. P. 1315216; abst. C. A. 1919, **13**, 3028; J. S. C. I. 1919, **38**, 834-A.

5. G. Barr and E. Wilson, Advisory Committee for Aeronautics (England) T. 961 A., Oct. 1917.

6. C. Dreyfus, E. P. 100180; abst. J. S. C. I. 1916, **35**, 887.

7. *Ibid.* E. P. 127615; abst. C. A. 1919, **13**, 2444; J. S. C. I. 1919, **38**, 531-A; Ann. Rep. S. C. I. 1920, **5**, 324; Chem. Ztg. 1919, **43**, 581.

1919, and the use of boiled linseed oil with acetated cellulose in conjunction with such high boilers as acetnaphthalid, terpineol and castor oil[1]. A series of suggested formulas for cellulose acetate aircraft dopes was published by C. Dreyfus[2] in 1915.

The first acetated cellulose manufacturing process using pre-cooling of the esterizing components in order to ensure uniformity of esterification was evolved by H. Dreyfus[3] and issued in 1915. It is one of the stellar contributions in this field. He found that cellulose acetates insoluble in chloroform and in alcohol-chloroform, but soluble in absolute or diluted acetone (and this is the class of cellulose acetate giving maximum tensile strength and tenuity in film form) could be prepared by acetylating cellulose, using sulfuric acid as catalyst; the acetylating mixture being cooled prior to the introduction of the cellulose to a temperature usually 10° or lower (patent says below 20-30°). In fact, incipient crystallization of glacial acetic acid at these temperatures fulfills the function of disintegrating the cellulose by attrition while acetylation is proceeding, and thus admitting of an unusually uniform ester being produced. In order to obtain esters of relatively high viscosity[4], the acetylating bath is subjected to prolonged cooling

1. C. Dreyfus, E. P. 127678; abst. C. A. 1919, **13**, 2444; J. S. C. I. 1919, **38**, 531-A; Chem. Ztg. 1919, **43**, 581.

2. *Ibid.* E. P. 3321, 1915; abst. J. S. C. I. 1917, **36**, 28.

3. H. Dreyfus, E. P. 6463, 1915; abst. C. A. 1916, **10**, 2637; J. S. C. I. 1916, **35**, 629; Kunst. 1917, **7**, 83; Zts. ang. Chem. 1917, **30**, II, 308. See also E. P. 100009; abst. J. S. C. I. 1916, **35**, 629. F. P. 475160; abst. J. S. C. I. 1916, **35**, 40. See E. P. 20852, 1912; abst. C. A. 1913, **7**, 891; 1914, **8**, 1010. E. P. 20977, 1911. U. S. P. 1278885; abst. C. A. 1918, **12**, 2687; J. S. C. I. 1918, **37**, 729-A. See U. S. P. 1217722. Re. 14338. Australia P. 12206, 1919. F. P. 478023; abst. C. A. 1916, **10**, 1433; J. S. C. I. 1916, **35**, 1152; Ann. Rep. S. C. I. 1917, **2**, 138; Kunst. 1917, **7**, 66. See F. P. 432046; and Addns. 14783, 16316, 16494. Swiss P. 93814, 94022.

4. *Ibid.* E. P. 14101, 1915; abst. C. A. 1917, **11**, 705; J. S. C. I. 1916, **35**, 1152; J. Soc. Dyers. 1917, **33**, 54; Chem. Ztg. 1916, **40**, 991; Kunst. 1918, **8**, 189. See also E. P. 21628, 1901; abst. J. S. C. I. 1901, **20**, 1293; J. Soc. Dyers. 1902, **18**, 24, 275; Mon. Sci. 1913, **77**, 392. E. P. 20977, 1911; abst. C. A. 1913, **7**, 891; J. S. C. I. 1913, **32**, 133; Chem. Ztg. 1913, **37**, 200; Chem. Ztg. Rep. 1913, **37**, 287; Kunst. 1913, **3**, 194. E. P. 20852, 1912; abst. J. S. C. I. 1913, **32**, 1063; C. A. 1914, **8**, 1010; J. Soc. Dyers. 1913, **29**, 56. D. R. P. 159524.

prior to the introduction of the cellulose, and acetylation stopped when the product shows insolubility in chloroform and solubility in alcohol-chloroform. Instead of using sulfuric acid as catalyst, a bisulfate as sodium bisulfate may be employed, the bisulfate being preferably formed in the acetylating mixture by addition of sodium carbonate or acetate[1].

In another method of cellulose acetate production by H. Dreyfus[2], the ester never reaches the chloroform-soluble stage, but is directly dissolvable in alcohol-chloroform. Condensing agents other than sulfuric acid are employed, and the cellulose is subjected to a preliminary hydrolysis or hydration at a temperature lower than that at which acetylation takes place. Where the cellulose and acetylating mixture are brought together in the presence of an amount of water, variations in solubility result[3]. To produce cellulose acetates substantially insoluble in either chloroform or alcohol, cellulose 10, is acted upon with sulfuric acid 2.5, and acetic anhydride 15-30, at not over 40°, then precipitating in the usual manner[4]. In another process for cellulose esterification[5], the amount of acetic anhydride used is based upon the quantity of sulfuric acid catalyst employed, cellulose 10, sulfuric acid 1 requiring 1.8-3 acetic anhydride to give the solubility required.

In order to alter the solubility of cellulose acetates already formed[6], the precipitated ester is admixed with a

1. H. Dreyfus, E. P. 100009; abst. C. A. 1916, **10**, 1269; J. S. C. I. 1916, **35**, 629. Can. P. 191800, 191802; abst. C. A. 1919, **13**, 1927. See E. P. 21376, 1912.

2. *Ibid.* E. P. 101555; abst. C. A. 1917, **11**, 209; J. S. C. I. 1916, **35**, 1152; Chem. Ztg. 1916, **40**, 991. U. S. P. 1280975; abst. J. S. C. I. 1918, **37**, 765-A; Chim. et Ind. 1919, **2**, 831.

3. *Ibid.* U. S. P. 1280974, 1280975; abst. C. A. 1919, **13**, 73; J. S. C. I. 1918, **37**, 765-A; Chim. et Ind. 1919, **2**, 831. F. P. 475160; abst. J. S. C. I. 1916, **35**, 40; Ann. Rep. S. C. I. 1917, **2**, 138; J. Soc. Dyers. 1916, **32**, 78; Mon. Sci. 1916, **83**, 83; Chem. Ztg. 1917, **41**, 23; Kunst. 1917, **7**, 239.

4. *Ibid.* U. S. P. 1181857. Belg. P. 151294.

5. *Ibid.* U. S. P. Re. 14338, to 1181857. For acetic anhydride manufacture, see H. Dreyfus, Ital. P. 158373, 159477, 160188, 160300, 160301.

6. *Ibid.* U. S. P. 1217722, 1280974.

small proportion of inorganic or organic acid, the solubility (in acetone) increasing, and viscosity diminishing with length of treatment. Nitric acid 12% strength is said to be especially efficacious[1]. Where $NaHSO_4$ is used as catalyst instead of H_2SO_4, less attention to pre-cooling is required[2]. As cellulose acetate plastifying bodies, there has been patented ethers of phenols, cresols and naphthols as anisol, methyl-naphthol, ethyl-naphthol, veratrol, pyrocatechol diethyl ether, benzyl-methyl ether, safrol, *iso*safrol and diphenyl ether[3]. Benzyl alcohol, benzhydrol, ethoxy- or methoxy-benzyl alcohol, phenoxy-, chlor-, or nitro-benzyl alcohol have also been advocated as acetate plastifiers[4]. In uninflammable celluloid manufacture, cellulose acetate may be combined with triacetin in amount directly proportional to the viscosity of the cellulose ester used[5]. The celluloid may be subjected to a pressure of 300 kilos per sq. cm., which is about twice that normally employed, in order to make the product more resistant by increasing the compactness[6]. Among the non-nitrogenous plastifiers which have been patented in connection with cellulose acetate fab-

1. H. Dreyfus, U. S. P. 1286172; abst. Kunst. 1920, **10**, 101.

2. *Ibid.* Can. P. 191800, 191801, 191802; abst. C. A. 1919, **13**, 1927; Paper Trade J. 1921, **73**, No. 25, 56; Paper, 1921, **29**, No. 14, 191.

3. *Ibid.* U. S. P. 1181859; abst. C. A. 1916, **10**, 1789; J. S. C. I. 1916, **35**, 687; Mon. Sci. 1917, **84**, 29; Chem. Ztg. 1916, **40**, 659. See F. P. 432264; abst. J. S. C. I. 1912, **31**, 24.

4. *Ibid.* U. S. P. 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. 164868, 167158. F. P. 459539. Swiss P. 65459.

5. *Ibid.* U. S. P. 1325931; abst. C. A. 1920, **14**, 629; J. S. C. I. 1920, **39**, 153-A; Chem. Ztg. 1920, **44**, 258. E. P. 114304; abst. C. A. 1918, **12**, 1512; J. S. C. I. 1918, **37**, 687-A; Mon. Sci. 1919, **86**, 39; Chem. Ztg. 1918, **42**, 614. F. P. 494453; abst. Chim. et Ind. 1920, **4**, 667; Chem. Ztg. 1920, **44**, 5.

6. *Ibid.* E. P. 118891; abst. C. A. 1919, **13**, 73; J. S. C. I. 1918, **37**, 651-A; Chem. Ztg. 1918, **42**, 529. U. S. P. 1315480; abst. C. A. 1919, **13**, 3011; J. S. C. I. 1919, **38**, 814-A. See E. P. 128274; abst. J. S. C. I. 1919, **38**, 484-A. U. S. P. 1280974; abst. C. A. 1919, **13**, 73.

rication[1], are cyclohexanone, methyl- and dimethyl-cyclohexanone.

In acetating cellulose[2], excellent range of solubilities may be obtained at will, by a preliminary cooling of the acetylizing bath to 0° before the cellulose is added, keeping the temperature below 10° and allowing the operation to take a correspondingly longer time. In acetate celluloid substitutes[3], a mixture of alcohol and trichlorethylene, or alcohol and tetrachlorethane[4] have received patent protection. In the formation of transparent fabric suitable for aircraft construction and of low visibility[5], cellulose acetate dissolved in tetrachlorethane is used to reinforce a metallic fabric. Acetylacetone and ethylideneacetone[6] were patented in 1918 as cellulose acetate solvents in conjunction with plastifiers as methyl phthalate.

Xylenemonomethyl- and xylenemonoethyl-sulfonamide[7], with mono-, di-, or tri-methylurea or mono- or di-ethylurea; *o*-toluenemonoethyl-, *o*-toluenemonomethyl-sulfonamide[8] are also examples of substituted sulfonamides which were first drawn to the attention of the world as extensifiers and plas-

1. H. Dreyfus, E. P. 128215; abst. C. A. 1919, **13**, 2444; J. S. C. I. 1920, **39**, 388-A; 445-A; Chem. Ztg. 1920, **44**, 545. Third Addn. 19680 to F. P. 432264; abst. J. S. C. I. 1916, **35**, 40.

2. *Ibid.* U. S. P. 1278885; abst. C. A. 1918, **12**, 2687; J. S. C. I. 1918, **37**, 729-A; Mon. Sci. 1919, **86**, 31. F. P. 478023; abst. J. S. C. I. 1916, **35**, 1152.

3. *Ibid.* U. S. P. 1242783; abst. J. S. C. I. 1917, **36**, 1232; Kunst. 1918, **8**, 143.

4. *Ibid.* U. S. P. 1181858. F. P. 419530, Addn. F. P. 13237.

5. H. Dryvers, E. P. 128274. F. P. 493493; abst. Chim. et Ind. 1920, **3**, 353.

6. H. Dreyfus, E. P. 131669; abst. C. A. 1920, **14**, 346; J. S. C. I. 1919, **38**, 834-A. Ital. P. 164867. 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.

7. *Ibid.* E. P. 132283; abst. C. A. 1920, **14**, 346; J. S. C. I. 1919, **38**, 896-A; Chim. et Ind. 1920, **4**, 798; Chem. Ztg. 1919, **43**, 797; Caout. et Gutta. 1920, **17**, 10659. U. S. P. 1353384; abst. C. A. 1920, **14**, 3792; J. S. C. I. 1920, **39**, 745-A; Phot. Abst. 1921, **3**, 84. F. P. 498726, and Addn. 21381. See also E. P. 114304, 133353. F. P. 675745.

8. *Ibid.* E. P. 133353; abst. J. S. C. I. 1920, **39**, 14-A. U. S. P. 1353385; abst. C. A. 1920, **14**, 3793; J. S. C. I. 1920, **39**, 745-A; Paper, 1921, **27**, #21, 27.

tifiers for cellulose acetate by H. Dreyfus, and have found extensive use since.

In the preparation of acetic acid from acetaldehyde[1], copper or platinum is used as the oxidant, a temperature in excess of 150° being maintained. A. Dubosc[2] published in 1918 a review of the state of the cellulose acetate art, with particular reference to the selection of the type of cellulose for esterification to obtain specific results. In the recovery of formic esters used as solvents of cellulose esters[3], the vapors are first absorbed in an alkaline solution, acid added with an excess of methyl or ethyl alcohol, and the formic acid ester produced recovered by distillation. Acetaldehyde is obtainable from acetylene[4] by oxidizing the latter by means of a mercury compound in presence of ferric sulfate.

Flexible products having cellulose acetate as a base[5], result from the addition thereto of *o*- and *p*-oxybenzyl (hydroxybenzyl) alcohols such as are produced by the action of formaldehyde upon phenol in the presence of dilute alkali. Anhydrides and chlorides of fatty acids (acetic anhydride, acetyl chloride)[6] are formed by treatment of the corresponding chlorine substituted product with phosphorus and distilling. Methods have been described for the preparation of phenylacetic anhydride, butyric anhydride, benzoyl chloride and propionyl chloride.

1. F. P. 487412, 489688. Ital. P. 158637, 159478, 160302, 164852.
2. Caout. et Gutta. 1918, **15**, 9501; abst. C. A. 1919, **13**, 660.
3. J. Duclaux, U. S. P. 1127871; abst. C. A. 1915, **9**, 861; Mon. Sci. 1915, **82**, 44. E. P. 2465, 1913; abst. C. A. 1914, **8**, 2624; J. S. C. I. 1913, **32**, 82. F. P. 439721; abst. J. S. C. I. 1912, **31**, 714; Mon. Sci. 1913, **79**, 181; Kunst. 1912, **2**, 333. F. P. 16214, Addn. to 439721; abst. J. S. C. I. 1913, **32**, 133; Kunst. 1913, **3**, 53. Belg. P. 245532; abst. Chem. Ztg. 1912, **36**, 909; Kunst. 1912, **2**, 399.
4. P. Duden and G. Peters, U. S. P. 1151928, 1151929; Norw. P. 26693, 26694; E. P. 24153, 1914; abst. J. S. C. I. 1915, **34**, 1031. For manufacture of ethylene dichloride and propylene dichloride, see Electric Furnace Products Co., Norw. P. 31349, 31703.
5. J. Dupont, U. S. P. 1317276; abst. J. S. C. I. 1920, **39**, 103-A; C. A. 1919, **13**, 3316.
6. T. Durrans, A. Boake and Roberts & Co., E. P. 128282, 130399, 131379; abst. C. A. 1919, **13**, 2882; 1920, **14**, 187, 285; J. S. C. I. 1919, **38**, 285-A; 739-A; 1920, **39**, 174-A; Mon. Sci. 1922, **77**, 32; Rev. Prod. Chim. 1920, **23**, 197. See E. P. 124542; abst. C. A. 1919, **13**, 1750. U. S. P. 1326040.

J. Edwards and I. Moore[1] have investigated the relative degradation of various coated and uncoated fabrics under ultraviolet light, and find that the deterioration is not directly comparable with that experienced in outdoor service. In molding cellulose acetate[2], the ester is finely divided, small amounts of low-boiling solvents added, and heat and pressure applied, and continued until substantially all of the solvent has dissipated. In phonograph record production[3], in obviating the formation of impure tones caused by microscopic injuries to the edges of the sound grooves or phonetic characters, a base impressionable layer is formed, and over this is flowed a cellulose acetate solution containing plasticizers and softening elements. After volatile solvent has been removed by evaporation, the phonetic indentations are made in the usual manner by combined heat and pressure. Acetylmethylanilid and ethyl lactate are recommended as plasticizers especially useful in this connection[4]. The solvent portion used should be insufficient in amount to cause the cellulose acetate to dissolve until combined heat and pressure are applied[5]. The acetate plastics formed are found in the trade under the names Cellon and Lonardit. An article on Cellonation by M. Bottler precipitated a somewhat acrimonious polemic between

1. Aerial Age Weekly, 1919, **9**, 734; abst. C. A. 1919, **13**, 2136. See J. Edwards et al, U. S. Nat. Adv. Comm. Aeronautics, 1917, 459-78.

2. Cellon-Werke A. Eichengruen, E. P. 147904; abst. Chem. Met. Eng. 1920, **23**, 1228; Caout. et Gutta. 1921, **18**, 10962. D. R. P. Anm. C-27801; abst. Kunst. 1922, **12**, 24; Chem. Ztg. 1921, **45**, 1128. Swiss P. 93296; abst. Chem. Ztg. 1922, **46**, 59. Chem. Ind. 1921, **44**, 183. Ital. P. 147233, 173152.

3. A. Eichengruen, U. S. P. 1175728; abst. C. A. 1916, **10**, 1415.

4. *Ibid.* U. S. P. 1185074, 1916; 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, 1910; abst. J. S. C. I. 1911, **30**, 79; Mon. Sci. 1913, **79**, 551. D. R. P. 287745, 1910; abst. C. A. 1916, **10**, 2145; Kunst. 1915, **5**, 274; Chem. Zentr. 1915, **86**, II, 864; Chem. Ztg. Rep. 1915, **39**, 422.

5. *Ibid.* D. R. P. 296205, Addn. to D. R. P. 287745; abst. Chem. Zentr. 1917, I, 463; Chem. Ztg. Rep. 1917, **41**, 64.

A. Eichengruen and Quittner & Co.[1] in 1916 in which the subject of acetate plastics was reviewed in detail.

In the preparation of so-called "granular" cellulose acetate[2] which is freely soluble in acetone, fibrous acetated cellulose is treated with acetic anhydride in a glacial acetic acid solution of the cellulose ester, and a small proportion of catalyst added, treatment being continued until the solubility desired has been attained. In the shaping of cellulose acetate bodies of considerable wall-thickness[3], the form or mold is dipped into the acetylcellulose solution which contains no softening agent, the solvent expelled and another coating applied, until a plurality of applications builds up the wall to the thickness or strength required. Pinacone diacetate, obtained in quantitative yield by treatment of pinacone with acetic anhydride with addition of a sulfo acid (toluene-, naphthalene- or anthraquinone sulfonic acid) has a solvent action upon some forms of acetated cellulose[4].

Acetylcellulose solution may be made in the absence of volatile solvents[5] by the use of metallic salts dissolved in water (zinc chloride or thiocyanate). In addition to water-soluble products of the condensation of aldehydes with resorcinol or pyrogallol[6], or basic dyestuffs brought to a definite strength by the use of urea instead of dextrin[7], cellulose acetate dissolved in calcium sulfocyanide is employed as a basic dyestuff fixative on cotton for printing on textiles[8]. In a process for the manufacture of acetic anhy-

1. Kunst. 1916, **6**, 56, 99, 151, 152. In this connection see M. Bottler, Kunst. 1916, **6**, 56. Dr. Quittner & Co., Kunst. 1916, **6**, 99.
2. G. Esselen and H. Mork, U. S. P. 1275884; abst .C. A. 1918, **12**, 2248; J. S. C. I. 1918, **37**, 651-A.
3. J. Faber, D. R. P. 368119; abst. Chem. Zentr. 1923, II, 769; Chem. Ztg. 1922, **46**, 1141.
4. Farbenfabriken vorm. Bayer & Co., D. R. P. 281374, 327128; abst. Kunst. 1921, **11**, 13.
5. *Ibid.* D. R. P. 281374; Addn. to D. R. P. 256922; abst. Kunst. 1916, **6**, 113; Chem. Zentr. 1913, I, 1156; 1915, I, 235.
6. *Ibid.* D. R. P. 347131; abst. J. S. C. I. 1922, **41**, 325-A.
7. *Ibid.* D. R. P. 347359; abst. J. S. C. I. 1922, **41**, 325-A.
8. *Ibid.* D. R. P. 347276; abst. J. S. C. I. 1922, **41**, 325-A.

dride and acetaldehyde from ethylidene diacetate[1], the latter is heated in the presence of granulated zinc, thus avoiding resinification of the acetaldehyde which results when sulfuric acid or mercuric sulfate is used. For the preparation of fatty acid esters[2], acetylene is brought in contact at high temperature with an equimolecular mixture of a fatty acid and alcohol in the presence of the mercury salt of a mineral acid. Formic acid and ethyl alcohol yield ethyl formate, and propionic acid and ethyl alcohol, ethyl propionate.

The softness and pliability of cellulose acetate masses may be increased by the addition of ethylenethiohydrin[3]. In the preparation of a metal decorative leaf[4], aluminum or other finely divided metal is admixed with a cellulose acetate lacquer containing resins (copal, sandarac, mastic) and this either sprayed on a surface or floated on water, thus producing imitation gold or silver leaf. In 1916, E. Fischer[5] reviewed the patent literature of the newer cellulose ester solvents, and J. Foltzer[6] illustrated his patented method for producing imitation textile products from cellulose acetate solutions. The applicability of Cellon and Cellonlacquer for impregnating purposes[7], together with tables showing the strength, expansion and extensibility

1. Farbenfabriken vorm. Bayer & Co., D. R. P. 360325; abst. Chem. Zentr. 1923, II, 404; Chem. Tech. Rep. 1922, **46**, 366.

2. Farbwerke, vorm. Meister, Lucius and Bruening, D. R. P. 315021; abst. J. S. C. I. 1920, **39**, 206-A; Chem. Zentr. 1919, IV, 1104; Chim. et Ind. 1920, **4**, 373; Kunst. 1920, **10**, 79. See Farbenfabr. vorm. F. Bayer and Co., D. R. P. 299782; abst. J. S. C. I. 1921, **40**, 717-A; Chem. Zentr. 1921, IV, 513; Kunst. 1922, **12**, 21. D. R. P. 305182; abst. J. S. C. I. 1921, **40**, 561-A; Chem. Zentr. 1921, IV, 40; Chim. et Ind. 1922, **7**, 332.

3. *Ibid.* D. R. P. 366115; abst. J. S. C. I. 1923, **42**, 348-A; Kunst. 1923, **13**, 34.

4. J. Fichtmueller, U. S. P. 1160979.

5. Kunst. 1916, **6**, 210, 225, 244; abst. C. A. 1917, **11**, 1316.

6. J. Foltzer, U. S. P. 1133548; Belg. P. 178221. D. R. P. 209923; abst. Wag. Jahr. 1909, **55**, II, 395. Ital. P. 199587.

7. Sonderabdruk aux der Fach- und Export, Zts. Elektrotechnik. "Helios," 1915, No. 32, 1. Kunst. 1915, **5**, 36.

appeared in an article published in 1915. H. Freter[1] detailed his method for preparing cellulose acetate solutions in 1917.

In coating fabrics with plastic cellulose acetate mixtures[2], adhesion is increased by applying the coating in a stiff condition and causing it to adhere by a long-continued rubbing pressure. The method[3] and apparatus[4] of D. Frothingham and R. Sawyer for preparing coated fabrics with cellulose esters is designed primarily for the utilization of celluloid scrap. As binders for lacquers are recommended metallic resinates or linoleates (aluminum, tin, zinc, manganese, cobalt) dissolved in cyclohexanols or cyclohexanone[5].

A cellulose acetate substitute for celluloid has been patented[6] comprising a resin extract (from which have been removed the acid products, aldehydes and light hydrocarbons as amylene and hexylene) added to acetylcellulose dissolved in a chlorinated hydrocarbon (tetra- or pentachlorethane) and alcohol, an apparatus[7] having been patented for carrying the operation into effect on a commercial scale. Acetaldehyde received patent grant in 1919 as a cellulose acetate solvent[8], in combination with other volatile liquids, or the aldehyde may be replaced by butyl or *iso*butyl formates[9].

1. H. Freter, D. R. P. Anm. F-42400, 1917; abst. Kunst. 1920, **10**, 11; Chem. Ztg. 1919, **43**, 851.
2. U. S. P. 1316782; abst. C. A. 1919, **13**, 3011.
3. U. S. P. 1316783; abst. C. A. 1919, **13**, 3011.
4. D. Frothingham and R. Sawyer, U. S. P. 1316784; abst. C. A. 1919, **13**, 3011.
5. P. Friesenhahn, D. R. P. 334761; abst. J. S. C. I. 1921, **40**, 399-A. D. R. P. 327180; abst. J. S. C. I. 1921, **40**, 459-A; Kunst. 1920, **10**, 197.
6. B. Gaisenband and C. Piestrak, F. P. 483316; abst. C. A. 1918, **12**, 995.
7. *Ibid.* F. P. 485068; abst. C. A. 1919, **13**, 1927; Rev. Chim. Ind. 1917, **28**, 87.
8. R. Gilmour and W. Dunville & Co., E. P. 131647; abst. C. A. 1920, **14**, 346; J. S. C. I. 1919, **38**, 896-A; Chem. Ztg. 1919, **43**, 733; Kunst. 1920, **10**, 79; 1921, **11**, 61 ;Chem. Age, (London), 1919, **1**, 453; Caout. et Gutta. 1920, **17**, 10659.
9. *Ibid.* E. P. 132996; abst. C. A. 1920, **14**, 358.

In dyeing artificial leathers formed of cellulose ester coatings[1], the latter are mixed with substances (aluminum hydroxide, acetate or silicate) which readily form lakes with aniline dyes, then applying the cellulose ester composition to the fabric and subsequently treating with dyestuffs. In finishing the edges of leather[2], particularly those used in shoe uppers so as to produce smoothly rounded edges, a cellulose ester plastic is applied to the abraded edges and dried. In the coating of fabrics used in the manufacture of balloons and dirigibles[3], the coating of gelatin is applied between the plies of the fabric, and as an exterior coat a cellulose ester is superposed, which may be pigmented to lessen hydrogen permeation and actinic effect.

Alkyl- or aryl-carbamates of cellulose(i.e. cellulose phenylcarbamate)[4] may be made by reacting upon cellulose with an aliphatic or aromatic isocyanic ester as phenyl isocyanate, the reaction being carried out in the presence of tertiary bases as dry pyridine. In the B. Goldsmith new composition of matter[5], acetylcellulose is admixed with oils (soy bean, cottonseed, olive, linseed, sperm, corn, castor) with sufficient nitric acid to oxidize but not to nitrate them, the stuff pastes being recommended for insulating pur-

1. E. Girzik, D. R. P. 281304, 1913; abst. C. A. 1915, **9**, 2153; Chem. Zentr. 1915, **86**, I, 228; Chem. Ind. 1915, **38**, 81; Chem. Ztg. Rep. 1915, **39**, 88; Kunst. 1915, **5**, 21; Wag. Jahr. 1914, **60**, II, 483; Zts. ang. Chem. 1915, **28**, 88. E. P. 4668, 1913; abst. C. A. 1915, **9**, 2152. D. R. P. 286120, 1915; abst. C. A. 1916, **10**, 973; Chem. Zentr. 1915, **86**, II, 447; Chem. Tech. Rep. 1915, **39**, 311; Chem. Ztg. 1915, **39**, 487; Kunst. 1915, **5**, 202; Wag. Jahr. 1915, **61**, II, 289; Zts. ang. Chem. 1915, **28**, II, 468. Aust. P. 3034; abst. C. A. 1914, **8**, 2229.

2. P. Glass and H. Halloran, U. S. P. 1181758.

3. R. Glazebrook, W. Rouse and A. Johnston, E. P. 124520; abst. C. A. 1919, **13**, 1770; J. S. C. I. 1919, **38**, 557-A.

4. P. Goissedet, U. S. P. 1357450; abst. C. A. 1921, **15**, 436; J. S. C. I. 1920, **39**, 817-A; Caout. et Gutta. 1921, **18**, 11074; Paper. 1921, **27**, 26. E. P. 130277; abst. C. A. 1920, **14**, 122; J. S. C. I. 1919, **38**, 714-A. F. P. 496526; abst. Mon. Sci. 1921, **88**, 25; Chim. et Ind. 1920, **4**, 668; Textilber. 1921, **3**, 202; Paper, 1921, **28**, 38. D. R. P. Anm. G-47759; abst. Chem. Ztg. 1922, **46**, 600. Swiss P. 88193. Ital. P. 172228.

5. U. S. P. 1152625; abst. C. A. 1915, **9**, 2800; Mon. Sci. 1916, **83**, 78.

poses. As an acetylcellulose dope for aeroplanes, he[1] recommends adding to the cellulose ester in solution, either acetanilid alone or with triacetin.

Where an acetone-soluble cellulose acetate is used for dopes and varnishes[2], plasticizers are recommended of *n*-butyl, *iso*-butyl or *iso*amyl neutral tartrates or citrates. In the production of acetaldehyde by passing acetylene into acid solutions of mercury salts, the mercury sludge formed in the process may be revivified by adding to the reaction liquid a small quantity of hydrogen dioxide and agitating the mixture[3]. The W. Grosvenor moving-picture film[4] comprises mechanical features for utilizing cellulose acetate film base.

In order to obviate the variation in tautness of cellulose acetate coated fabric used in airplane construction due to varying humidity in the atmosphere[5], the ester lacquer has incorporated therein, hygroscopic salts soluble in organic solvents as calcium, magnesium, zinc or tin chlorides, in 1-3% of the weight of the dope. Ammonium chloride may be used for the same purpose[6]. A mixture of xylene and ethyl lactate was patented in 1916 as a cellulose plasticizer combination[7], in which year[8] the E. de Haen cellulose acetate manufacturing process appeared.

1. B. 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.

2. J. Grolea and J. Weyler, E. P. 123712; abst. J. S. C. I. 1919, **38**, 714-A; Kunst. 1922, **12**, 6. F. P. 489037.

3. Crosfield & Sons, J. Warrington and T. Hilditch, E. P. 124702, 125926, 131084; abst. C. A. 1919, **13**, 1715, 2218; 1920, **14**, 72; J. S. C. I. 1919, **38**, 274-A, 346-A, 388-A, 440-A; Mon. Sci. 1922, (5), **12**, 21.

4. U. S. P. 1226655.

5. S. Groves and T. Ward, E. P. 128659; abst. C. A. 1919, **13**, 3028; J. S. C. I. 1919, **38**, 518-A; Kunst. 1921, **11**, 71.

6. *Ibid.* E. P. 131093; abst. C. A. 1920, **14**, 227; Kunst. 1922, **12**, 6.

7. R. Grueter, U. S. P. 1195673; abst. C. A. 1916, **10**, 2646; J. S. C. I. 1916, **35**, 1026. F. P. 464617; abst. J. S. C. I. 1914, **33**, 557.

8. E. de Haën, Chemische Fabrik "List," D. R. P. Anm. H-67436; abst. Kunst. 1916, **6**, 52.

For use as a dielectric for electrical condensers[1], extremely thin tissue paper is coated with cellulose acetate solution, the thin paper being supported by a heavier backing. The K. Haring leather substitute[2] comprises felt impregnated with cellit in solution, the solvent then evaporated and a coating of pitch in benzene applied. In the formation of fatty acids and aldehydes[3], ozonides of unsaturated aliphatic oils derived from petroleum, or from tar products of lignites, shales, peats or asphalts, are decomposed in solution to form aldehydes, which are removed from the mass by solvent extraction. In obtaining esters from crude pyroligneous acid[4], the latter is neutralized and evaporated until, on cooling, sodium acetate crystallizes out, the methyl alcohol being recovered by distillation. A solvent rich in methyl acetate or other alkyl acetate is obtained by treating pyroligneous acid with a condensing agent (sulfuric acid) and maintaining the mass at a temperature capable of effecting esterification. It is claimed there is no production of methyl sulfate[5].

P. Hewitt has been granted three patents for producing light-transforming compositions, by a class of devices employed for combining with light rays deficient in some portion of the spectrum; efficiency, durability and retentiveness is increased by using rhodamine dissolved in a cellulose acetate lacquer[6], together with alcohol[7], glycerol[8], or

1. F. Haigh, E. P. 138226; abst. J. S. C. I. 1920, **39**, 292-A. See E. P. 24981, 1911.
2. U. S. P. 1179357; abst. C. A. 1916, **10**, 1608.
3. C. Harries, R. Koetschau and E. Albrecht, D. R. P. 324663; abst. J. S. C. I. 1920, **39**, 1920.
4. Haschkowerke Eberhard & Jakob, D. R. P. 325639; abst. J. S. C. I. 1921, **40**, 27-A.
5. A. Helbronner and G. Criquebeuf, U. S. P. 1260977; abst. C. A. 1918, **12**, 1511; J. S. C. I. 1918, **37**, 283-A. F. P. 464646; abst. J. S. C. I. 1914, **33**, 502. F. P. 18975, Addn. to 464646.
6. P. Hewitt, U. S. P. 1188655; abst. C. A. 1916, **10**, 2157; J. S. C. I. 1916, **35**, 898; Kunst. 1916, **6**, 266. E. P. 16271, 1911. D. R. P. 254083; abst. C. A. 1914, **8**, 1065; Chem. Zentr. 1914, I, 136. See U. S. P. 907598.
7. *Ibid.* U. S. P. 1188775; abst. C. A. 1916, **10**, 2157; J. S. C. I. 1916, **35**, 898; Mon. Sci. 1917, **84**, 60; Kunst. 1916, **6**, 264.
8. *Ibid.* U. S. P. 1188776; abst. C. A. 1916, **10**, 2157; J. S. C. I. 1916, **35**, 898; Mon. Sci. 1917, **84**, 60.

acetone[1]. As a substitute for leather[2], the bast bark or birch is soaked in a hardening solution to fill the pores and waterproof the bast without deleteriously affecting the flexibility (?), after which an acetylcellulose is applied. H. Hibbert[3] detailed the innovations in acetic acid and acetone manufacture up to 1919.

The C. Higgins stiffening compound of acetylcellulose[4] is applied in the undissolved condition between layers of felt, the stiffening action being afterwards developed by the addition of solvent which is subsequently dissipated. In the preparation of pliable cellulose ester lacquers[5] glycol esters of such fatty acids as those obtained from rape oil (colza oil) as glycol erucate, linoleate and linolenate are advocated.

C. Hudson and co-workers in a series of four papers have investigated the acetylated polysaccharides, and determined the physical constants and reactions of *b*-maltose octa-acetate, cellose octa-acetate[6], the lactose octa-acetates[7], mannose penta-acetates[8] and *d*-fructose penta-acetate[9]. J. Huebner[10] prepares cellulose acetate solutions suitable for artificial fiber formation by dissolving the ester in a mixture of formic or acetic acids and methyl or ethyl alcohols. A waterproof line used for fishing has been de-

1. P. Hewitt, U. S. P. 1188777; abst. C. A. 1916, **10**, 2157; J. S. C. I. 1916, **35**, 898; Mon. Sci. 1917, **84**, 60.
2. von Heynitz, D. R. P. 320629; abst. C. A. 1921, **15**, 774; J. S. C. I. 1920, **39**, 633-A; Kunst. 1920, **10**, 134; Chem. Zentr. 1920, IV, 149.
3. H. Hibbert, Chem. Met. Eng. 1918, **19**, 397; abst. C. A. 1918, **12**, 2324; J. S. C. I. 1918, **37**, 671-A; Chem. Zentr. 1919, II, 928.
4. C. Higgins, E. P. 3278, 1915; abst. Kunst. 1916, **6**, 298.
5. A. Hildesheimer, D. R. P. 338475; abst. Chem. Zentr. 1921, IV, 471; Chem. Tech. Uebers. 1923, **47**, 55; Chim. et Ind. 1922, **8**, 647.
6. C. Hudson and J. Hudson, J. A. C. S. 1915, **37**, 1276; abst. C. A. 1915, **9**, 1770.
7. C. Hudson and J. Johnson, J. A. C. S. 1915, **37**, 1270; abst. C. A. 1915, **9**, 1770.
8. C. Hudson and J. Dale, J. A. C. S. 1915, **37**, 1280; abst. C. A. 1915, **9**, 1771.
9. C. Hudson and D. Brauns, J. A. C. S. 1915, **37**, 1283; abst. C. A. 1915, **9**, 1771.
10. E. P. 127027; abst. C. A. 1919, **13**, 2443; J. S. C. I. 1919, **38**, 678-A; Chem. Ztg. 1919, **43**, 589.

scribed[1], in which acetylcellulose 100, castor oil 250 is dissolved in amyl acetate 400, to which is added urea 2 as antacid and a mixture of dichlorhydrin and methyl alcohol 600. Such a line is nearly invisible in the water.

In the manufacture of cellulose formate solutions[2], resorcinol 30 to cellulose ester 10 has been patented, as well as chloral hydrate and chloral alcoholate[3]. Also[4], the following salts are employed as solvents: sodium, potassium, ammonium, calcium, copper chlorides and bromides; ammonium, calcium, magnesium, strontium nitrates; alkali xanthates, aniline salts and alkali salts of mono- and polysulfonic acids. The cellulose formate is stirred into the previously prepared salt solution with heat. Ammonium bichromate 30, dissolved in water 100 and cellulose formate 20, gives a transparent but yellow solution[5]. In the manufacture of patent leather coatings[6], the leather is first treated with a solution of gelatin in acetic acid and then a cellulose acetate lacquer applied as a top coat. Ethyl formate as a solvent of cellulose acetate[7] is said to be especially useful in film formation. In 1918 M. Jenett and M. List[8] described various methods for the employment of acetylcellulose plastics.

1. J. Hyde, U. S. P. 1165179; abst. C. A. 1916, **10**, 393; Kunst. 1916, **6**, 150. See U. S. P. 673955.

2. Internationale 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. *Ibid.* D. R. P. 265911; abst. C. A. 1914, **8**, 573; J. S. C. I. 1913, **32**, 1104; Chem. Zentr. 1913, II, 1635.

4. *Ibid.* D. R. P. 266600; abst. C. A. 1914, **8**, 573; J. S. C. I. 1914, **33**, 196.

5. *Ibid.* D. R. P. 267557; Addn. to D. R. P. 266600; abst. C. A. 1914, **8**, 822; J. S. C. I. 1914, **33**, 196.

6. *Ibid.* D. R. P. 300908; abst. Chem. Zentr. 1917, II, 716.

7. B. Jaillard, F. P. 487350 and Addn. 22415; abst. Rev. Prod. Chim. 1921, **24**, 712; Caout. et Gutta. 1921, **18**, 11148.

8. Chem. Tech. Wochschr. 1918, **2**, 287; abst. Chem. Zentr. 1919, II, 428.

W. Jones has shown[1] whereby acetated cellulose may be introduced at any stage of the reaction prior to the final hardening in the manufacture of phenol-aldehyde condensates, phenyl or cresyl acetates being also present to assist in the solution of the cellulose ester. The toxic effects of acetate lacquer used in airplane wing coating, as developed at the Johannisthaler Flying Material Factory has been detailed by Jungfer[2]. For increasing the softness and pliability of cellulose acetate films[3], the methyl, ethyl and amyl sulfones of benzene, toluene and xylene, or ethyl phenylsulfonacetate have been brought forward, being stable to both acids and alkalis. Phenylethylsulfone, ethyl phenylsulfonacetate and *m*-xylylethylsulfone are especially recommended. As a face protector, W. Kemp[4] proposes to use a mask composed of transparent cellulose acetate, claiming it is "fire resisting." As a non-blushing brush lacquer, J. Kessler[5] has claimed acetaldol with cellulose acetate and methyl acetate, ethyl formate and methylethyl ketone as volatile solvents. Acetaldol (*b*-oxybutyraldehyde, aldol) boils at 88° at 20 mm. pressure. The use of acetate plastics in the airplane industry for coating and tautening purposes was detailed in 1918 by G. Kippenberger[6].

Combinations of cellulose acetate with polymerized vinyl acetate or chloracetate produce plastic products readily moldable[7]. It is well understood that dry acetylcellulose threads, especially those produced from the primary acetylizing solution, become easily electrified when unwound

1. U. S. P. 1209165; abst. C. A. 1917, **11**, 710; J. S. C. I. 1917, **36**, 225.
2. Farben Ztg. 1916, **21**, 544; abst. Kunst. 1916, **6**, 131.
3. M. Schmidt and Kalle & Co., D. R. P. 366116; abst. J. S. C. I. 1923, **42**, 348-A; Kunst. 1923, **13**, 34; Chem. Ztg. 1922, **46**, 1051.
4. U. S. P. 1238154.
5. U. S. P. 1303563; abst. C. A. 1919, **13**, 1938; J. S. C. I. 1919, **38**, 531-A; Chim. et Ind. 1921, **5**, 578.
6. "Der Weltmarkt," 1918, 149; abst. Kunst. 1918, **8**, 288.
7. 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.

from the bobbin[1]. This may be remedied by passing the threads through a bath of soap or soluble oil. In order to produce plastics without the interposition of volatile solvents requiring subsequent removal[2], swollen, chloroform-soluble acetylcellulose is directly submitted to combined heat and pressure until the moisture has been expelled. In order to obviate depolymerization of the cellulose molecule in partial hydration immediately succeeding acetylation[3], the acetylating mixture is cooled to a lower temperature, and water added in such small portions that the temperature is not allowed to rise.

Resorcinol monoacetate[4], on account of the fact that with cellulose acetate a mass is produced which becomes soft on warming and hardens upon cooling, is said to play a role similar to camphor as a thermoplasticizer with nitrocellulose. Instead of sulfuric acid, ammonium chloride or nitrate or ferric chloride[5] is said to produce readily soluble cellulose acetate when used in the acylating bath with acetic acid and anhydride. The change[6] of cellulose acetate difficulty soluble in acetone to that easily dissolvable therein may be brought about in the absence of a catalyst by treatment of the cellulose acetate in solution with a mixture of acetic acid containing 6% water at a temperature of 100°. Where the water is added in small portions and at a low temperature[7], it is possible to transform the

1. Knoll & Co., D. R. P. 286173; abst. J. S. C. I. 1915, **34**, 1138. They (D. R. P. 284726, Addn. to D. R. P. 203178; Ital. P. 172678; abst. Wagn. Jahr. 1915, **61**, II, 15) prepare stable acetylcellulose solutions by esterizing in the presence of acid sulfates and an indifferent solvent or diluent, potassium bisulfate being used.
2. *Ibid.* D. R. P. 293261; abst. Kunst. 1916, **6**, 250.
3. *Ibid.* D. R. P. 297504; abst. Chem. Zentr. 1917, I, 1038.
4. *Ibid.* D. R. P. 298806; abst. J. S. C. I. 1920, **39**, 483-A; Chim. et Ind. 1921, **5**, 335; Chem. Zentr. 1920, II, 542; Chem. Ztg. 1919, **43**, 901; Kunst. 1920, **10**, 22, 69; Caout. et Gutta. 1921, **18**, 11157.
5. *Ibid.* D. R. P. 303530, Addn. to D. R. P. 297504; abst. Chem. Zentr. 1918, I, 499; Kunst. 1918, **8**, 102.
6. *Ibid.* D. R. P. 305348, Addn. to D. R. P. 297504; abst. Chem. Zentr. 1918, I, 977; Chem. Ztg. 1918, **42**, 154.
7. *Ibid.* D. R. P. 305884, D. R. P. 297504; abst. Chem. Zentr. 1918, II, 236; Chem. Ztg. 1918, **42**, 190.

acetic anhydride into acid, and partially hydrate the esterified cellulose to an acetone-soluble condition without essentially decomposing the cellulose ester. Or[1], acetone-insoluble acetylcellulose may be changed to the acetone-soluble modification by means of heat alone, the cellulose acetate being first precipitated, washed free from reactants, then heated with 8-10 times its weight of acetic acid at 100°. The addition of 0.1 part methylamine bisulfate containing 10% methylamine sulfate assists the change in solubility. When cellulose acetate solutions in chloroform or acetone containing water are heated to 90-100° in the absence of catalysts, the ester is gradually transformed into a product dissolving completely in ethyl acetate[2]. This change may be more quickly brought about by the introduction of bodies other than water containing hydroxyl groups as glycerol, the acetins or glycols[3].

E. Knoevenagel[4] modifies the solubility of acetylcellulose to an acetone-soluble form, by heating an acetone-insoluble ester in the presence of a substance which will induce only slight hydrolytic decomposition, until the solubility desired has been reached. Proposed for cellulose acetylation[5], methylene sulfate obtained by causing fuming sulfuric acid to react upon trioxymethylene[6] was added to

1. Knoll & Co., D. R. P. 306131, Addn. to D. R. P. 297504; abst. Chem. Zentr. 1918, II, 325; Kunst. 1918, **8**, 120; Chem. Ztg. 1918, **42**, 226.

2. *Ibid.* D. R. P. 346672, Addn. to D. R. P. 297504; abst. J. S. C. I. 1922, **41**, 248-A; Chem. Tech. Uebers. 1922, **46**, 74; Chim. et Ind. 1923, **9**, 354.

3. *Ibid.* D. R. P. 347817, Addn. to D. R. P. 297504; abst. J. S. C. I. 1922, **41**, 410-A; Chim. et Ind. 1923, **9**, 354; Chem. Tech. Uebers. 1922, **46**, 97; Chem. Ztg. 1921, **45**, 1255.

4. U. S. P. 1241995; F. P. 453835; D. R. P. 297504, 305348; abst. J. S. C. I. 1913, **32**, 785; 1917, **36**, 1174; C. A. 1918, **12**, 223; Chem. Zentr. 1918, **89**, I, 499, 977. In this connection see U. S. P. 838350; F. P. 371447; 14558, Addn. to F. P. 432046; D. R. P. 203178.

5. J. Koetschet and M. Theumann, U. S. P. 1191439; F. P. 478436; E. P. 10822, 1915; Swiss P. 77663; abst. C. A. 1916, **10**, 2298, 2299; 1917, **11**, 209; 1918, **12**, 2439; J. S. C. I. 1915, **34**, 1086; 1916, **35**, 1009; 1918, **37**, 2439.

6. M. Delepine, Compt. rend, 1899, **129**, 831.

the list of catalysts in 1916, and trioxymethylene[1] the next year. As a pretreatment to acetylation[2], it is recommended subjecting cellulose to the action of glacial acetic acid with a small amount of acetic anhydride and catalyst until a fluid mass is obtained, which is then acetylated in the usual manner, forming acetylcellulose of very low viscosity and high solubility. The addition of a small amount of nitric acid[3] is said to facilitate the transformation.

When acetaldehyde is allowed to slowly run into furfurol at low temperatures[4] in the presence of a small amount of NaOH, pale yellow crystals of furfuracrolein are obtained which combine with acetylcellulose in the presence of volatile solvents to produce a moldable composition. In the preparation of fabrics and fibers as a substitute for wool[5] hair, horn or leather refuse is treated with solutions of acetylcellulose with the addition of glycerol and triphenyl phosphate. The material is formed into fibers and these spun into yarn or cloth in the same manner as paper yarn.

La Soie Artificielle[6] have described a compound obtained by the action of trioxymethylene upon cellulose in the presence of a substance facilitating the reaction as alum or calcium chloride, the product formed being transparent and very resistant to water. A projection screen has been patented[7], made by treating a textile backing with cellulose acetate dope to render it waterproof, coating one sur-

1. J. Koetschet and M. Theumann, U. S. P. 1216462; abst. C. A. 1916, **10**, 1301; J. S. C. I. 1917, **36**, 383. E. P. 7773, 1915; abst. J. S. C. I. 1916, **35**, 302. Swiss P. 71695.
2. J. Koetschet, U. S. P. 1258913; F. P. 473399; E. P. 13696, 1914; Swiss P. 59412, 68996; abst. C. A. 1915, **9**, 3358; 1918, **12**, 1420; J. S. C. I. 1915, **34**, 488, 606; 1918, **37**, 265-A. Swiss P. 78108.
3. J. Koetschet and M. Theumann, U. S. P. 1286025; E. P. 8046, 1915; abst. C. A. 1919, **13**, 261; J. S. C. I. 1916, **35**, 39; 1919, **38**, 102-A.
4. W. Koenig and K. Hey, D. R. P. 330358; abst. Kunst. 1921, **11**, 29.
5. P. Krais, D. R. P. 302611; abst. J. S. C. I. 1918, **37**, 332-A.
6. Swiss P. 74231. Same as E. Bloch-Pimental, U. S. P. 1234720; abst. C. A. 1917, **11**, 2611; J. S. C. I. 1917, **36**, 1044.
7. W. Lawrence, E. P. 143748; abst. C. A. 1920, **14**, 2977.

face with adhesive material, and depositing aluminum powder on the adhesive material while it is still tacky.

The L. Lederer product resembling celluloid[1], comprises cellulose acetate with chloral hydrate or chloral alcoholate as plasticizing bodies, a small amount of tetrachlorethane being added, while F. Lehmann and J. Stocker combine acetylcellulose with coumarone resin[2] for the same purpose, the cumarone resin being first purified if transparent products are desired[3]. A mixture suitable for forming tough, flexible films or sheets results by combining cellulose acetate 85, nitrocellulose 12 and partly oxidized China wood oil 3, a mixture of acetone 30, acetic acid 30, being used to dissolve the ingredients[4]. Or[5], a softening agent as castor, palm, China wood or rape oil may be incorporated with the cellulose ester in the presence of volatile solvents to produce a similar effect.

According to L. Lilienfeld[6], merchantable artificial leather may be produced by combining cellulose acetate with a phenol ester which remains liquid at 0° (*o*-tricresyl phosphate), dissolving in volatile solvents, and coating a fabric alternately with a coating of the above and then one of viscose until a sufficient number of layers have been built up. Castor oil[7] is featured as a desirable addition to the above composition to induce softness.

1. L. Lederer, 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, 1904.
2. F. Lehmann and J. Stocker, U. S. P. 1185514; abst. C. A. 1916, **10**, 1939. Aust. P. 71287; abst. Chem. Ztg. 1916, **40**, 196; Kunst. 1917, **7**, 12.
3. *Ibid.* 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.
4. H. Levey, U. S. P. 1295533; abst. C. A. 1919, **13**, 1255; J. S. C. I. 1919, **38**, 357-A.
5. *Ibid.* U. S. P. 1316311; abst. C. A. 1919, **13**, 3011; J. S. C. I. 1919, **38**, 897-A; Caout. et Gutta. 1920, **17**, 10659; Chim. et Ind. 1921, **6**, 818.
6. U. S. P. 1140174; abst. C. A. 1915, **9**, 1856; Kunst. 1913, **3**, 474. E. P. 28210, 1912; abst. C. A. 1914, **8**, 1886; J. S. C. I. 1914, **33**, 432.
7. L. Lilienfeld, U. S. P. 1217123; abst. J. S. C. I. 1917, **36**, 396. F. P. 456261; abst. C. A. 1914, **8**, 2277; J. S. C. I. 1913, **32**, 953.

A series of 36 patents was issued to W. Lindsay in the cellulose ester art during this five year period, the majority of them disclosing new direct or ancillary solvents and/or ways of utilizing them. They comprehend triphenyl or tricresyl phosphates in conjunction with methyl or ethyl alcohol[1], or a mixture of tetrachlorethane and acetone[2]; tetrachlorethyl- and trichlormethyl-acetanilid[3]; ethyl acetate with methyl alcohol[4]; benzene, methyl alcohol and *p*-ethyltoluenesulfonamid[5]; ethylacetanilid, tetrachlorethylacetanilid, methylacetanilid or *p*-ethyltoluenesulfonamid with chloroform and methyl or ethyl alcohol[6]; triphenyl phosphate in conjunction with *p*-ethyltoluenesulfonamid[7], or with trichlorethylene[8]; to both of which methyl alcohol and benzene may constitute the volatile solvent portion[9]. Diphenylamine[10]; fusel oil (propyl, butyl, amyl alcohols) with triphenyl phosphate[11]; or fusel oil alcohols with chloroform and ethyl alcohol[12]. *p*-Ethyltoluenesulfonamid,

1. U. S. P. 1128468, 1915; abst. C. A. 1915, **9**, 1114, 1546; J. S. C. I. 1915, **34**, 349; Mon. Sci. 1915, **82**, 44; Kunst. 1915, **5**, 131.

2. U. S. P. 1133385, 1915; abst. C. A. 1915, **9**, 1282; J. S. C. I. 1915, **34**, 488; Mon. Sci. 1915, **82**, 45. F. P. 415517, 1910; abst. J. S. C. I. 1910, **29**, 1299; 1911, **30**, 679; 1915, **34**, 488; Mon. Sci. 1912, **77**, 9; 1913, **79**, 392; Rev. Chim. Ind. 1910, **21**, 385; 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.

3. U. S. P. 1136245, 1915; abst. J. S. C. I. 1915, **34**, 606; Mon. Sci. 1915, **82**, 45.

4. U. S. P. 1143979, 1915; abst. C. A. 1915, **9**, 2311; J. S. C. I. 1915, **34**, 830; J. Soc. Dyers. 1915, **31**, 195; Mon. Sci. 1916, **82**, 77. See also U. S. P. 1128468, 1133385, 1136248, 1915.

5. U. S. P. 1188797; abst. C. A. 1916, **10**, 2146; J. S. C. I. 1916, **35**, 887; Chem. Ztg. 1916, **40**, 805.

6. U. S. P. 1188798; abst. C. A. 1916, **10**, 2145; J. S. C. I. 1916, **35**, 887; Chem. Ztg. 1916, **40**, 805.

7. U. S. P. 1188799; abst. C. A. 1916, **10**, 2145; J. S. C. I. 1917, **36**, 887.

8. U. S. P. 1188800; abst. C. A. 1916, **10**, 2145; J. S. C. I. 1917, **36**, 887.

9. U. S. P. 1199395; abst. C. A. 1916, **10**, 3158; J. S. C. I. 1916, **35**, 1215.

10. U. S. P. 1199798; abst. C. A. 1916, **10**, 3159; J. S. C. I. 1916, **35**, 1215.

11. U. S. P. 1199799; abst. C. A. 1916, **10**, 3159; J. S. C. I. 1916, **35**, 1215.

12. U. S. P. 1199800; abst. C. A. 1916, **10**, 3159; J. S. C. I. 1916, **35**, 1215.

triphenyl phosphate, ethyl acetate and methyl alcohol[1]; tetrachlorethyl- or trichlormethyl-acetanilid and ethyl alcohol[2]; methyl alcohol, water and benzene in conjunction with the above named plasticizers[3]; and epichlorhydrin and methyl alcohol[4]; methyl acetate and methyl alcohol[5] alone, or with *p*-ethyltoluenesulfonamid[6]. Continuing, Lindsay combined sulfonamids, triphenyl phosphate with epichlorhydrin and methyl alcohol[7], or chloroform with methyl or ethyl alcohol as the volatile portion of the formula[8]. Trichlorethylene and methyl alcohol[9]; chloroform and methyl or ethyl alcohol[10]; and benzyl benzoate completes the category. All have been patented as especially useful in connection with the acetone-soluble class of cellulose acetates. A cellulose acetate which is not completely soluble in anhydrous acetone is of diminished commercial value. If the partial hydration has not been carried to the point of complete solubility in anhydrous acetone then the tenuity of films prepared therefrom is lacking. If carried beyond the point of solubility in dry acetone to solubility in acetone containing water therein, then hydration has proceeded too far, and the tensile strength in film form is impaired (the cellulose acetate has "rotted")[11].

1. U. S. P. 1203756; abst. C. A. 1917, **11**, 99; J. S. C. I. 1916, **35**, 1256.
2. U. S. P. 1216581; abst. C. A. 1917, **11**, 1301; J. S. C. I. 1917, **36**, 450.
3. U. S. P. 1226339; abst. C. A. 1917, **11**, 2153; J. S. C. I. 1917, **36**, 707; Kunst. 1918, **8**, 9.
4. U. S. P. 1226340; abst. C. A. 1917, **11**, 2153; J. S. C. I. 1917, **36**, 707; Kunst. 1918, **8**, 9.
5. U. S. P. 1226341; abst. C. A. 1917, **11**, 2157; J. S. C. I. 1917, **36**, 707.
6. U. S. P. 1226342; abst. C. A. 1917, **11**, 2157; J. S. C. I. 1917, **36**, 707; Kunst. 1918, **8**, 9.
7. U. S. P. 1226343; abst. C. A. 1917, **11**, 2157; J. S. C. I. 1917, **36**, 707.
8. U. S. P. 1229485; abst. C. A. 1917, **11**, 2276; J. S. C. I. 1917, **36**, 869.
9. U. S. P. 1229486; abst. C. A. 1917, **11**, 2276; J. S. C. I. 1917, **36**, 869.
10. U. S. P. 1229487; abst. C. A. 1917, **11**, 2276; J. S. C. I. 1917, **36**, 869.
11. U. S. P. 1233374; abst. C. A. 1917, **11**, 2612; J. S. C. I. 1917, **36**, 1004; Kunst. 1918, **8**, 57.

Lindsay treats cellulose in a preliminary bath of hydrous acetic acid, which, without altering the physical appearance of the cellulose increases its reactivity, and hence augments danger of too rapid or of uncontrollable esterification[1]. In order to obviate this, acetylation is conducted in the presence of an inert diluting medium (benzene) and the ester thereby obtained in a fibrous form. It is not clear why additional expense of non-solvent diluent should be made in any esterizing bath, for the acetated celluloses have no commercial applications in the *dry* state. When cellulose 100 is treated with 90% acetic acid 200, and zinc chloride 50 (an unduly large amount), and this impregnated material then subjected to the action of an acetylizing bath in the presence of an excess of benzene, a fibrous acetate results soluble in tetrachlorethane and with difficulty in chloroform free from alcohol[2].

A composition suitable for films or molded articles is prepared from acetone soluble acetylcellulose when the ester is dissolved in a chloroform-alcohol mixture with either *p*-ethyltoluenesulfonamid[3] or methyl- or ethyl-acetanilid. In a series of three patents of adjacent numbers, methyl or ethyl alcohol is the volatile solvent employed, and ethyl-*p*-toluenesulfonamid[4], alkylacetanilid[5], or chloroform are the combinations specified and claimed[6]. Triphenyl phosphate, acetone and dichlorhydrin[7], or other chlorine substituted hydrocarbon (epichlorhydrin, acetodichlorhydrin, dichlorethylene, ethylene chloride, trichlorethylene, aceto-

1. U. S. P. 1236578; abst. C. A. 1917, **11**, 2963; J. S. C. I. 1917, **36**, 1092; Kunst. 1918, **8**, 69; L'Ind. Chim. 1918, **5**, 93.
2. U. S. P. 1236579; abst. C. A. 1917, **11**, 2963; J. S. C. I. 1917, **36**, 1092; Kunst. 1918, **8**, 69.
3. U. S. P. 1244107; abst. C. A. 1918, **12**, 424; J. S. C. I. 1917, **36**, 1269; Chem. Ztg. 1918, **42**, 178.
4. U. S. P. 1244108; abst. J. S. C. I. 1917, **36**, 1269; Chem. Ztg. 1918, **42**, 178.
5. U. S. P. 1244347; abst. C. A. 1918, **12**, 424; J. S. C. I. 1917, **36**, 1269; Chem. Ztg. 1918, **42**, 118.
6. U. S. P. 1244348; abst. C. A. 1918, **12**, 424; J. S. C. I. 1917, **36**, 1269; Chem. Ztg. 1918, **42**, 118.
7. U. S. P. 1244349; abst. C. A. 1918, **12**, 424; J. S. C. I. 1917, **36**, 1269; Chem. Ztg. 1918, **42**, 118.

chlorhydrin, tetra- and penta-chlorethane, ethyl chloracetate, diacetochlorhydrin)[1] completes the enumeration.

In another method for the production of fibrous acetated cellulose[2], cotton rovings are pretreated with 90% acetic acid, then added to the usual acetylizing bath in the presence of an ample amount of benzene at a temperature of about 20°. After 24 hours the product is found soluble in tetrachlorethane-alcohol, dichlorhydrin, epichlorhydrin or nitrobenzene. The ester is then freed from excess esterizing liquid by centrifugalization and immersed for 1 hr. in a hot solution of calcium nitrate to remove free sulfuric acid and sulfonic acid esters.

A flowable solution of acetylcellulose is formed by means of a mixture of ethylene chloride and alcohol, then adding camphor, triphenyl phosphate or *p*-toluenesulfonamide, and either propyl, butyl or amyl alcohols. Presence of the higher alcohols is said to impart toughness, flexibility and elasticity to films formed from the solution[3]. Salol (phenyl salicylate)[4], a white solid, is a feeble cellulose acetate plasticizing body. W. Lindsay has specified, claimed and illustrated a method of making an aeroplane fabric, and of coating with acetate dope[5]; likewise a composition particularly applicable to photographic films[6], combining acetylcellulose, triphenyl phosphate and a liquid monohydroxy aliphatic alcohol having more than 2 carbon atoms. R. Löffler avers that certain lignoproteins obtained from cellulose sulfite waste or a mixture of their components, when added to cellulose acetate[7] forms solutions pe-

1. U. S. P. 1245476; abst. C. A. 1918, **12**, 424; J. S. C. I. 1918, **37**, 27-A.
2. U. S. P. 1265216; abst. C. A. 1918, **12**, 1699; J. S. C. I. 1918, **37**, 461-A; Chem. Ztg. 1918, **42**, 494.
3. U. S. P. 1265217; abst. C. A. 1918, **12**, 1700; J. S. C. I. 1918, **37**, 461-A; Chem. Ztg. 1918, **42**, 494.
4. U. S. P. 1319229; abst. C. A. 1920, **14**, 223; J. S. C. I. 1920, **39**, 14-A.
5. U. S. P. 1325363.
6. Can. P. 175107; abst. C. A. 1918, **12**, 95.
7. R. Loeffler, D. R. P. 346832; abst. Chem. Zentr. 1922, IV, 76; Chem. Ztg. 1921, **45**, 1155.

culiarly effective for filament formation. A weather-resistant cellulose acetate lacquer alleged to be superior for purposes of coating wood was granted patent protection[1] in 1920.

W. Main[2] in 1915 gave a general review and discussion of the cellulose acetate art; and Manchester Oxide Co.[3] their process for dissolving cellulose in the thiocyanates, while M. Marshall and G. Shaw[4] disclosed their method of acetic acid and acetaldehyde manufacture from ethylidene diacetate, in which phosphoric acid is added to the diacetate as a catalyst to facilitate decomposition. A cellulose ester coated surface may be rendered fire-resistant by incorporating with the ester in solution, dissolved phenol-formaldehyde condensate[5]. H. Matheson[6] in a series of 5 patents, has described a process and apparatus for transforming acetaldehyde into acetic acid, and the recovery of the latter in concentrated form.

Cements suitable for attaching glass to glass, or celluloid to glass[7], owes its claim to novelty and originality to dissolving elemi with cellulose acetate in a solvent mixture harmonious to both (tetrachlorethane). In the protection of a photographic film against abrasion and other injury[8] especially staining, the film is coated with a cellulose acetate lacquer in a sufficient number of coats so that it is incapable of absorbing deleterious matters. The K.

1. Luftfahrzeugbau Schutte-Lanz., D. R. P. Anm. L-40426, 1918; abst. Kunst. 1920, **10**, 83.
2. Rev. Gen. Chim. 1915, **18**, 73; abst. C. A. 1915, **9**, 1831.
3. Manchester Oxide Co., R. Clayton, J. Huebner and H. Williams, E. P. 123784; abst. C. A. 1919, **13**, 1637; J. S. C. I. 1919, **38**, 282-A. U. S. P. 1301652; abst. C. A. 1919, **13**, 1928; J. S. C. I. 1919, **38**, 460-A. F. P. 494234; abst. Mon. Sci. 1921, **88**, 22. Ital. P. 171138.
4. Can. P. 217576.
5. H. Matheson, U. S. P. 1309581; abst. C. A. 1919, **13**, 2278; J. S. C. I. 1919, **38**, 678-A.
6. *Ibid.* Can. P. 217575, 217624, 217625, 217626, 218373.
7. J. Matray, F. P. 477294; abst. J. S. C. I. 1916, **35**, 597; Kunst. 1918, **8**, 46; Zts. Farben. Ind. 1918, **16**, 78.
8. A. McCurdy, U. S. P. 1261747, 1261748. E. P. 122391; abst. C. A. 1919, **13**, 1679. Can. P. 186045. See D. R. P. 129484; Brit. J. Phot. 1900, **47**, 104.

McElroy process for chlorhydrin production[1] as a cellulose acetate dissolvant, involves the interaction of olefine, chlorine and water under such conditions that little hypochlorous acid is formed in the sphere of reaction, and comprises establishing and maintaining a body of aqueous boiling liquid in a suitable reaction chamber having a vapor space, and introducing olefin and chlorine in the chamber in predetermined proportions[2]. A variant of the process is treatment of the olefine with hot cupric chloride[3].

Weight per given area is reduced in aircraft fabrics[4] by using fine linen and covering the same with a plurality of cellulose acetate coatings. When cellulose ester solutions are treated with cinnamic acid or cinnamic esters, especially the amyl ester, it is claimed lacquers made therefrom retain their[5] flexibility and durability unimpaired for an indefinite length of time. G. Mersereau[6] has found that cellulose acetate will readily dissolve in the more or less complex chlorine compound containing heavy oil formed when petroleum oils are pyrolized, and the gaseous product then treated with chlorine to form largely addition products, provided such heavy oil is mixed with methyl alcohol or other volatile co-solvent.

Furfural, pure or in admixture with alcohol or acetone[7] is an excellent cellulose acetate solvent and has been patented for that purpose. In the F. Meyer plastic com-

1. U. S. P. 1253615.
2. K. McElroy, U. S. P. 1253616; abst. C. A. 1918, **12**, 703.
3. *Ibid.* U. S. P. 1315229; abst. Chim. et Ind. 1920, **4**, 659; J. S. C. I. 1919, **38**, 847-A. See U. S. P. 1255617, 1295339. E. P. 113955. Can. P. 186632, 186633; abst. C. A. 1918, **12**, 2325.
4. J. McKechnie, U. S. P. 1301955; abst. C. A. 1919, **13**, 1936. J. McKechnie, Ryan and Vickers, Ltd., E. P. Appl. 7465, 1919; abst. J. S. C. I. 1919, **38**, 238-A. Vickers, Ltd., and J. McKechnie, E. P. 125617, 125636; abst. J. S. C. I. 1919, **38**, 344-A.
5. F. Medicus, D. R. P. 351228; abst. Chem. Zentr. 1922, II, 1144; Chem. Ztg. 1922, **46**, 239.
6. U. S. P. 1308803; abst. C. A. 1919, **13**, 2278.
7. G. Meunier, F. P. 472423; abst. J. S. C. I. 1915, **34**, 500. Addn. 23822 thereto; abst. Chim. et Ind. 1922, **8**, 643. The use of furfurol has been patented by G. Bonwitt, E. P. 138078; abst. Chem. Met. Eng. 1920, **23**, 25. Chem. Fabr. von Heyden, A. G., D. R. P. 302460; abst. J. S. C. I. 1920, **39**, 430-A. F. Steimmig, D. R. P. 307075. P. Goissedet and H. Guinot, F. P. 512850; abst. Chim. et Ind. 1921, **6**, 647.

position[1], acetylcellulose is mixed with a solvent and with sufficient non-solvent such as petroleum to inspissate the solution before precipitating the ester in the colloided state, pigments being afterwards incorporated. When ethylene dichloride is heated to about 230° with anhydrous sodium acetate in the presence of a small amount of glycol diacetate, the latter is formed in almost theoretical yield. Like the monoacetate, it is an excellent cellulose acetate solvent[2].

G. Miles[3] recovers partially hydrated cellulose acetate from photographic film by treatment with benzol and commercial methyl or ethyl alcohol heated to about 60°, the glue or gelatin remaining undissolved. Useful plastic and moldable products result from combining yeast and acetylcellulose with glyceryl phthalate or naphthalate[4]. Aldehydes (formaldehyde, paraldehyde, trioxymethylene) may afterwards be added to harden the yeast. As a covering for bottles or jars where high contractility is desired in passing from the humid to the dry state[5], a cellulose acetate solution is poured onto water to produce a film, which is used in the swollen condition. To impart both permanent flexibility and fire-retarding qualities to a cellulose acetate film, there is admixed therewith in the presence of volatile solvents[6], a mixture of triphenyl phosphate and phenyl salicylate. H. Mork in 1919 contributed a retrospective article on the development and future of the acetated celluloses[7].

1. U. S. P. 1175791; abst. C. A. 1916, **10**, 1434; J. S. C. I. 1916, **35**, 534. F. P. 393963; abst. J. S. C. I. 1909, **28**, 257. Swiss P. 44833.
2. K. Meyer, D. R. P. 332677; abst. Chem. Zentr. 1921, II, 646; Kunst. 1921, **11**, 94; Chem. Ztg. 1921, **45**, 21; Chem. Tech. Uebers. 1921, **45**, 76; Chim. et Ind. 1922, **7**, 1161.
3. U. S. P. 1196799; abst. C. A. 1916, **10**, 2853. See U. S. P. 838350.
4. W. Mooser-Schiess, U. S. P. 1317721; abst. C. A. 1919, **13**, 3289.
5. J. Morford, U. S. P. 1149532.
6. H. Mork and G. Esselen, U. S. P. 1193178; abst. C. A. 1916, **10**, 2404; J. S. C. I. 1916, **35**, 961.
7. J. I. E. C. 1919, **11**, 474; abst. C. A. 1919, **13**, 1390; Chem. Zentr. 1920, II, 699. Caout. et Gutta. 1919, **16**, 9930; abst. Kunst. 1920, **10**, 19. J. Frank. Inst. 1917, **184**, 353; abst. Chem. Zentr. 1920, II, 651; Paper Making, **35**, 372; Paper Makers Monthly, 1918, **56**, 7. See also H. Mork, 8th Int. Cong. Appl. Chem. 1912, **13**, 195; abst. Kunst. 1913, **3**, 273.

In attaching fabric panels to the longerons or other rigid elements of aircraft[1], a reinforcing strip of cellulose ester is used. Cellulose destined for acetylation purposes is bleached, centrifuged, disintegrated, freed from larger particles by means of a fan, then dried at a comparatively low temperature[2]. Pneumatic tire covers are usually constructed of several plies of canvas cemented together. W. Muntz[3] proposes to provide a rotproof foundation by impregnating the fabric before being built up with a cellulose acetate solution, or partially formylating or acetylating the original fabric.

Cellulose may be acetylated by glacial acetic acid, sulfuric acid and acetic anhydride after a preliminary treatment of the cellulose with acetic and sulfuric acids. The cellulose is first treated for at least 10 hrs. at ordinary temperature in the presence of acetic acid free from anhydride, sulfuric acid is then added in the proportion of 4-10% of the cellulose, and the action continued[4]. A cinematograph projection shutter has been described[5] which has a masking blade with a balance part, and a detachable balance blade, both blades being made of uncolored cellulose acetate. A cellulose acetonitrate (nitroacetylcellulose) has been described[6], obtainable by heating partially nitrated cellulose (11.68% N) with large excess of acetic anhydride at 90° for 12 hrs., a product being obtained which apparently is a monoacetyl derivative of a six-carbon dinitrocellulose.

1. W. Morton, E. P. 125261.

2. R. Mueller, D. R. P. 400190, Addn. to D. R. P. 387685; abst. J. S. C. I. 1925, **44**, 351-B. F. P. 507472; abst. Rev. Prod. Chim. 1920, **23**, 511. Nor. P. 35856; abst. Chem. Ztg. 1922, **46**, 919.

3. U. S. P. 1184257; abst. C. A. 1916, **10**, 1950.

4. Naamlooze Vennootschap Fabrik van Chemische Produkten, F. P. 494832; abst. Mon. Sci. 1921, **88**, 23; Chim. et Ind. 1920, **3**, 353; Chem. Ztg. 1920, **44**, 5. Holl. P. 3146; abst. C. A. 1920, **14**, 1439; Chem. Ztg. 1919, **43**, 405. See Norsk Alkali A. S., Nor. P. 31377; abst. Chem. Ztg. 1921, **45**, 10; Chem. Tech. Uebers. 1921, **45**, 47.

5. C. Notter, E. P. 145318. See also E. P. 273, 1914; 107839.

6. B. Oddo, Gazz. chim. Ital. 1919, **49**, II, 140; abst. J. S. C. I. 1920, **39**, 12-A; Caout. et Gutta. 1920, **17**, 10662; J. C. S. 1920, **118**, i, 16.

H. Ost[1] in 1919 painstakingly reviewed the published knowledge on the chloroform-soluble and acetone-soluble cellulose acetates.

In the manufacture of self-luminous masses[2], radioactive zinc sulfide is incorporated with cellulose acetate plastic, the sulfide being ground until cryptocrystalline in character. A non-inflammable cinematograph film has been described[3] in which the cellulose acetate plasticizing agent is isoprene, its homologues or analogues, they being substances elastic at high boiling point, and soluble in acetone and methyl acetate, besides dissolving cellulose acetate in the cold. The S. Peachey varnish coating[4] combines trichlorethylene and tetrachlorethane as a solvent. A. Pellerin[5] has described the preparation of a purified hydrated cellulose especially suitable for cellulose acetate manufacture, being a finely divided form of cellulose xanthate precipitated and washed free from sulfur compounds. Such a cellulosic material would be excellent for nitration, acetation and etherification purposes, were it not unduly expensive to produce.

In the multiplication of pictures as oil paintings[6], a photographic reproduction is made on a readily impressionable material, and then an intaglio to be used as a die, by supporting the painting in a horizontal position and pouring on a solution of cellulose acetate 10, tetrachlorethane 80, dichlorhydrin 5. The A. Piestrak lacquer comprises[7] ace-

1. Zts. ang. Chem. 1919, **32**, 66, 76, 82; abst. C. A. 1919, **13**, 2760; J. S. C. I. 1919, **38**, 355-A; Chem. Zentr. 1919, IV, 794; Kunst. 1920, **10**, 8. See H. Ost, Ann. 1913, **398**, 313; abst. C. A. 1913, **7**, 3836. H. Ost and T. Katayama, Zts. ang. Chem. 1912, **25**, 1467; abst. C. A. 1913, **7**, 2303.
2. E. Parade, D. R. P. 311500; abst. Chem. Zentr. 1919, II, 689; Kunst. 1919, **9**, 180.
3. Cie Generale des Etablissements Pathe Freres Phonographe et Cinematographs, E. P. 2067, 1915; abst. C. A. 1917, **11**, 2077.
4. S. Peachey, E. P. 121091; abst. J. S. C. I. 1919, **38**, 110-A. See also E. P. 1894, 1915; abst. J. S. C. I. 1916, **35**, 479.
5. A. Pellerin, U. S. P. 1128624; abst. C. A. 1915, **9**, 1114.
6. H. Peters, U. S. P. 1143860.
7. C. Piestrak, F. P. 501236; abst. Chim. et Ind. 1921, **5**, 330; Kunst. 1921, **11**, 38.

tylcellulose 8, methyl acetate 50, acetone 20, benzene 9.5, benzyl alcohol 3.5 and dye 9. E. Pin[1] forms a film on a temporary support, comprising coating the support with soap solution, then depositing cellulose acetate thereon.

To produce moldable plastics[2], a phenol-formaldehyde or similar condensate is admixed with cellulose acetate by means of volatile solvents; or formaldehyde, or substances yielding formaldehyde[3] are added to swelled or dissolved cellulose acetate, and then can be flowed or worked into molded structures. In the fabrication of artificial sponge[4], acetated cellulose is admixed with fibers and a granular solid substance, a solution of which substance will harden the cellulose ester, then shaping the mass into the form desired, and dissolving out the water-soluble components, thus inducing a porous structure.

In the partial hydration of acetated cellulose, instead of the usual introduction of water, J. Radcliffe[5] prefers to use a finely divided salt containing water of crystallization as alum, because "the water has an exaggerated local effect and cannot be distributed through the mass quickly." Sodium acetate and sulfate are also specified. The use of cellulose acetate produced in this manner has been advocated for artificial silk manufacture. H. Rauch[6] in 1919 reviewed our knowledge of cellulose acetylation with special

1. U. S. P. 1184772; abst. J. S. C. I. 1916, **35**, 1273. E. P. 102066; abst. J. S. C. I. 1916, **35**, 755.

2. F. Pollak, U. S. P. 1216728; abst. C. A. 1917, **11**, 1734; J. S. C. I. 1917, **36**, 396. Plausons Forschungsinstitut, Nor. P. 35448; abst. Chem. Ztg. 1922, **46**, 665.

3. *Ibid.* D. R. P. 375640, 375641; abst. J. S. C. I. 1924, **43**, 52-B. See A. Eichengruen, Ital. P. 140664. V. Pauthonier and J. Antoine, Ital. P. 144105. F. Lehmann, Ital. P. 141905.

4. G. Pum and A. Glaessner, U. S. P. 1142619; abst. C. A. 1915, **9**, 1978.

5. J. Radcliffe, E. P. 131357; abst. C. A. 1920, **14**, 123; J. S. C. I. 1919, **38**, 759-A; Chem. Ztg. 1919, **43**, 685; Chim. et Ind. 1921, **5**, 577.

6. Chem. tech. Wochenschrift, 1919, 81; abst. Kunst. 1919, **9**, 177; Chem. Zentr. 1919, IV, 631; Chim. et Ind. 1921, **6**, 358. Reference is made to U. S. P. 1195673. F. P. 359079, 371497. D. R. P. 135474, 281373, 288267, 296205.

reference to the catalysts employed. F. Redlich[1] produces a plastic by combining acetylcellulose 10 with diethyl tartrate 12.

In the compounding of medicinal, cosmetic or edible salve-like products[2] aqueous alcoholic solutions of cellulose hydroacetates or sulfacetates are mixed with medicaments which either possess a direct dissolving power for cellulose acetate or dissolve in indifferent softening agents or liquids which in themselves exert a solvent action on the ester. J. Reitstoetter[3] reviewed the acetylcellulose patent situation, covering the ground to 1920.

In the formulation of printing or stamping dies, plates or blocks[4], a cellulose acetate plastic is prepared of relatively low melting point but hard when cold, and this used as the impressionable backing. In the use of amyl acetate (a non-solvent) in cellulose acetate mixtures[5], and as a substitute for tetrachlorethane in this respect, the maximum of amyl acetate is added to a cellulose acetate solution, then sufficient acetone incorporated to restore transparency. Upon evaporation of such a solution in a dry atmosphere, high-strength and lustrous films and threads are said to be obtained.

As a fireproof composition combining plasticity with covering power[6], a cellulose lacquer is incorporated with such bodies as ammonium magnesium phosphate, ammonium phosphate, ammonium manganese phosphate, ammonium manganese arsenate, these double salts being dissolvable in a mixture of acetone and acetaldol with the addition

1. D. R. P. 304224; abst. J. S. C. I. 1920, **39**, 264-A; Chem. Zentr. 1920, I, 38; Chem. Ztg. 1920, **44**, 55; Wag. Jahr. 1919, **65**, II, 346; Chim. et Ind. 1921, **5**, 578.
2. Reichhold, Flügger & Boecking Stadlauer Lackfabrik, Aust. P. 70772; abst. C. A. 1916, **10**, 1407.
3. Kunst. 1919, **9**, 185; abst. C. A. 1920, **14**, 2262; Chem. Ztg. 1920, **44**, 164; Chim. et Ind. 1920, **4**, 383.
4. J. Richter, U. S. P. 1132384.
5. L. Riley, E. P. 15428, 1915; abst. J. S. C. I. 1916, **40**, 794; Zts. ang. Chem. 1916, **29**, II, 506; Chem. Ztg. 1916, **40**, 794.
6. E. Robinson, U. S. P. 1310841; abst. C. A. 1919, **13**, 2443.

of small amounts of resin. As an artificial leather[1], E. Roggenkämper proposes to admix acetyl- and nitro-cellulose in varying proportions, incorporating therewith a vegetable colloid. In stearic aldehyde, benzaldehyde, *p*-oxybenzaldehyde and butaldehyde manufacture[2], chlorstearic acid (stearic acid chloride), benzoyl bromide, *p*-carbomethoxybenzoyl chloride, or butyryl chloride respectively, are heated with halogen acids in liquid form in the presence of catalysts and hydrogen-containing gases[3].

In manufacturing non scatterable glass[4], A. Roosevelt plasticizes acetylcellulose or celluloid with camphor, and interposes between two glass sheets, forming a unitary body by the simultaneous application of heat and pressure. Adhesion may be increased by interposing a thin layer of gelatin between cellulose ester and glass, using a solvent (formic or acetic acids) of both gelatin and acetylcellulose. In driving-belt manufacture[5], a solution having a base of acetylcellulose is applied in a plurality of coats to give the degree of impregnation and water-proofing effect desired.

It is claimed that with the aid of weak acting catalysts as sulfuryl chloride of phosphorous pentachloride[6], wholly acetylated celluloses may be obtained which are distinguished from the cellulose acetates of the art prior to 1918 by a hitherto unattained viscosity in their solutions, the acetylation being carried out under 20°. Based on the cellulose, 2-4% of catalyst is used. The following year (1919)

1. D. R. P. 319966; abst. Chem. Zentr. 1920, IV, 52; Chim. et Ind. 1922, **7**, 550. D. R. P. 321251; abst. Chim. et Ind. 1922, **7**, 763.
2. W. Robinson-Bindley, A. Weller and E. Dulcken, E. P. 134565.
3. K. Rosenmund, D. R. P. 333154; abst. Chem. Zentr. 1921, II, 737.
4. U. S. P. 1210987; abst. C. A. 1917, **11**, 693.
5. N. Roy, E. P. 104780; abst. Kunst. 1918, **8**, 214.
6. F. Ruppert, U. S. P. 1263119; abst. C. A. 1918, **12**, 1598; J. S. C. I. 1918, **37**, 367-A; Kunst. 1915, **5**, 72, 95. Swiss P. 62359, 66046, 66047. Observe that whereas the patent above protects the use of sulfuryl chloride and phosphorus pentachloride or pentoxide as catalyst for the acetation of weakly nitrated cellulose, A. Jacquet (E. P. 29882, 1913) has described the same thing for the acetation of celluose.

A. Rusch[1] published a general description for preparing and applying cellulose acetate dopes to airplane fabrics.

To prepare a leather substitute[2], cellulose acetate alone or mixed with esters of naphthenic acids, are incorporated with insoluble metallic naphthenates (aluminum, chromium, iron, cobalt), particularly aluminum-magnesium naphthenate. Phenyl, glyceryl and glycol naphthenates[3] may also be used. In waterproofing the soles of footwear[4], a layer of cellulose acetate to which may be added a little *b*-naphthol as a germicide, is inserted between the inner and outer sole of the shoe. Matchbox igniting strips[5] may be similarly waterproofed. In 1916 M. Schall published a general article on the use of cellulose acetate lacquers in the arts[6].

The E. Scheller process of acetaldehyde production[7] is based on the action of steam on acetylene by the aid of oxides (of aluminum, zinc, iron, nickel) at an elevated temperature, removing the impurities from the acetylene which is then passed over steam in the presence of a catalyst. As cellulose ester plasticizers[8] acetyldicyclohexylamine and *p*-toluenesulfodicyclohexylamine have been patented. A process has been described for obtaining cellulose acetate solvents[9], in which rice hulls are distilled and the furfural,

1. Textile World J. 1919, **56**, 53; abst. C. A. 1919, **13**, 2136; Kunst. 1920, **10**, 77.
2. G. Ruth and E. Asser, D. R. P. 332866; abst. J. S. C. I. 1921, **40**, 400-A; Kunst. 1920, **10**, 47.
3. *Ibid.* D. R. P. 334983; abst. Kunst. 1921, **11**, 87.
4. A. St. Armande, E. P. 12839, 1915; abst. J. S. C. I. 1916, **35**, 1057; Kunst. 1917, **7**, 10.
5. *Ibid.* E. P. 106375; abst. J. S. C. I. 1917, **36**, 736; Kunst. 1918, **8**, 10.
6. M. Schall, Kunst. 1916, **6**, 113.
7. E. Scheller, U. S. P. 1244901, 1244902; abst. C. A. 1918, **12**, 155; J. S. C. I. 1918, **37**, 20-A; Chem. Ztg. 1918, **42**, 106.
8. O. Schmidt, U. S. P. 1200886; abst. 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. D. R. P. 284672; abst. Chem. Zentr. 1915, II, 111. F. P. 459006; abst. Mon. Sci. 1914, **81**, 129.
9. F. Scurti and C. Zay, Staz. sperim. agrar, 1919, **52**, 278; abst. Chem. Zentr. 1919, IV, 1105.

acetic acid and other components recovered. In an article on the death of B. Seifert in 1919, is a resume of his discoveries of cellulose plasticizing agents such as *p*-toluenesulfonates and cresol carbonate[1]. In the continuous manufacture of acetaldehyde[2], acetylene is treated with 6% sulfuric acid at 40-65° reaction temperature in the presence of mercury compounds.

The S. Sheppard photographic film[3] owes its alleged novelty to the discovery that cellulose acetate tends to hold basic dyes in a fixed relation. Chloracetic acid is produced by subjecting trichlorethylene 100 to the action of 92% sulfuric acid 450 at 160° and separating the products by distillation[4]. Ethyl alcohol may be added directly to the reaction mixture to obtain ethyl monochloracetate. For the preparation of odorless respirators[5], they are treated with a cellulose acetate solution containing a high-boiling softening agent. If a film obtained from acetylcellulose solutions be immersed for a short time in concentrated ethyl alcohol[6] and then dried in air, it becomes quite insensitive to alcohol and is a satisfactory gutta-percha substitute.

For the waterproofing of fabrics and rendering them impervious to gases[7], a lacquer of cellulose acetate 60, caoutchouc 20, tetrachlorethane 600 has been patented. Glycol chlorhydrin may be made by agitating ethylene with

1. Kunst. 1920, **10**, 83.
2. The Shawinigan Water and Power Co., Nor. P. 32779; abst. Chem. Tech. Uebers. 1922, **46**, 3.
3. U. S. P. 1290794; abst. C. A. 1919, **13**, 818; J. S. C. I. 1919, **38**, 200-A.
4. L. Simon and G. Chavanne, U. S. P. 1304108; abst. C. A. 1919, **13**, 2039. E. P. 129301; abst. C. A. 1919, **13**, 2878. F. P. 503158; abst. Chem. Tech. Uebers. 1922, **46**, 3. Swed. P. 44929; abst. C. A. 1920, **14**, 1341.
5. Firma Oskar Skaller, D. R. P. 301758; abst. Kunst. 1920, **10**, 69.
6. O. Skaller, D. R. P. 317145; abst. J. S. C. I. 1920, **39**, 445-A; Chim. et Ind. 1922, **7**, 550; Chem. Zentr. 1920, II, 462.
7. Soc. Anon. des Etablissements Hutchinson, E. P. 129630; abst. C. A. 1919, **13**, 3027; Kunst. 1920, **10**, 135; J. S. C. I. 1920, **39**, 482-A.

chlorine and hydrochloric acid[1]. In the acetylation of cellulose[2], methylene sulfate (10% on the weight of cotton) is recommended as a mild catalyst, or[3], trioxymethylene for the same purpose. Ethylidene diacetate may be formed by the action of acetic acid on acetylene in the presence of[4] mercury salts of sulfonic acids (benzenesulfonic, naphthalenesulfonic, camphorsulfonic) at 40-65°. In order to obtain a partially saponified cellulose acetate[5], soluble in acetone and in a mixture of tetrachlorethane and alcohol, and whose acetone solutions are more viscous than those obtained with other cellulose acetates, the acetylation is carried out in the presence of methylene sulfate, and the product partially saponified.

In coating compositions for airplane fabrics, cellulose acetate plastified with diethyl *iso*phthalate or ethyl cinnamate has been patented. A little eugenol (a cellulose acetate solvent) is recommended, perhaps from an odoriferous point of view[6]. To diminish the visibility of airplanes in projected beams of artificial light[7], colored cellulose coatings that successively absorb the rays are applied. Cellu-

1. Soc. Camar et P. Dumesnil, F. P. 493541; abst. Mon. Sci. 1921, **88**, 20.

2. Soc. Chim. des Usines du Rhone Anciennement Gillard, P. Monnet. et Cartier, E. P. 10822, 1915; abst. C. A. 1917, **11**, 209; J. S. C. I. 1915, **34**, 1086. U. S. P. 1191439. F. P. 478436; abst. C. A. 1916, **10**, 2299; J. S. C. I. 1916, **35**, 1009. Swiss P. 68996; abst. Chem. Ztg. 1915, **39**, 311. Swiss P. 71991; Addn. to Swiss P. 68996; abst. Kunst. 1916, **6**, 173; Chem. Ztg. 1916, **40**, 162.

3. *Ibid.* E. P. 7773, 1915; abst. C. A. 1916, **10**, 3160; J. S. C. I. 1916, **35**, 302; Chem. Ztg. 1916, **40**, 130. U. S. P. 1216462. F. P. 477620; abst. J. S. C. I. 1916, **35**, 357. Swiss P. 71695; abst. C. A. 1916, **10**, 2637; Chem. Ztg. 1916, **40**, 54. Swiss P. 77663; abst. Chem. Ztg. 1918, **42**, 166; C. A. 1918, **12**, 2439.

4. Soc. Chim. Des Usines Du Rhone, D. R. P. 334554; abst. C. A. 1923, **17**, 1801; Chem. Ztg. 1921, **45**, 137.

5. Soc. Chim. des Usines du Rhone Anciennement Gillard, P. Monnet et Cartier, Swiss P. 77663; abst. C. A. 1918, **12**, 2439; Chem. Ztg. 1918, **42**, 166.

6. Societe Nauton Freres and de Marsac and T. Tesse, E. P. 126989; abst. J. S. C. I. 1919, **38**, 531-A; Ann. Rep. S. C. I. 1920, **5**, 324. E. P. 124763; abst. J. S. C. I. 1919, **38**, 319-A. F. P. 492698; abst. Chim. et Ind. 1920, **3**, 352.

7. *Ibid.* E. P. 131369; abst. J. S. C. I. 1919, **38**, 759-A; Ann. Rep. S. C. I. 1920, **5**, 324.

lose acetate dissolved in a mixture of acetone, methyl acetate, benzyl alcohol and ethyl acetoacetate is recommended, colors as red alizarin lake being incorporated therein. As a useful solvent for acetated cellulose[1], creosote with furfural, acetone and alcohol has been brought forward, the lacquer being especially useful for application to airplane wing fabric and for the manufacture of artificial leather.

A cellulose acetate lacquer containing cork dust[2] has been granted patent protection as an airplane dope. H. Staier[3] prepares a composition for match heads of potassium chlorate, phosphorus sulfide and a binder of feculose (acetated starch). In the use of furfurol (furfural, furfuryl alcohol) as a solvent[4], F. Steimmig claims the acetone-soluble as well as the chloroform-soluble forms of cellulose acetate yield satisfactory results, whether the furfural is used alone or with other organic solvents. The solvent action is not diminished by admixture of other liquids in which cellulose acetate is but partially soluble, e.g. methyl alcohol, ethyl acetate, ethyl chloride, benzene and toluene.

The W. Stevenson method of acetylcellulose manufacture involves zinc chloride as catalyst[5], bleached sulfite paper pulp being used as the cellulose source, cellulose 10, glacial acetic acid 28, acetic anhydride 40, and zinc chloride 2 being mixed and allowed to stand 7-8 hrs. at 60-70°, then precipitated. The D. Sutherland formula for cellulose

1. Societe Palewski & Morin, F. P. 491490; abst. Chim. et Ind. 1920, **3**, 811; Chem. Ztg. 1919, **43**, 733.

2. *Ibid.* F. P. 492265; abst. Chim. et Ind. 1920, **3**, 352.

3. U. S. P. 1144076 abst. C. A. 1915, **9**, 2313. See J. Traquair, J. S. C. I. 1909, **28**, 289.

4. D. R. P. 307075; abst. J. S. C. I. 1920, **39**, 153-A; Chem. Zentr. 1919, IV, 913; Caout. et Gutta. 1920, **17**, 10662.

5. U. S. P. 1441541; abst. C. A. 1923, **17**, 1141; J. S. C. I. 1923, **42**, 180-A; Chem. Met. Eng. 1923, **28**, 735; Chem. Age, 1923, **31**, 81. E. P. 130029; abst. J. S. C. I. 1919, **38**, 714-A; C. A. 1920, **14**, 123; Chim. et Ind. 1921, **5**, 335; Chem. Ztg. 1919, **43**, 589. F. P. 506706; abst. Caout. et Gutta. 1921, **18**, 10893. Ital. P. 180766, 1919.

acetate airplane wing dope[1] is acetylcellulose 6-12, acetone 36-44, 90% benzene 24, borated benzol (boric acid 1, benzene 9) 24-25 and benzyl alcohol 2-3. A mixed solvent for acetyl- and nitro-cellulose has been described comprising methyl alcohol and methyl acetate, and obtained by distillation of neutralized pyroligneous acid[2]. A fireproof, insulating building material (that seems unduly expensive)[3], comprises powdered magnesium oxide and granulated cork with a solution of cellulose acetate as binder. A composition for coating aeroplane cloth and which gives "a very fine aesthetic effect"[4], consists of first applying a plurality of cellulose acetate coats, and a top coat of linseed oil fatty varnish, usually pigmented. Or[5], a layer of cellulose acetate containing an excess of high boilers or plasticizers (and hence too soft for exposure) is imprisoned between two layers deficient in cellulose acetate softeners. This method of coating was highly successful during the War in giving maximum suppleness together with satisfactory constringency.

In a table of properties of condenser electrics published in 1915, the specific inductive capacity of cellulose acetate[6] is given as 4.5-6.5, per cent power factor 0.70-1.10, and breakdown strength volts per mil. 400-900. Stotz & Co.[7] have pointed out the uses of plastic cellulose acetate as an insulating material in electrical technique. The J. Thornton

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

2. D. Sutherland and W. McLaren, E. P. 28613, 1897; abst. J. S. C. I. 1897, **16**, 1013.

3. B. Sutter, U. S. P. 1183694.

4. T. Tesse, E. P. 124763; abst. J. S. C. I. 1919, **38**, 319-A. See E. P. 20975, 1911.

5. *Ibid.* E. P. 124844; abst. C. A. 1919, **13**, 1771; J. S. C. I. 1919, **38**, 319-A; Chim. et Ind. 1921, **6**, 89.

6. P. Thomas, "Standard Handbook for Electrical Engineers," 1915, 157.

7. Chem. Apparatur, 1917, 92; abst. Kunst. 1918, **8**, 56; Chem. Zentr. 1918, II, 489; Chem. Ztg. 1918, **42**, 266.

moving-picture film[1] comprises gelatin, glue, Iceland moss, agar-agar, chondrin or albumin as the base and over this a cellulose ester layer to induce the necessary waterproof effect. In producing two-color value positive pictures for cinematograph films from a single strip of negative film[2], and having the picture negatives of different color values arranged in alternate sequence, one side of a transparent cellulose acetate film is printed upon, the positive picture being printed in register on the opposite side. For silver monochrome films[3], cellulose acetate of 0.005 inch thick is used.

A. Trivelli[4] renovates cinematograph film of either acetyl- or nitro-cellulose and removes the "rain" therefrom by filling up the scratches with a cellulose ester varnish containing drying oils, the solvent portion being ethyl alcohol, methyl valerianate and benzene. F. Tully has described a tea-ball[5], in which the fabric holding the individual portion of tea, in order to make it withstand hot or boiling water, is coated with a cellulose acetate solution.

In the manufacture of solidified alcohol, the addition of the alcohol to form a solid mass of soap[6], stearic acid[7], shellac[8], stearin[9], rosin and paraffin[10], gum lac[11], sodium silicate[12], sodium stearate[13], ammonium oleate[14], nitrocellulose[15] and cellulose acetate[16], the latter being sold under the name of Smaragdine, are a few of the materials which have been proposed. Lithosprit[17] is made from alcohol and kieselguhr.

1. U. S. P. 1183698.
2. J. Thornton, U. S. P. 1245822.
3. *Ibid.* U. S. P. 1250713.
4. U. S. P. 1205822; abst. J. S. C. I. 1917, **36**, 101; E. P. 7956, 1915; abst. J. S. C. I. 1916, **35**, 754.
5. U. S. P. 1247906.
6. R. Hirsch, D. R. P. 134165.
7. H. Hempel, D. R. P. 152682.
8. J. Rosenthal, D. R. P. 117896.
9. *Ibid.* D. R. P. 145400.
10. H. Meyer, Seifens, 1915, 602.
11. Seifens, 1901, 801.
12. E. Raynaud, D. R. P. 115594.
13. F. P. 453122.
14. C. F. Boehringer & Soehne, D. R. P. 204708.
15. A. G. fur Spiritus-Beleuchtung und Heizung, D. R. P. 126090.
16. R. Duncan, "Chemistry of Commerce," 146. See also U. S. P. 919759.
17. Manufactured by Th. Teichgraeber, A. G. (Berlin).

Alcoheat, Alcofuel, Sterno, Solol, Theroz, Solid Sunbeams and Solakol are commercial names for similar preparations[1].

Ethylene dichloride is prepared by reacting upon ethylene with liquid chlorine, the chlorine being previously mixed with either ethylene dichloride or an inert solvent[2]. Monochloracetic acid is purified from sulfuric acid normally present by distillation at 25 mm. pressure[3]. Acetatrosshaar is a coarse cellulose acetate filament of the horsehair size which apparently has been but little used[4]. In the production of acetic acid from acetaldehyde[5], the latter is treated with oxygen under pressure in a confined space separate from the oxygen to avoid explosions.

An hydraulic packing has been described[6] suitable for machinery stuffing boxes, formed of fibers of cotton, flax or jute waterproofed with an acetylcellulose solution, and then coated with a lubricant as tallow. As a filler and polish for wood surfaces[7], cellulose acetate lacquer dissolved only in volatile solvents has been patented. The Vereinigte Glanzstoff Fabr. have described cellulose ester filaments in tubular form[8], made by extruding an acetylcellulose solution through a slit into a setting bath, and then twisting the ribbons so formed. When cellulose acetate is incorporated with the proper proportions of triphenyl phosphate[9] to form a homogeneous mass, upon application of

1. For details of solid alcohol manufacture, see E. Worden, "Technology of Cellulose Esters," 1916, p. 2598. A. von Unruh, Kunst. 1916, **6**, 253.
2. Union Carbide Co., E. P. 136489; abst. Kunst. 1920, **10**, 158.
3. Usines Electriques de la Lonza Suisse, F. P. 502218; abst. Chim. et Ind. 1921, **5**, 323.
4. Utz, Neue Faser. 1919, **1**, 41; abst. Chem. Zentr. 1919, II, 613.
5. S. Uthelm, E. P. 116279; abst. Mon. Sci. 1922, (5), **12**, 21; Chem. Ztg. 1919, **43**, 493. Nor. P. 28501, 1918.
6. C. Vance and J. Vetter, U. S. P. 1295241; abst. C. A. 1919, **13**, 1248.
7. Verein f. Chemische Industrie in Mainz, D. R. P. 296206; abst. Chem. Zentr. 1917, I, 462.
8. D. R. P. 369560; abst. Chem. Zentr. 1923, II, 768; Textilber. 1923, **4**, 144; Chem. Ztg. 1923, **47**, 52.
9. Verein fur Chemische Industrie, D. R. P. 303018; abst. J. S. C. I. 1918, **37**, 367-A; Kunst. 1918, **8**, 36.

heat the plastic merely melts without igniting (depending upon the degree of heat applied).

In order to prepare cotton fabric impervious to moisture and gases, and thereby adapt it to use in airplane fabrics or for balloons[1], the cotton is superficially acetylated in the piece form, and after neutralizing and drying, is submitted to sufficient solvent action to colloid the mass and fill the interstices between the threads of the warp and weft—an ingenious idea. E. Walen discussed in detail in 1918 the desirable properties of airplane fabrics and proper methods for coating and preserving them[2].

In preparing waterproof and moistureproof paper[3], cellulose esters are added to paper pulp, and the paper, after drying, is treated with a solvent to induce incipient gelatinization. In the case of paper textiles, the solvent is not added until after the weaving process. For the dyeing of artificial leather[4], non-dyed fabrics are impregnated with layers consisting of cellulose esters having aniline mordants therein (aluminum hydroxide, acetate or silicate), and after drying, the artificial leather is dyed by immersion in an aniline bath.

For the formation of leather substitutes[5], a textile fabric is converted into substitute leather by applying a plurality of coats of leatherfying dope, the latter comprising a cellulose ester dissolved in volatile solvents to which castor oil or other oil has been added, the fluidity of the dope being constantly maintained during the coating process by heat. In the production of glycols[6], dichlor paraffins which have their chlorine atoms attached to different carbon atoms,

1. Vickers, Ltd., J. McKechnie and A. Ryan, E. P. 142615; abst. C. A. 1920, **14**, 2863; J. S. C. I. 1920, **39**, 482-A; Kunst. 1921, **11**, 21; Ann. Rep. S. C. I. 1920, **5**, 325.
2. Aviation, 1918, **5**, 621. Amer. Soc. Mech. Eng. J. 1918, **40**, 933. Textile World, 1918, **54**, 741, 1207.
3. H. Wandrowsky, D. R. P. 323816; abst. J. S. C. I. 1920, **39**, 779-A; Paper, 1921, **28**, 38.
4. R. Weeber, U. S. P. 1186052; abst. J. S. C. I. 1916, **35**, 834.
5. E. Weinheim, U. S. P. 1263171; abst. C. A. 1918, **12**, 1604.
6. C. Weizmann, E. P. 131628; abst. Chem. Age (London), 1919, **1**, 453.

are treated in aqueous suspension in an autoclave with aluminum hydroxide, lead or calcium carbonates, borax or sodium bicarbonate at 100-200°.

A suitable dope for the fabrics of airplanes and kites[1] consists of acetylcellulose with amber oil in a volatile solvent as the plasticizing medium. For the sizing and "surface stretching" of paper[2], the paper is led through a series of wet-presses and while passing between the last pair of press rolls a size compound of feculose (acetated starch) is applied to both sides of the moist web of paper by means of press rolls, which transfer the acetated starch to the paper. E. Worden[3] summarized our knowledge of cellulose acetate in 1919 in an article with about 300 references to the literature, which was translated into German and amplified the same year[4]. Equal weights of cellulose acetate and cresylic acid thinned to the desired consistency with volatile solvents[5] is said to produce a relatively inexpensive but satisfactory dope for fabrics, wood or metal. F. Zimmer[6] published a summation on cellulose ester lacquers in 1918, and F. Zippel disclosed his process for the recovery of cellulose acetate from fabrics[7] the next year.

Acetylcellulose Advancement, 1920-1924. In the quinquennial period following the close of hostilities, technicians in this and cognate fields appear to have gone back to normalcy as evidenced by an almost *nil* number of contributions printed and patents granted involving what might

1. R. Whestley, E. P. 112483; abst. C. A. 1918, **12**, 1002; J. S. C. I. 1918, **37**, 120-A. See E. P. 105137; abst. J. S. C. I. 1917, **36**, 544-A.

2. H. Wheelwright, U. S. P. 1195888; abst. J. S. C. I. 1916, **35**, 1009.

3. J. S. C. I. 1919, **38**, 370-T; abst. C. A. 1920, **14**, 1038; Chem. Zentr. 1920, II, 303; Chim. et Ind. 1920, **4**, 666; Caout. et Gutta. 1920, **17**, 10664.

4. Kunst. 1921, **11**, 1, 44. Not a true translation.

5. A. Zimmer, J. Bryce and G. Davies, E. P. 124807; abst. C. A. 1919, **13**, 1771; J. S. C. I. 1919, **36**, 379-A; Chem. Ztg. 1919, **43**, 493; Kunst. 1920, **10**, 90.

6. Farben Ztg. 1918, **23**, 331; abst. Kunst. 1918, **8**, 92; Chem. Zentr. 1919, II, 852.

7. D. R. P. Anm. Z-11159, 1919; abst. Kunst. 1919, **11**, 8.

properly be classed as the warlike arts in contradistinction to those activities embraced under the peaceful pursuits. A distinct recrudescence is noticeable in this respect, and a quickening of research activity and inventive ingenuity as evidenced by the over eight hundred contributions involving the organic cellulose esters as indicated in this abbreviated resume as covering this cycle.

In the manufacture of acetylated celluloses[1], the cellulose is pretreated with equal parts of 85% nitric acid and nitrobenzene during 20 minutes at 25°, the cellulose containing 2.6% N. This is then acetated in the usual manner, bromine being used as a catalyst. Or[2], the acetylation may be carried out in two stages. In the first, a catalyst other than sulfuric acid is used (i.e. bromine), the finished product containing the cellulose fibers in the original condition, but slightly swollen, and 37% acetic acid in combination. Acetic and sulfuric acids are then added and the esterification completed, the finished ester showing about 61.5% acetic acid in combination with the cellulose. If it is desired to obtain thin films[3], particularly those containing metal powder and serving as substitutes for metal leaf, a concentrated solution of acetylcellulose is spread upon a smooth surface and then dried without further treatment.

"Borated cellulose" may be produced by dissolving a cellulose ester in methyl acetone (methylethyl ketone) and adding thereto a boric acid saturated in the solvent[4]. A translucent film is produced of a pleasing quality of brilliance, being soft, mellow and lustrous[5]. In 1921 the trade-

1. Act. Ges. für Anilin-Fabrikation, E. P. 145524; abst. C. A. 1920, **14**, 3529; J. S. C. I. 1921, **40**, 494-A; Kunst. 1921, **11**, 14; Rev. Prod. Chim. 1920, **23**, 606. Swiss P. 88131 Addn. of 61424; abst. Textilber. 1921, **2**, 360. Faser, 1921, **3**, 60. Cites E. P. 10706, 1912; 1156, 1914.

2. *Ibid.* E. P. 145525; abst. Chem. Met. Eng. 1920, **23**, 990; Kunst. 1921, **11**, 14; Rev. Prod. Chim. 1920, **23**, 606.

3. *Ibid.* E. P. 181706; abst. Chem. Met. Eng. 1922, **27**, 755.

4. W. Alexander and J. Clegg, U. S. P. 1358914.

5. Allegre, Mondon & Co., F. P. 550142; abst. Chem. Zentr. 1923, IV, 164; Chem. Ztg. 1923, **47**, 517. F. P. Addn. 25779 to 550142; abst. Chem. Zentr. 1924, I, 378; Chem. Ztg. 1923, **47**, 517.

marks "Dreyfusilk"[1] and "Amcella"[2] were registered. Plastic compositions consisting of cellulose acetate impregnated with a small proportion of glycerol[3], are prepared by heating the acetate with excess of glycerol, washing until the relatively small amount of softener desired remains, and then removing the water by evaporation.

In the manufacture of substantially anhydrous organic acids as acetic[4], the reaction between salt of the acid and strong inorganic acid is carried out in the presence of a substantially anhydrous, non-volatile liquid, inert with respect to the reactants as paraffin oil. In the art of protectively treating materials as wood, paper and fabrics[5], cellulose acetate lacquer in which has been incorporated antimony trichloride dissolved in amyl acetate is recommended. Solution of antimony trichloride or oxychloride in creosote is claimed to be equally efficient as a fire-retardant when combined with dissolved acetylcellulose[6]. Antimony trichloride[7], amyl acetate and linseed oil[8], or the trichloride dissolved in ethyl acetate[9] has been the subject of patent issuance.

To prepare an impermeable and non-hygroscopic material[10], M. Arosio coats vulcanized fiber with acetated cellulose, care being taken that the coating substance be evenly distributed over the surface and caused to penetrate the pores. Airplane propellers are strengthened and waterproofed by bandaging with vulcanized fiber and then treat-

1. American Cellulose & Chem. Mfr. Co., Ltd., U. S. Trademark, 148859 of 1921.
2. *Ibid.* U. S. Trademark, 148912 of 1921.
3. *Ibid.* E. P. 190269; abst. Chem. Ztg. 1923, **47**, 73.
4. R. Andreau, U. S. P. 1381782; abst. C. A. 1921, **15**, 3499; Mon. Sci. 1922, (5), **12**, 5.
5. A. Arent, U. S. P. 1388825.
6. *Ibid.* U. S. P. 1388826.
7. *Ibid.* U. S. P. 1388827.
8. *Ibid.* U. S. P. 1388828.
9. *Ibid.* U. S. P. 1451313.
10. U. S. P. 1355586; abst. C. A. 1921, **15**, 173.

ing to a coat of acetylcellulose[1]. In producing matrices for sound-records[2], any suitable solid impressionable material may be used, being coated with a solution of cellulose acetate in order to enhance the rigidity and diminish deterioration due to abrasion of the stylus upon repeated reproduction. Or[3], the matrix may be lightly coated with a thin acetylated cellulose solution after the sound wave impressions have been placed on and in the surface of the matrix.

A series of five patents were granted to A. Backhaus during this period 1920-1024, one[4] a catalyzer of granular pumice stone impregnated with cupric or nickel nitrate to transform acetaldehyde into acetic acid; an apparatus for the manufacture of ethyl acetate[5], and a process for producing the same[6]. Ethyl or propyl acetoacetate or propionate, propyl acetopropionate, propyl acetobutyrate or ethyl acetobutyrate[7] are obtained by heating the respective esters and alcohols with metallic sodium, and separating the products of reaction. Acetaldehyde[8] is produced by heating alcohol with a finely divided metallic catalyzer (copper, nickel, chromium or iron), and separating the acetaldehyde and hydrogen produced.

Cellulose acetate silk or fabric is dyed by means of amino anthraquinones in fine suspension. 1.4-Diamino- or 1.4.5.8-tetramino-anthraquinone condensed with salicylic

1. M. Arosio, U. S. P. 1356847; abst. C. A. 1921, **15**, 296. F. P. 519721; abst. Mon. Sci. 1923, (5), **13**, 5; Chim. et Ind. 1922, **7**, 542. D. R. P. 331024; abst. Chem. Tech. Uebers. 1922, **46**, 98.
2. J. Aylsworth and E. Aiken, U. S. P. 1345115. Cites U. S. P. 1020593.
3. J. Aylsworth and E. Aiken, U. S. P. 1347668. Cites U. S. P. 1020593.
4. A. Backhaus, U. S. P. 1400203; abst. Mon. Sci. 1922, (5), **12**, 66.
5. *Ibid.* U. S. P. 1425624; abst. Chem. Tech. Uebers. 1923, **47**, 53.
6. *Ibid.* U. S. P. 1425625; abst. Chem. Tech. Uebers. 1923, **47**, 53.
7. *Ibid.* U. S. P. 1425626.
8. A. Backhaus and F. Arentz, U. S. P. 1388841; abst. Chem. Met. Eng. 1921, **25**, 1191.

sulfochloride gives bluish-red tints on acetyl silk[1]. Use is also made of soluble aminoazo dyes containing one or more carboxyl groups and also a diazotizable amino group[2], so that after dyeing with the carboxylated azoamino dye, different shades are obtainable by diazotizing the dye on the fiber and developing. *m*-Aminoazobenzoic acid, *o*-anisidine or anthranilic acid produce scarlet, red, magenta or bluish-red dyeings when developed with *b*-naphthol or *b*-hydroxynaphthoic acid. 1.4-Diaminoanthraquinone condensed with phenylglycidic acid or methylglycidic acid in glacial acetic acid solution in the presence of copper or copper acetate[3], dyes acetyl silk bright blue. 1-Aminoanthraquinone and 1-amino-4-hydroxyanthraquinone give red and purple dyes respectively with phenylglycidic acid.

Acid dyestuffs giving blue to green shades on acetate silk[4] are obtained by condensing 4.8-dihalogenanthrarufin with 2 molecules of an aminobenzoic acid, or by condensing 4.8-dinitro-1.5-dichloranthraquinone as above, and reducing the nitro groups of the product. To produce monomethylxylenesulfonamide[5], xylenesulfochloride is treated with monomethylamine chloride in the presence of sodium carbonate. The monomethylamine[6] is obtained in excess of 80% theoretical yield by treating acetamide with calcium hypochlorite and hydroxide. Plastic cellulose acetate solutions result by admixing cyclohexanone or methylcyclohexanone dissolved in ethyl acetate with acetone-soluble acetyl-

1. British Dyestuffs Corp., J. Baddiley and A. Shepherdson, E. P. 211720; abst. C. A. 1924, **18**, 1914.
2. J. Baddiley, J. Hill and E. Anderson, U. S. P. 1498315; abst. C. A. 1924, **18**, 3279; J. S. C. I. 1924, **43**, 629-B; Textile Colorist, 1924, **46**, 526. E. P. 202157; abst. J. S. C. I. 1923, **42**, 972-A. Refer to E. P. 182830.
3. J. Baddiley, W. Tatum and British Dyestuffs Corp., Ltd., E. P. 224363; abst. C. A. 1925, **19**, 1351.
4. British Dyestuffs Corp., J. Baddiley and W. Tatum, E. P. 227923; abst. Chem. Zentr. 1925, I, 2664.
5. W. Bader and D. Nightingale, U. S. P. 1433925.
6. *Ibid.* U. S. P. 1489380; abst. J. S. C. I. 1924, **43**, 450-B. E. P. 169536; abst. J. S. C. I. 1921, **40**, 827-A.

cellulose[1]. Acetyldicyclohexylamine[2], and *p*-toluenesulfodicyclohexylamine are similarly acting plastifiants. The methylcyclohexanones[3], instead of being obtained from a cresol, may be produced from mixed isomeric cresols.

By heating cellulose with chloral and a tertiary base as quinoline or pyridine to 90°, a clear, stable, viscous solution is rapidly formed. On treating this solution with water[4], the cellulose is precipitated as a chloral compound, in the form of a clear, transparent film. Dyeing cellulose acetates is carried out with water-soluble sulfamic acids of the dye[5], 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 continued diazotization and treatment with *b*-naphthol produces a red-violet color.

The alkaline saponification of cellulose acetate prior to or during dyeing[6], is effected in the presence of soluble aldehydes or hydroxyaldehydes, or of aromatic sulfonic or carboxylic acids or their salts. When a mixture of ammonium formate and formamide is decomposed with sulfuric acid[7], and in the presence of at least one molecular proportion of water to formamide, concentrated formic acid is obtained. A celluloid-substitute results from admixing acetylcellulose with water and a gelatinizing media as tri-

1. 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; Textilber. 1921, **2**, 408. D. R. P. 251351; abst. Farben-Ztg. 1912, **17**, 2815.

2. *Ibid.* D. R. P. 281225; abst. Chem. Zentr. 1915, I, 238.

3. *Ibid.* D. R. P. 334871; Addn. to D. R. P. 284672; abst. Chem. Zentr. 1921, II, 1068. D. R. P. 284672; abst. Chem. Zentr. 1915, II, 111.

4. *Ibid.* D. R. P. 408821; abst. J. S. C. I. 1925, **44**, 351-B.

5. *Ibid.* E. P. 204280; abst. C. A. 1924, **18**, 909. D. R. P. 420017; abst. J. S. C. I. 1926, **45**, 317-B. Belg. P. 309771. F. Guenther and Badische Anilin & Soda-Fabrik, U. S. P. 1526142; abst. C. A. 1925, **19**, 1202; J. S. C. I. 1925, **44**, 204-B.

6. *Ibid.* E. P. 209849; abst. C. A. 1924, **18**, 1757. Belg. P. 317800.

7. *Ibid.* E. P. 217467; abst. C. A. 1923, **19**, 300; J. S. C. I. 1924, **43**, 731-B.

chlorethylacetanilid or ethylacetanilid in quantity more than sufficient to gelatinize the ester. The water is then evaporated therefrom, and the acetylcellulose plastic molded by heat[1].

Cellulose acetate when treated with aldehydes in the presence of saponifiable agents, acquire the property of fixing dyestuffs without there being any marked change in the properties of the fibers themselves[2]. Sulfonic acids (cresolsulfonic, naphthalenesulfonic, and naphthoic acids) may be substituted for aldehydes. A compound or non-shattering glass[3] is produced by first coating each piece of glass with a thin gelatin layer, then with a cellulose ester film; or a cellulose ester plastic solution may be sprayed upon the gelatin coating. According to the experience of W. Barnett[4], use of a mixed catalyst of chlorine and sulfur dioxide gives satisfactory results with the minimum amount of change in the parent cellulose complex in acetylating. As no signs of discoloration occur owing to the ease of control of the reaction, no special precautions are necessary. The acetate, propionate, butyrate, and benzoate and acetobenzoate (using benzoyl chloride in acetic acid) are cellulose esters readily produced by this method. Acetylcellulose-phenylhydrazines and acetylcellulose-*p*-bromphenylhydrazones[5] are obtained by treating solutions of various acetylcelluloses with the hydrazines. The first compound has m. pt. 229-265°, the second, 243-287°.

The viscosity and density of 5% cellulose acetate solutions in acetone, and mixtures of acetone with water, ben-

1. Badische Anilin & Soda Fabrik, U. S. P. 1468222; abst. C. A. 1923, **17**, 3789. E. P. 154157; abst. C. A. 1921, **15**, 1092.

2. Badische Anilin & Soda Fabrik, F. P. 558900; Addn. 29098; abst. J. Soc. Dyers, 1923, **39**, 329; Chem. Zentr. 1923, IV, 987; 1928, I, 2758.

3. A. Bardin, D. R. P. 320339; abst. Kunst. 1920, **10**, 109.

4. W. Barnett, J. S. C. I. 1921, **40**, 8-T; abst. C. A. 1921, **15**, 1396; Chim. et Ind. 1921, **6**, 511; Paper 1921, **29**, #3, 19; Cellulosechemie 1921, **2**, 102.

5. *Ibid.* J. S. C. I. 1921, **40**, 61-T; abst. J. C. S. 1921, **120**, i, 308; Chim. et Ind. 1921, **6**, 771.

zene and ethyl alcohol have been determined[1]. Benzene causes a progressive increase in viscosity with increase in concentration, whereas water and ethyl alcohol give an initial rapid fall in viscosity. H. Bassett[2] recommends acetylating cotton in a mixture of 80% acetic anhydride 300, benzene or toluene 1200, sulfuric acid 10, the fibrous ester formed being separated and treated with sulfur chloride or chlorine to form the ester. In manufacturing filaments from cellulose acetonitrate[3], glacial acetic acid and acetone constitute the solvent used for spinning, the precipitating bath being dilute acetic acid. In the preparation of aldehyde from acetylene[4], the latter is continuously passed through a bath containing an acid mercury compound, the acetic acid formed being led off and fresh water added.

In preparing masses non-sensitive to water[5], cellulose is dissolved in calcium thiocyanate solution and paper coated with this mixture, or the paper may be passed through a thiocyanate solution under such conditions that there is superficial solution and gelatinization of the paper. E. Becker[6] detects oxycellulose, owing to its acidity by addition of barium hydroxide solution, chemical combination taking place. Storage battery separators[7], positioned between the active plates, and having all the advantages of a

1. G. Barr and L. Bircumshaw, Trans. Faraday Soc. 1921, **16**, 72; abst. C. A. 1922, **16**, 2988; J. C. S. 1922, **122**, i, 232; Ann. Rep. S. C. I. 1922, **7**, 138.

2. H. Bassett, U. S. P. 1466329; abst. C. A. 1923, **17**, 3789.

3. H. Bassett and T. Banigan, U. S. P. 1497321; abst. J. S. C. I. 1924, **43**, 706-B; Textile Colorist, 1924, **46**, 525.

4. E. Baum and M. Mugdan, U. S. P. 1489915; abst. C. A. 1924, **18**, 1836; J. S. C. I. 1924, **43**, 450-B; Chem. Age (N. Y.) 1924, 205. Swiss P. 71990. D. R. P. Appl. 25173, July 15, 1914. Swed. P. 43001. F. P. 475183. Belg. P. 269317. E. P. 16957, 1914; abst. J. S. C. I. 1915, **34**, 888. Ital. P. 144187. Norw. P. 25625. Span. P. 58940.

5. F. Beck, D. R. P. 357972; abst. Chem. Zentr. 1922, IV, 962; Kunst. 1923, **13**, 35. D. R. P. 367212, Addn. to 357972; abst. Chem. Zentr. 1923, II, 1006. D. R. P. 353662; abst. Chem. Zentr. 1922, IV, 646.

6. E. Becker, Zellstoff u. Papier, 1921, **1**, 3; abst. Chem. Zentr. 1921, IV, 439; J. S. C. I. 1921, **40**, 653-A; Paper Trade J. 1921, **73**, 52; J. C. S. 1922, **122**, ii, 94. Cf. J. S. C. I. 1921, **40**, 295-A.

7. L. Bent, U. S. P. 1463864.

perforated celluloid plate, are obtained by incorporating sodium sulfate finely divided with cellulose acetate, shaping to the form of the plate, evaporating off the volatile solvent portion, then immersing in warm water to dissolve out the sodium sulfate and thereby induce the degree of porosity desired.

Metallic tubes for cosmetic substances are coated on the inside with tin[1], but through use continually gives off small amounts of lead which contaminates the preparation contained in them. A cellulose acetate coating of the tube interior obviates this. Acetic anhydride is prepared without the use of chlorine or phosphorus[2], by passing a current of nitrogen trioxide or tetroxide and oxygen over freshly fused and pulverized sodium acetate, the yield being about 50%.

In a research upon the behavior of artificial silks upon dyeing[3] it was found that in dyeing with sulfur black the loss in weight went up to 0.84%, but a favorable influence is exerted with regard to tenacity and elasticity. The G. Blenio patent describes[4] a flame-proof fabric for airplane wing covering, embracing a cellulose acetate impregnated cotton or linen fabric in which anhydrous, non-delinquescent salts (ammonium sulfate or phosphate with aluminum sulfate or phosphate) have been dissolved. A film may be made of this same material and attached to the fabric[5].

J. Bloom[6] has described a process and shown an apparatus for the electrical treatment in the dyeing of cellulose acetate films and fibers, and in 1923 appeared the

1. A. Beythien, Ztschr. Unters. Nahr. u. Genussm. 1922, **43**, 47; abst. Chem. Tech. Uebers, 1922, **46**, 291. See also K. Neukam, Chem. Ztg. 1921, **45**, 301.
2. J. Bielecki and J. Ciechanowski, Roozniki Chem. 1923, **2**, 453; abst. C. A. 1925, **19**, 38; J. S. C. I. 1924, **43**, 653-B. Cf. R. Muller and Deutsche Celluloid Fabr., F. P. 468963; abst. J. S. C. I. 1914, **23**, 985.
3. K. Biltz, Textile Forschung, 1921, **3**, 157; abst. Chem. Tech. Uebers, 1922, **46**, 98.
4. G. Blenio, U. S. P. 1427941.
5. *Ibid.* U. S. P. 1436231; abst. C. A. 1923, **17**, 618.
6. J. Bloom, U. S. P. 1333700.

Bombrini, Parodi and Delfino process for acetylcellulose preparation[1]. In the manufacture of dissolved or gelatinized cellulose acetates[2], furfural alone or dissolved in alcohol or other solvents has been described, and its uses in the industry pointed out. G. Bonwitt[3] has indicated the variations in physical constants obtained by dissolving cellulose acetates or hydroacetates in various solvents and dissolving combinations, especially as applied to the manufacture of films.

The G. Bouffe process for acetate filament formation[4] involves spinning in a closed apparatus (which is illustrated), a "dry" spinning operation being preferred. Air or inert gas traverses the apparatus, which is electrically heated. In the treatment of acetate silk before dyeing[5], a hank of 100 gms. is plunged into a 2 liter bath containing crystallized sodium sulfate 800 gm. (350 gm. anhydrous salt) and 17 gm. sodium carbonate, a temperature of 85° for 30-45 minutes being used. The hank is then withdrawn and dyed in the usual manner. Cloth may be fireproofed by first impregnating it with cellulose acetate[6], and afterwards a solution containing alginic acid or an alginate. J. Brandenberger[7] has described details of manufacture of a band of cellulosic material as cellulose acetate, by folding over the edges and coating them, so as to avoid the normal small serrations on a cut edge, and also to increase rigidity of the film edge.

1. Bombrini, Parodi & Delfino, Ital. P. 181812, 196070.

2. G. Bonwitt, E. P. 138078; abst. C. A. 1920, **14**, 1762; J. S. C. I. 1920, **39**, 504-A, 541-A; Paper, 1921, **27**, #27, 33; Chem. Ztg. 1920, **44**, 617. F. P. 519536; abst. Caout. et Gutta. 1921, **18**, 11148.

3. *Ibid.* Chem. Ztg. 1920, **44**, 973; abst. Phot. Abst. 1921, **3**, 83. Chem. Ztg. 1921, **45**, 194; abst. Chem. Tech. Uebers, 1922, **46**, 202.

4. G. Bouffe, F. P. 523590; abst. Chim. et Ind. 1922, **8**, 653; Rev. Prod. Chim. 1921, **24**, 712; Caout. et Gutta. 1922, **19**, 11195. E. P. 160859; abst. Chem. Met. Eng. 1921, **25**, 33.

5. M. Bouvier, U. S. P. 1489814; abst. C. A. 1924, **18**, 1914; J. S. C. I. 1924, **43**, 465-B. Compare E. Prince, U. S. P. 1366023.

6. P. Bradley, E. P. 151396. U. S. P. 1372478.

7. J. Brandenberger, U. S. P. 1406148.

J. Briggs in 1920 published an article on the dyeing of acetate silk[1], and the next year[2] appeared the dyeing process of J. Briggs and C. Palmer, in which the cellulose acetate is pretreated with a thiocyanate solution to augment its tinctorial receptivity[3]. Briggs prepared acetate filaments for dyeing[4] by treating cellulose acetates lower than the triacetate, by subjecting the filaments to a superficial or peripheral saponification treatment in an aqueous bath containing 0.1-0.5% NaOH, afterwards dyeing with direct dyes the hydrated cellulose or deacetylated cellulosic layer so formed. The dyeing of cellulose acetate by means of insoluble or difficultly soluble dyes is effected by solubilizing the dye by pretreatment with higher fatty acids or their sulfo derivatives or salts (sulfo-ricinoleic, -oleic, -stearic or -palmitic acids or their potassium, sodium or ammonium salts)[5]. Examples of suitable dyes are benzeneazobenzeneazo-*b*-naphthol (Sudan III), 4-nitro-2-methoxybenzene-1-azodiphenylamine and aminoazonaphthalene. Pyrazolone dyes containing no sulfo group are also useful for dyeing acetylcellulose[6], especially azo dyes prepared by coupling non-sulfonated diazo compounds with 1-phenyl-3-methyl-5-pyrazolone or 1.3-dimethyl-5-pyrazolone. In 1924 the trade-

1. J. Briggs, J. S. C. I. 1920, **39**, 286-R; abst. Faser. 1921, **3**, 54.

2. J. Briggs and C. Palmer, U. S. P. 1398357; abst .C. A. 1922, **16**, 836.

3. J. Briggs, Canadian Dyer and Color User, 1922, **2**, 5; J. S. Dyers Col. 1921, **37**, 287; abst. C. A. 1922, **16**, 2226; J. S. C. I. 1922, **41**, 54-A; J. I. E. C. 1922, **14**, 253.

4. J. Briggs, U. S. P. 1425364; abst. C. A. 1922, **16**, 3402; J. S. C. I. 1922, **41**, 705-A; Chem. Tech. Uebers, 1923, **47**, 32. E. P. 169741; abst. C. A. 1922, **16**, 836; J. S. C. I. 1921, **40**, 795-A; Textilber. 1922, **3**, 375. India P. 5687, 1920. Compare E. P. 20672, 1910; 20977, 1911; 6463, 1915; 14101, 1915; 100009, 158340.

5. British Celanese, Ltd., and G. Ellis, E. P. 219349; abst. C. A. 1925, **19**, 579; J. S. C. I. 1924, **43**, 906-B. U. S. P. 1618413; abst. C. A. 1927, **21**, 1361; J. S. C. I. 1927, **46**, 249-B. See also E. P. 211720.

6. British Celanese, Ltd., G. Ellis, F. Stevenson and C. Croft, E. P. 224681; abst. C. A. 1925, **19**, 1352; J. S. C. I. 1925, **44**, 39-B. U. S. P. 1600277; abst. C. A. 1926, **20**, 3578; J. S. C. I. 1926, **45**, 977-B. Can. P. 260530, abst. C. A. 1926, **20**, 3578.

mark Celfect as applied to yarns and threads of cellulose acetate was registered in Canada[1].

If cellulose acetate filaments or fibers are treated with hot water or steam, solutions of ammonium, calcium or potassium thiocyanate or acetic acid[2] and dried without tension, they will appear more or less crinkled in appearance, softer to the touch, of reduced luster and resemble greatly wool or hair. In 1921 appeared the British Cellulose & Chemical Manufacturing Co. process for manufacture of cellulose acetate filaments by a described method and apparatus[3]. A method for preparing methylamine and other primary alkylamines from acetamide, propionamide, etc., was published in 1921, as having a softening effect on cellulose esters[4]. When using the thiocyanates in the pretreatment of acetate silk[5], acid wool dyes and basic and vat dyes may be used.

Goods containing acetylcellulose fibers are first dyed in the usual manner with substantive or other dyes[6], and then subjected to a slight alkaline soaping, whereby the dye first absorbed bleeds off, especially when cotton is present. The dyeing is continued for a sufficiently long time so that cotton and acetated cotton have the same depth of shade. As a soaping agent in this connection come into consideration sodium hydroxide, carbonate, sulfide, silicate and borate. The details of a rotary pump were published in 1922, especially useful for acetylcellulose filament production[7].

1. British Celanese, Ltd., Can. Trade Mark 35266 of 1924.
2. British Cellulose & Chemical Mfrg. Co., Ltd., H. Dreyfus, J. Briggs and H. Clotworthy, E. P. 165164; abst. C. A. 1922, **16**, 650; Chem. Met. Eng. 1921, **25**, 802. U. S. P. 1554801; abst. C. A. 1925, **19**, 3593. Compare E. P. 158340.
3. British Cellulose & Chemical Mfrg. Co., Ltd., and H. Roy, E. P. 165519.
4. British Cellulose & Chemical Mfrg. Co., D. Baden and D. Nightingale, E. P. 169536; abst. J. S. C. I. 1921, **40**, 756-A.
5. British Cellulose & Chemical Mfrg. Co., Ltd., J. Briggs and C. Palmer, E. P. 158340; abst. Chim. et Ind. 1922, **7**, 131; Caout. et Gutta. 1922, **19**, 11334.
6. British Cellulose & Chemical Mfrg. Co., Ltd., J. Briggs and L. Richardson, E. P. 178946; abst. Chem. Tech. Uebers, 1922, **46**, 318.
7. British Cellulose & Chemical Mfrg. Co., Ltd., and H. Mallock, E. P. 181085. Compare E. P. 28320, 1912.

Sodium, potassium, ammonium and calcium thiocyanates have also been proposed as swelling agents for cellulose acetate filaments[1], so that immediately after extrusion of the plastic filament, the swelling agent of the thiocyanate minimizes the normal contractility induced by evaporation of the volatile solvent (acetone) in which the cellulose acetate was dissolved prior to extrusion into filament form. This swelling and coagulation controlling effect may also be induced by certain acetate solvents which are miscible in water, as diacetone alcohol, ethyl alcohol, and formic and acetic acids[2].

In the preparation of acetate filament for dyeing[3], the partial saponification action with sodium hydroxide may be intensified by the addition of sodium acetate, chloride or sulfate in small quantity or in low concentration, or sodium silicate, aluminate or borate (borax)[4]. Sodium acetate is especially beneficial in this respect[5], particularly when the alkaline saponification takes place in the cold, or without heating[6]. The addition of calcium or magnesium chloride[7], or suspending in the saponifying liquid colloidal bodies such as clay, alumina, silicic acid gel (the two latter prepared so as to be insoluble in dilute alkali), calcium or magnesium oxide or carbonate or calcium or aluminum oleate[8], produce analogous results.

1. British Cellulose & Chemical Mfrg. Co., Ltd., C. Palmer and W. Dickie, E. P. 177868; abst. C. A. 1922, **16**, 3208; Chem. Tech. Uebers, 1922, **46**, 292.
2. *Ibid.* E. P. 179234; abst. C. A. 1922, **16**, 3394; Caout. et Gutta. 1923, **20**, 11687; Chem. Tech. Uebers, 1922, **46**, 327. Cites E. P. 177868.
3. British Cellulose & Chemical Mfrg. Co., Ltd., and L. Richardson, E. P. 175485; abst. J. S. C. I. 1922, **41**, 202-A; Caout. et Gutta. 1922, **19**, 11496; Chem. Tech. Uebers, 1922, **46**, 259. India P. 5688, 1920. Compare E. P. 169741.
4. *Ibid.* E. P. 175486; abst. J. S. C. I. 1922, **41**, 202-A; Caout. et Gutta. 1922, **19**, 11496; Chem. Tech. Uebers, 1922, **46**, 259. India P. 5689, 1920.
5. *Ibid.* E. P. 176034; abst. J. S. C. I. 1922, **41**, 237-A. India P. 5690, 1920.
6. British Cellulose & Chemical Mfrg. Co., Ltd., and W. Bader, E. P. 193912. Compare E. P. 20672, 1910.
7. *Ibid.* E. P. 194244.
8. *Ibid.* E. P. 195920.

As a plasticizing agent for the acetylcellulose[1], 30% of 1.1.1.-trichlor-2-methylpropanol (trichlor*ter*butyl alcohol) alone or with triphenyl phosphate or castor oil has been advocated. An apparatus especially useful for cutting plastic cellulose esters[2], comprises a heated cutting knife with or without auxiliary means for heating the surface layer of the material, the latter being dovetailed to a carrier, held to a reciprocating table.

Dyestuffs of the aryl- or substituted arylbenzo- or naphtho-quinonemonoimide series (indophenols) are used for dyeing cellulose acetate[3], applied to the material as their leuco compounds, which are subsequently oxidized to the dyestuffs by air or oxidizing agents. For example, the dyestuff is reduced by sodium hydrosulfite in an NaOH bath containing dimethyl - *p* - phenyl - 1.4 - naphthoquinoneimide maintained at 60°. A description of Celastoid, a cellulose acetate plastic[4] was published in 1920. Cellulose acetate is dyed in fast greenish-yellow shades free from phototrophy by means of monazo dyestuffs obtained by coupling 1-3-dihydroxyquinoline with diazotized aniline, halogenated aniline, toluidine, 1.3-dihydroxyquinoline, or *o*-chlor-*p*-nitraniline[5]. Yellowish-red tintings are produced[6] with

1. British Cellulose & Chemical Mfrg. Co., Ltd., W. Bader and W. Dickie, E. P. 195849; abst. C. A. 1923, **17**, 3789; J. S. C. I. 1923, **42**, 546-A. U. S. P. 1536052; abst. C. A. 1925, **19**, 1948. See also E. P. 190269; abst. C. A. 1923, **17**, 2957.

2. British Cellulose & Chemical Mfrg. Co., Ltd., F. Small and W. Dickie, E. P. 200922; abst. J. S. C. I. 1923, **42**, 748-A.

3. British Cellulose & Chemical Mfrg. Co., Ltd., and G. Ellis, E. P. 220505; abst. J. S. C. I. 1924, **43**, 865-B.

4. British Cellulose & Chemical Mfrg. Co., Ltd., J. I. E. C. 1920, **12**, 515; Kunst. 1921, **11**, 87; Die Chem. Ind. 1921, **44**, 143.

5. British Dyestuffs Corp., J. Baddiley and J. Hill, E. P. 236037; abst. C. A. 1926, **20**, 993; J. S. C. I. 1925, **44**, 708-B. U. S. P. 1611986; abst. C. A. 1927, **21**, 655. See also E. P. 11205, 1905; abst. J. S. C. I. 1905, **24**, 840.

6. British Dyestuffs Corp., J. Baddiley, A. Shepherdson, H. Swann, J. Hill and L. Lawrie, E. P. 224077; abst. C. A. 1925, **19**, 1202; Chem. Age (London), 1924, **11**, 582; Chem. Zentr. 1925, I, 1017. U. S. P. 1616103; abst. C. A. 1927, **21**, 1018; J. S. C. I. 1927, **46**, 216-B. F. P. 587570; abst. Rayon J. 1926, **1**, 41. Ital. P. 253044. E. P. 246984 Addn. to 224077; abst. J. S. C. I. 1926, **45**, 317-B. U. S. P. 1534019; abst. C. A. 1925, **19**, 1781. British Dyestuffs Corp., J. Baddiley and A. Shepherdson, E. P. 211720.

a dispersion (by use of sulfonated naphthalene condensates with formaldehyde) of a monoazo dye prepared from diazotized *p*-nitraniline and diphenylamine, or violet red with a dispersion of 1.4-diaminoanthraquinone. Bluish-red red shades result[1], when 1.4 diaminoanthraquinone is condensed with *o*-cresotinic sulfochloride (sulfochloride of *o*-cresotinic acid). A deep black shade is obtained[2] by immersing acetylcellulose silk in a hot colloidal solution of *a*-naphthylamine, benzidine, tolidine, or *pp'*-diaminodiphenylamine, diazotizing and developing in a slightly acid solution containing *b*-hydroxynaphthoic acid or resorcinol.

A fluorescent screen has been described[3] made from a composition which is not fluid at room temperature, consisting of the fluorescent material calcium tungstate in a fine state of subdivision and a binding material of cellulose acetate. A nearly pure alphacellulose, particularly suitable for making pure cellulose acetate[4] is obtained when cleaned wood in small pieces is treated with dilute sulfuric acid under pressure, drained, neutralized and boiled with calcium or magnesium bisulfate under pressure.

The gases obtained from cracking petroleum by the Burton process contain ethylene, propylene, amylene and hexylene. In the manufacture of chlorhydrins from these gases[5], they are passed admixed with chlorine, through a heated chamber and the chlorhydrins removed from the issuing gases by passing into an emulsion of a salt solution and an indifferent solvent (chloroform, carbon tetrachloride, tetrachlorethane, dichlorethane, benzene, toluene). In making chlorhydrins[6], ethylene or propylene is treated

1. British Dyestuffs Corp., J. Baddiley and W. Wyndham, E. P. 225678; abst. Chem. Zentr. 1925, I, 2664.
2. British Dyestuffs Corp., L. Lawrie, H. Blackshaw, E. P. 224359; abst. C. A. 1925, **19**, 1352; J. S. C. I. 1925, **44**, 39-B.
3. British Thomson-Houston Co., Ltd., E. P. 190792; abst. J. S. C. I. 1923, **42**, 203-A.
4. E. Bronnert, E. P. 170964; abst. C. A. 1922, **26**, 1013.
5. B. Brooks, U. S. P. 1394664.
6. *Ibid.* U. S. P. 1446873; abst. Chem. Tech. Uebers, 1923, **47**, 151.

with hypochlorous acid in cold, dilute aqueous solution. A float for steam traps has been described[1], in which the core, instead of being electroplated with copper as is usual, is immersed in an acetylcellulose lacquer carrying finely divided metallic copper in suspension, or[2], the core may be dipped in acetate lacquer, then copper dusted on and afterwards electrolytically deposited. The anaesthetic properties of propylene, methane and dimethyl ether have been detailed[3].

Cellulose acetate may be dyed with dyestuffs[4], for which in the ordinary way it has little or no affinity, by employing them in colloidal solution (addition of gelatin, casein, saponin) to the dye bath, followed by a precipitant (molybdate, tungstate, stannate, tannin), and for acid sulfur or vat colors, a salt of an organic compound containing basic groups (aniline, benzidine, dianisidine). Acetylcellulose goods are dyed by means of alkylaminoazo compounds containing no sulfonic nor carboxylic acid groups, suitable dyes being those prepared by coupling methylaniline or dimethylaniline with the diazo compounds of aniline, chloranilines, nitroanilines, nitroanisidines, aminomethylanilines, aminodimethylaniline, naphthylamines or aminoazobenzenes, or with tetrazo compounds of benzidine, dianisidine or diaminodiphenylmethane. Examples, aminoazotoluene, -naphthalenes, -naphthols or -naphthylamines[5].

Compounds obtained by reacting upon cellulose with sulfur chlorides, thionyl chloride, sulfuryl chloride, pyrosulfuryl chloride, phosphoryl chloride or chlorsulfonic acid

1. J. Brown and J. Mullinnix, U. S. P. 1492349. For process of dehydrating chlorhydrins, see B. Brooks, U. S. P. 1446874; abst. Chem. Tech. Uebers, 1923, **47**, 151.

2. *Ibid.* U. S. P. 1492350.

3. W. Brown, J. Pharmacol. 1924, **23**, 485; abst. C. A. 1924, **18**, 2921; J. S. C. I. 1924, **43**, 889-B.

4. Burgess, Ledward & Co., Ltd., and W. Harrison, E. P. 179384; abst. C. A. 1922, **16**, 3402; J. S. C. I. 1922, **41**, 543-A; Chem. Ztg. 1922, **46**, 919; Chem. Tech. Uebers, 1922, **46**, 318.

5. *Ibid.* E. P. 190313; abst. C. A. 1923, **17**, 2964; J. S. C. I. 1923, **42**, 34-A, 141-A; Chem. Ztg. 1922, **47**, 73. Compare E. P. 182830; abst. C. A. 1922, **16**, 4356.

have been described[1], alkalicellulose being treated with the chlorinated inorganic compound. The products obtained are not decomposed by alkali metal hydroxides, and fabrics so treated are used for the production of wool-like effects.

In a single-bath process for forming azo dyes upon cellulose acetate silk[2], the amino component and the second component are absorbed by the silk from a hot bath, the nitrite added, and diazotization effected at 30-50°, the color being rapidly developed. The manufacture of benzyl succinate has been described[3], having dissolving action on acetone-soluble acetylcellulose. A. Caille[4], in 1923, published his objections to the views of M. Deschiens (see p. 448, n. 2), and a resume of the applications[5] and stabilities[6] of the acetated celluloses, including their methods of preparation[7].

In pattern ornamentation, acetate silk[8] is treated in selected areas only with mercerizing agents other than NaOH (sulfuric, phosphoric, hydrochloric, or nitric acids, zinc chloride or calcium thiocyanate), the solutions being applied by a printing press, or the fabrics may be printed with a resist and then immersed in a mercerizing solution. In the manufacture of acetaldehyde by passing acetylene through an aqueous solution containing a mercury catalyst, the acetylene is passed through at such rate that a large proportion is not absorbed[9], a much greater output of ace-

1. Burgess, Ledward & Co., Ltd., and W. Harrison, E. P. 192173.
2. *Ibid.* E. P. 193646; abst. C. A. 1923, **17**, 3794; J. S. C. I. 1923, **42**, 250-A, 397-A.
3. M. Bye and L. Carlson, U. S. P. 1439605; abst. C. A. 1923, **17**, 771.
4. A. Caille, Bull. Soc. Ind. Rouen, 1920, **48**, 431; abst. C. A. 1923, **17**, 1139.
5. *Ibid.* Caout. et Gutta. 1920, **17**, 10447; abst. C. A. 1920, **14**, 3790; Chem. Zentr. 1920, IV, 372.
6. *Ibid.* Bull. Soc. Ind. Rouen, 1922, **50**, 382; abst. C. A. 1923, **17**, 2500; Caout. et Gutta. 1924, **21**, 12438.
7. *Ibid.* Chim. et Ind. 1924, **12**, 441; abst. C. A. 1925, **19**, 171; J. S. C. I. 1924, **43**, 937-B.
8. Calico Printers' Assoc., Ltd., and F. Roberts, E. P. 215860; abst. C. A. 1924, **18**, 3481.
9. Canadian Electro-Products Co., Ltd., E. P. 208689; abst. J. S. C. I. 1925, **44**, 114-B. Can. P. 242537.

taldehyde being obtained and a larger yield. Acetic anhydride is prepared by acting upon powdered, fused sodium acetate with sulfur chloride which has absorbed chlorine to the extent of 50% of its weight at —14°, 76% of theoretical being obtained[1].

The viscosity of dissolved cellulose acetate may be materially diminished by treating in an autoclave at 120° for 1 hour[2]. The inflammability of cellulose nitrate[3], or acetate[4], is materially reduced by adding thereto tri- or tetra-chlornaphthalenes or -chloranthracenes. Composite films are produced in a manner to avoid the trapping of air bubbles[5] by charging one compartment of an apparatus illustrated with a cellulose acetate solution and another compartment with a different composition (nitrocellulose), both esters being dissolved in acetone, and flowing them in about equal dry weights onto a movable base. Moulded cellulose acetate articles are obtained by compressing a plastic under high pressure (1000 kilos per sq. cm.) at temperatures approaching its decomposition point, and allowing to cool under pressure. The operation may be carried out in three stages[6], the hot plastic being extruded into the air when any volatile solvent vaporizes, leaving a dry, friable mass, which is then pressed into moulds at 140-160° at 100 atm. pressure. Or[7], the three-phase above described may be carried out in a single operation.

1. G. Capelli, Giorn. chim. ind. applicata, 1921, **3**, 356; abst. C. A. 1922, **16**, 238; J. S. C. I. 1921, **40**, 902-A; Chim. et Ind. 1922, **7**, 673; Chem. Tech. Uebers, 1922, **46**, 295.

2. O. Carlsson and E. Thall, U. S. P. 1375208; abst. C. A. 1921, **15**, 2724. E. P. 136141; abst. C. A. 1920, **14**, 1219. D. R. P. 359311.

3. S. Carroll, U. S. P. 1354725; abst. C. A. 1921, **15**, 172.

4. *Ibid.* 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.

5. *Ibid.* U. S. P. 1476392.

6. Cellon-Werke A. Eichengrün, E. P. 147904; abst. C. A. 1921, **15**, 173; J. S. C. I. 1921, **40**, 874-A; 1922, **41**, 52-A. F. P. 520101; abst. Chem. Zentr. 1921, IV, 533. Swiss P. 93296.

7. *Ibid.* E. P. 171432, Addn. to 147904; abst. J. S. C. I. 1922, **41**, 52-A.

The manufacture of very thin acetylcellulose films is carried out by flowing the acetate solution upon a base which is[1], or is not[2], soluble in the solvents used to dissolve the cellulose ester, the film being removed from the base before all the solvent has evaporated, i.e., as soon as possible after solidification. Cellulin[3] has been described, apparently a cellulose acetate film. A. Chapman in his lecture on the "Chemistry of Aeronautics" in 1920, detailed the manufacture of acetylcellulose and its application to airplane dopes[4]. The addition to cellulose esters as a plasticizer[5] of ethylacetanilid, especially in the dissolved form is said to lower the water-sensitivity and raise the crystal-turbidity.

As solvents for cellulose esters[6] have been patented alkyl acrylates and crotonates, especially the methyl and ethyl esters, in combination with alcohol and benzene. Diacetylaniline and formylacetyl-*o*-toluidine have been proposed[7], being acetylcellulose gelatinizers, even in the cold. Phenoxyacetic acid-ethyl-anilide (ethylanilide phenoxyacetate) and cresoxylacetic acid-*o*-toluidide (*o*-toluidide cresoxylacetate)[8] have also been proposed, an example being acetone-soluble acetylcellulose 10, acetone 90, above arylaminoarylide of phenoxyacetic acid 5.

When an equal weight of fuming sulfuric acid containing 60% free SO_3 is allowed to flow with stirring into pentachlorethane heated to 50-60°, dichloracetyl chloride is obtained[9]. Chlorethylsulfuryl chloride is prepared by

1. Cellon-Werke A. Eichengrün, E. P. 202306.
2. *Ibid.* E. P. 224848, Addn. to 202306. Cellon-Werke, India Rubber World, 1923, **68**, 458.
3. Cellulin Corp., Paper, 1922, **30**, #24, 12.
4. A. Chapman, Chem. Age (London), 1920, **2**, 438; abst. C. A. 1920, **14**, 2089.
5. Chem. Fabr. vorm. Weiler-ter Meer, D. R. P. 343182; abst. Chem. Zentr. 1922, II, 101.
6. *Ibid.* D. R. P. 367294; abst. Chem. Zentr. 1923, II, 634.
7. G. Racky and Chemische Fabriken vorm. Weiler-ter Meer, D. R. P. 391873; abst. J. S. C. I. 1924, **43**, 553-B; Plastics, 1925, **1**, 26.
8. Chemische Fabriken vorm. Weiler-ter Meer, D. R. P. 395703; abst. J. S. C. I. 1925, **44**, 68-B.
9. *Ibid.* D. R. P. 362748; abst. J. S. C. I. 1923, **42**, 332-A; Chem. Tech. Uebers, 1922, **46**, 383.

subjecting ethylene chloride, a mercury salt and fuming sulfuric acid (65-80%) to heat, and the finished product separated by addition of water[1]. Plastic combinations result by incorporating with acetylcellulose[2], glyceryl esters containing both aromatic and lower aliphatic carboxylic acid radicals as monobenzoyldiacetylglycerol (glyceryl monobenzoyldiacetate), or glyceryl diacetomonophenylacetate, the last in conjunction with ethyl formate. Or[3], the acetylcellulose may be mixed with an alkyl ester of *o*-cyanocinnamic acid as the amyl ester, which may be obtained by the action of sulfonic chlorides on *a*-nitroso-*b*-naphthol in the presence of alkali.

A method for the manufacture of acetaldehyde by passing acetylene into acid solutions containing mercury salts has been evolved[4], in which the catalyst is continuously regenerated in the reaction liquid by electrolytic oxidation, the arrangement being such that excess of metallic mercury is always present at the anode. As softeners and plastifiants for acetylcellulose[5], alkyl- or alkylidene glyceryl ethers have been proposed as methyl-, ethyl- or methyleneglyceryl chlorhydrin. Acyloxyfatty acid esters, as amyl acetylglycollate dissolved in alcohol-ether for nitrocellulose, or ethyl acetyloxyacetate for cellulose acetate have received patent recognition[6]. Acetic anhydride may be prepared by treating anhydrous alkali- or alkaline-earth acetates with a cold solution of sulfur trioxide in sulfuryl chloride[7].

1. Chemische Fabriken vorm. Weiler-ter Meer, D. R. P. 374141; abst. J. S. C. I. 1923, **42**, 1201-A; Chem. Tech. Uebers, 1923, **47**, 165.
2. *Ibid.* D. R. P. 402752; abst. J. S. C. I. 1925, **44**, 68-B.
3. *Ibid.* D. R. P. 412884; abst. J. S. C. I. 1925, **44** ,707-B; Plastics, 1926, **2**, 99 Cites D. R. P. 411955.
4. Chemische Fabrik Griesheim-Elektron, E. P. 143891. D.R.P. 360417, 360418; abst. Chem. Zentr. 1923, II, 403; Chem. Tech. Uebers, 1922, **46**, 366.
5. Chemische Fabrik von Heyden A. G., D. R. P. 288267; abst. J. S. C. I. 1916, **35**, 356. See A. Verley, Bull. Soc. Chim. 1899, (3), **21**, 375; abst. J. C. S. 1899, **76**, i, 665.
6. *Ibid.* D. R. P. 324786; abst. J. S. C. I. 1920, **39**, 779-A; Chem. Zentr. 1920, IV, 507. See D. R. P. 278487; abst. Chem. Zentr. 1914, II, 1012. Aust. P. 79427; abst. Kunst. 1920, **10**, 150.
7. *Ibid.* D. R. P. 358774; abst. J. S. C. I. 1923, **42**, 331-A; Chem. Ztg. 1922, **46**, 642.

When acetic acid vapor is passed over cast-iron turnings in an iron tube at 400°, acetone and carbon dioxide are formed[1]. In the preparation of thin bands to be more particularly used in the manufacture of cigarette mouthpieces[2], a solution of acetylcellulose in which has been incorporated powdered metal is uniformly spread over a revolving support in an exceedingly thin layer and the dried film detached. In the process of producing multicolor screens which are insoluble in water from compounds of basic dyes[3] with tannin, tungstic, molybdic or tungstic-phosphoric acid dissolved in alcohols or ammonia, the emulsification is effected in a cellulose acetate solution and dried. Emulsified particles of the different colors are prepared separately and mixed before application to the carrier. Furfural has also been patented as an acetylcellulose solvent[4], as has anhydrous liquid ammonia[5]. As desirable solvents of high dissolving power for nitrocellulose[6] and acetylcellulose[7] H. Clarke has described sulfones which are only slightly volatile or nonvolatile at ordinary temperatures, as *n*-dibutyl, di*iso*butyl, dimethyl, diethyl, *n*-dipropyl, di*iso*propyl, di*iso*amyl, methylethyl, diheptyl, ethyl-*iso*amyl and diphenyl sulfones. Likewise[8], phenolic esters of phthalic acid (diphenyl *o*-phthalate, phenyl phthalate).

Thioacetic acid may conveniently be prepared in about 70% yield[9] by passing hydrogen sulfide into acetic acid containing about 20% acetyl chloride, hydrochloric acid or

1. Chemische Fabrik von Heyden A. G., and R. Feibelmann, D. R. P. 435347; abst. J. S. C. I. 1927, **46**, 347-B.
2. *Ibid.* E. P. 157126; abst. J. S. C. I. 1922, **41**, 541-A.
3. J. Christensen, E. P. 216853.
4. C. Claessen, Belg. P. 292639, 295386, 296729, 296766, 296814, 299881.
5. J. Clancy and Nitrogen Corp., E. P. 182488; abst. C. A. 1922, **16**, 4346; J. S. C. I. 1923, **42**, 1171-A; Caout. et Gutta. 1923, **20**, 11688. Ital. P. 212137. Can. P. 234321.
6. H. Clarke, U. S. P. 1370878; abst. J. S. C. I. 1921, **40**, 296-A.
7. *Ibid.* U. S. P. 1370879; abst. J. S. C. I. 1921, **40**, 296-A; Chem. Ztg. 1921, **45**, 393.
8. *Ibid.* U. S. P. 1398939; abst. Chem. Ztg. 1922, **46**, 46.
9. H. Clarke and W. Hartman, J. A. C. S. 1924, **46**, 1731; abst. C. A. 1924, **18**, 2497; J. C. S. 1924, **126**, i, 1041.

acetyl bromide, the latter being the more effective catalyst. Direct dyeing of cellulose acetate films or filaments is possible by the addition of gelatin, gelatin soaps or acetic acid to the dyebath, in conjunction with soluble salts of zinc, tin or magnesium, as the chlorides[1]. According to the R. Clavel method[2], cellulose acetate goods are dyed directly in aqueous solution or suspension with non-sulfonates or mono-sulfonated dyes containing one or more of the following "active" groups: hydroxyl, amino, imino, amide, nitro, nitroso, *iso*nitroso, acylamino or azo groups. Example is given of dyeing in an aqueous bath of Gallocyanine DH. Differential dyestuffs may be used in the case of mixed goods[3], these methods being especially suitable for use with cellulose acetate in which depolymerization has been reduced to the minimum in the process of manufacture[4]. Cellulose acetates are also satisfactorily dyed by means of ice colors[5], provided that a relatively large quantity of a water-soluble salt (zinc, barium, magnesium, sodium, potassium chlorides), and a protective colloid (gelatin, boiled-off liquor, albumin, tannin) are present in the dyebath. Example, dianisidine hydrochloride, diazotized and de-

1. R. Clavel, 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. D. R. P. 355533; abst. Chem. Zentr. 1922, IV, 552; Chem. Tech. Uebers, 1922, **46**, 259. F. P. 528230; abst. Chim. et Ind. 1922, **8**, 879. F. P. Appl. 16012, 1921, Addn. to F. P. 528230; abst. Chim. et Ind. 1921, **6**, 828. F. P. Appl. 552, 1922, Addn. to F. P. 528230; abst. Chim. et Ind. 1922, **7**, 361. F. P. Appl. 554, 1922; abst. Chim. et Ind. 1922, **7**, 361. Swiss P. 92375; abst. Chem. Ztg. 1921, **45**, 1204. See E. P. 102310.

2. *Ibid.* E. P. 182830; abst. C. A. 1922, **16**, 4356; J. S. C. I. 1922, **41**, 616-A, 666-A; Phot. Abst. 1922, **2**, 164; Caout. et Gutta. 1923, **20**, 11688. F. P. 542892; abst. Chem. Zentr. 1923, II, 999; Chem. Ztg. 1922, **46**, 46. U. S. P. 1448432; abst. C. A. 1923, **17**, 1892; J. Text. Inst. 1923, **14**, 205-A; Rayon Record, 1930, **4**, #9, 483. See E. P. 102310, 176535.

3. *Ibid.* E. P. 182844; abst. J. S. C. I. 1922, **41**, 666-A. Can. P. 233420.

4. *Ibid.* E. P. 102310; abst. J. S. C. I. 1917, **36**, 80.

5. *Ibid.* E. P. 184964; abst. J. S. C. I. 1923, **42**, 884-A. See E. P. 176535; abst. J. S. C. I. 1922, **41**, 325-A. F. P. 542940; abst. Chem. Zentr. 1923, II, 576; Chem. Ztg. 1922, **46**, 868.

veloped with *a*-naphthylamine salt gives black, as does developing with 5-hydroxy-*a*-naphthylamine.

Acetate silk may be dyed with vat or sulfur dyes in such a weakly alkaline hydrosulfite vat that the silk is not attacked[1], under addition of salts, calcium or magnesium chloride, and protective colloids, or the acetate silk may be dyed in a hyposulfite vat kept weakly alkaline by ammonia, only sufficient alkali being present to form the leuco compound[2]. Examples are given of dyeing with bromindigo and Pyrogenindigo. If black shades are desired[3], the acetyl silk is impregnated with diphenyl black base and acids, and developed by oxidation. Satisfactory dyeings are obtained in the application of ice (developed) colors to cellulose acetate materials if *(a)* the bases and developers are employed in one bath[4], or *(b)* the base is applied and diazotization is effected in a second bath, or *(c)* the base or developer is applied in one bath and diazotization and development is carried on in a second bath, provided that a suitable protective colloid is present in one or both baths. Cellulose acetate is colored brownish-red by immersion in a bath of aminoazobenzene 20, *b*-naphthol 30 and Capri Blue 5 (for shading), afterwards diazotizing.

In the production of azo dyes upon acetate silk[5], the development is effected between 75-100°, and diazotization in a separate bath at low temperature. Supple woolly effects may be produced on acetylcellulose threads by heating the threads in the form of yarn in dilute formic or acetic acid at the boiling point[6]. The action is restrained and

1. R. Clavel, F. P. 542940; abst. Chem. Ztg. 1922, **46**, 868; Chem. Zentr. 1923, II, 576.

2. *Ibid.* E. P. 191553; abst. C. A. 1923, **17**, 3103; J. S. C. I. 1923, **42**, 125-A, 221-A. Can. P. 236696.

3. *Ibid.* E. P. 194840; abst. C. A. 1923, **17**, 3611; J. S. C. I. 1923, **42**, 336-A, 448-A; Chem. Tech. Uebers, 1923, **47**, 159.

4. *Ibid.* E. P. 199754; abst. C. A. 1924, **18**, 334; J. S. C. I. 1923, **42**, 826-A. Can. P. 236949. Cf. E. P. 24284, 1907.

5. *Ibid.* E. P. 204179; abst. C. A. 1924, **18**, 909; J. S. C. I. 1923, **42**, 1127-A. See E. P. 187964; abst. C. A. 1923, **17**, 1154.

6. *Ibid.* E. P. 206818; abst. J. S. C. I. 1924, **43**, 743-B. Can. P. 236697. Cites E. P. 165164.

the strength and elasticity unimpaired in the presence of protective colloids as gelatin soap or Turkey-red oil.

In the treatment of union and mixed fabrics in which acetylcellulose is present[1], R. Clavel has given methods involving the use of monoazo dyestuffs (Alizarin yellow R, Fat soluble orange, Silk ponceau G, Brilliant orange G), diazo dyestuff (Pyramidol brown BG), triphenylmethane dyestuffs (Fuchsine, Chrome violet), Rhodamine G as a phthalein dyestuff, Aniline black as an azine dye; Gallocyanine, Methylene blue B, and Brilliant alizarine blue G as oxazine and thiazine dyestuffs; indulin, oxyketone dyes (alizarin, Alizarin orange, Alizarin Bordeaux paste), anthracene vat dyes (Indanthrene X, Indanthrene Bordeaux B, Algol rose R, Algol scarlet G, Algol yellow WG, Algol violet B and of natural organic dyes (Cochineal, Logwood, Haemetin, Catechu).

It has been found that acetate silk possesses a pronounced affinity for aromatic nitro-, amino-, and hydroxy-compounds[2]. In the dyes with the amino group the two principal factors are *(1)* basicity of the dye, and *(2)* size of the molecule. Groups which tend to lessen the basicity of the dye make it less suitable. Owing to the small size of the pores in cellulose acetate fibers, dyestuffs with large molecules do not penetrate well. As an airplane covering material[3], especially one that is self-sustaining and does not require tension on the fibers to keep the material taut, N. Clay has devised an apparatus comprising a series of rolls whereby the cellulose acetate is frictioned on the cloth by a plurality of coatings. E. Clayton[4] has given a summation to 1921 of our knowledge of acetylcellulose silk.

1. U. S. P. 1517709. Ital. P. 210113, 210114. See U. S. P. 1448432.
2. R. Clavel and T. Stanisz, Rev. gen. mat. color. 1923, **28**, 145, 167; 1924, **29**, 94, 158, 222; abst. C. A. 1925, **19**, 401.
3. U. S. P. 1519239.
4. J. Soc. Dyers Col. 1921, **37**, 301; abst. C. A. 1922, **16**, 2999.

In dyeing fabrics containing cellulose acetate fibers[1], hydrolysis of the ester of alkalis is avoided by adding waste sulfite liquor or its active components. In dyeing cotton goods with acetylcellulose fibers, the latter remain white. Using waste sulfite liquor, suitable dye solutions may be formed of Pyrogen green 3G, Pyrogen deep black A and Pyrogen cutch 2GR in sodium sulfide baths. Comparative tests made by L. Clement[2] upon selected celluloid and non-inflammable cellulose acetate cinematograph films showed the celluloid was less elastic, had slightly higher tensile strength and was less fragile. The acetate shrank less than celluloid on storing, but when subjected to immersion in developing solutions and in the subsequent operations of washing and drying it behaved in the same manner as celluloid.

In rendering gas bags impermeable to hydrogen, a mixture of gelatin and glycerol (glycerinated gelatin) with cellulose acetate dissolved in acetone has been proposed[3]. A cellulose acetate lacquer especially useful as a bronzing liquid when powdered metals have been incorporated therein, comprises cellulose acetate plastified by mesityl oxide, phorone and diacetone alcohol[4]. Substituted phenylureas (dimethylphenyltolylurea), 60% of the weight of the cellulose acetate used, in volatile solvents[5] has also been recommended for the same purpose.

In the dynamometric examination of fabrics coated with acetylcellulose solutions[6], it has been found that the strength of the fabric is increased by the coating, a solution of the acetate in tetrachlorethane giving a slightly stronger

1. Clayton Aniline Co., Ltd., E. P. 214330; abst. C. A. 1924, **18**, 2609; J. S. C. I. 1924, **43**, 508-B.
2. Bull. Soc. Franc. Phot. 1921, **8**, 343; abst. C. A. 1922, **16**, 1914; J. S. C. I. 1922, **41**, 233-A; Phot. Abst. 1922, **2**, 52.
3. L. Clement and C. Riviere, F. P. 504323; abst. Mon. Sci. 1922, (5), **12**, 34.
4. *Ibid.* F. P. 505073; abst. Rev. Prod. Chim. 1921, **24**, 18; Caout. et Gutta. 1921, **18**, 10893.
5. *Ibid.* F. P. 505087; abst. Chim. et Ind. 1921, **6**, 89.
6. *Ibid.* Chim. et Ind. 1920, **3**, 440; J. S. C. I. 1920, **39**, 481-A.

coating than one in acetone or benzyl alcohol, neither tetrachlorethane or acetic acid having any injurious effect on linen. A general review of the preparation and application of various types of cellulose acetate varnishes was published in 1921, with a brief outline of a scheme of analysis[1], and in 1924 a review of our knowledge of the colloidal nature of cellulose and acetated cellulose[2], and of non-inflammable cinematographic films[3].

For the recovery of volatile solvents used in the coating of airplane wings[4], the air mixed with solvent is led into a column or tower packed with filling material through which an absorption liquid is flowing. In the manufacture of cigarette tubes[5], a frosted paper like film of cellulose acetate is used, obtained by permitting a solution of acetylcellulose in volatile solvents to evaporate on a roughened surface as on a frosted glass plate, the surface before application having been rubbed with chalk. In preparing rubber-like masses from cellulose acetate[6], high-boiling tar oils as creosote oil are used.

In 1921 the method of manufacturing cellulose acetate in Australia was to act upon cotton waste with 33-40% acetic anhydride in acetic acid, sulfuric acid being used as catalyst (20% on the weight of the cotton[7]. The fibers

1. L. Clement and C. Riviere, Chim. et Ind. 1921, **6**, 283; abst. C. A. 1921, **15**, 4054; Chem. Zentr. 1922, II, 38.
2. *Ibid.* Chim. et Ind. Special No. 1924, 578; abst. C. A. 1924, **18**, 3715; Chem. Zentr. 1924, II, 1785.
3. *Ibid.* Chim. et Ind. 1922, **8**, 322; abst. C. A. 1922, **16**, 3820; Chem. Zentr. 1923, II, 376.
4. *Ibid.* F. P. 22388, Addn. to F. P. 493459; abst. Kunst. 1921, **11**, 173; Chem. Zentr. 1922, II, 210.
5. E. Closmann, E. P. 196654; abst. C. A. 1923, **17**, 3790. Can. P. 222780. For cellulose acetate silk production see L. Clement, C. Riviere and Courtaulds, Ltd., E. P. 224404; abst. C. A. 1925, **19**, 1352.
6. F. Clouth, Rheinische Gummiwaarenfabrik m. b. H., 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. D. R. P. 324944; abst. Chem. Zentr. 1920, IV, 648.
7. J. Cochrane, Chem. Eng. Mining Rev. (Australia), 1920, **12**, 455; abst. C. A. 1921, **15**, 171.

lose their strength in half to one hour, and the product can then be mixed by power, the reaction requiring 10-11 hours. The acetate is then ripened at constant temperature for 13-15 hrs. until the syrup is homogeneous, and then hydrated by adding 50% acetic acid (80-120 parts per 100 parts cellulose being used), this requiring 12-16 hrs. The acetate obtained is plastic in chloroform and soluble in acetone, containing about 53% combined acetic acid.

In 1921 J. Cochrane[1] published a critical study leading to the development of a commercial process for the large-scale production of cellulose acetate. A bibliography is included. Properties and composition of dekalin (mixture of tetra- and deca-hydronaphthalene) were published[2] in 1922, and diacetylacetone[3] the same year. A composition suitable for phonograph record manufacture[4] consists of cellulose acetate, gelatinizing agents (diethyldiphenylurea, form-*o*-toluidide, phenylurethane, phenyloxamic ester, cyclohexanone), and acaroid resin. Phenyl oxamate 1, acaroid resin 1, and cellulose acetate 2 are given as an especially useful composition. In forming a disc record[5], the powdered plastic material is fed onto a plate heated to the temperature at which the mass softens and becomes coherent, and pressure is applied. Acetaldehyde may be prepared[6] by hydrating acetylene in the presence of a catalyzer, which comprises establishing a continuous circulation of the reaction liquid by partial vacuum through a circuit including the reaction chamber, and withdrawing the acetaldehyde. Acetic acid is made therefrom[7]. Ethyl

1. Commonwealth Australia Munitions Supply Board, Tech. Repts. 1921-2, 20; abst. C. A. 1924, **18**, 584.
2. J. Coleman and P. Bilham, Chem. Age, 1922, **7**, 554; abst. J. S. C. I. 1922, **41**, 904-A.
3. J. Collie and A. Reilly, J. C. S. 1922, **121**, 1984; abst. C. A. 1923, **17**, 68. Cf. J. C. S. 1921, **119**, 1550; abst. C. A. 1922, **16**, 96.
4. Columbia Graphophone Co., Ltd., W. Forse, F. Jones and G. Walters, E. P. 192108; abst. C. A. 1923, **17**, 3253.
5. Columbia Graphophone Co., Ltd., Can. P. 244792.
6. Compagnie des Produits Chimiques D'Alais et de la Camargue, Can. P. 214472. F. P. 514061; abst. Chim. et Ind. 1922, **7**, 105.
7. *Ibid.* Can. P. 214163. Norw. P. 32780; abst. Chem. Tech. Uebers, 1922, **46**, 3. Norw. P. 33459.

acetate may be prepared from acetaldehyde[1] by use of aluminum ethylate (prepared by mixing anhydrous aluminum chloride and aluminum filings gradually added to ethyl alcohol). When acetic acid vapor is passed over catalytic material (calcium, aluminum or zinc phosphates) heated to 600° acetic anhydride is formed[2], and may be separated from acetic acid and water by fractional distillation below 40 mm. pressure[3].

The R. Cox process of cellulose acetate manufacture comprises an apparatus in which a chloroform-soluble acetate is first formed[4], then a hydrolyzing mixture added which includes a relatively small amount of water. The apparatus includes a mechanical element whereby air is passed in circulation in contact with the esterifying mixture to take up and recover acetic vapors by means of a condenser unit. At a temperature not exceeding 35°, cellulose reacts with an ethereal solution of magnesium ethyl bromide[5], giving ethane and a greenish-gray, fibrous magnesium cellulosyl bromide, $C_6H_9O_5.MgBr(C_2H_5)_2O$, which reacts energetically with water with formation of cellulose and magnesium hydroxybromide, MgBrOH. As a precipitant for acetate filaments[6], it has been proposed to project the acetate solution into a bath of animal or vegetable oil (castor or linseed). Filaments so precipitated are said to be very clear, strong and pliable. "Splinterless" reinforced

1. Consortium für Elektrochemische Ind., F. P. 510949; abst. Mon. Sci. 1921, (5), **11**, 76. D. R. P. 386688; abst. J. S. C. I. 1924, **43**, 450-B. Ital. P. 212881.

2. *Ibid.* D. R. P. 410363; abst. J. S. C. I. 1925, **44**, 1013-B; Chem. Zentr. 1925, II, 2186. Can. P. 243849. U. S. P. 1570514; abst. C. A. 1926, **20**, 768; J. S. C. I. 1926, **45**, 386-B. E. P. 194719; abst. J. S. C. I. 1924, **43**, 34-B.

3. *Ibid.* D. R. P. 411106; abst. J. S. C. I. 1925, **44**, 569-B; Chem. Zentr. 1925, I, 2409.

4. R. Cook, U. S. P. 1494830; abst. C. A. 1924, **18**, 2249; J. S. C. I. 1924, **43**, 668-B.

5. D. Costa, Gazz. Chim. Ital. 1922, **52**, II, 362; abst. J. S. C. I. 1923, **42**, 219-A; J. C. S. 1923, **124**, i, 186.

6. Courtaulds, Ltd., L. Clement and C. Riviere, E. P. 224404; abst. J. S. C. I. 1925, **44**, 38-B. Holl. P. 15344. F. P. Appl. 3954, 1922; abst. Chim. et Ind. 1922, **7**, 777. F. P. Appl. 4082, 1922; abst. Chim. et Ind. 1922, **7**, 777.

glass is prepared by sealing a sheet of cellulose acetate between sheets of glass, the glass having had a preliminary treatment with a solution formed of "gum cornifan 28, nelkin oil 0.5" (to prevent ropiness), and water 112, the acetate having been softened by tetrachlorethane and acetic acid before adhesion. In case you should not know, "kornifan," properly spelled kordofan, is a species of gum acacia, and "nelkin" is an obsolete name for clove oil[1]. As a valuable adjunct to the cellulose esters for lacquer and varnish purposes[2], benzyl resinate or abietate has been proposed. Alkyl ethers of ethyleneglycol are prepared by allowing an alcoholate to act on ethylene oxide or ethylenechlorhydrin[3]. Physical constants of glycol monomethyl (or ethyl, *iso*propyl, propyl, *iso*butyl, butyl, amyl) ether have been determined. Their b. pts. at 743 mm. are 124.5°, 134.8°, 144°, 150°, 158.8°, 170.6° and 181° respectively.

In 1920, C. Cross contributed a note to the Society of Dyers and Colourists[4] to the effect that primary cellulose acetates of the H. Dreyfus processes do not support the generalizations of H. Ost in that they are not soluble in chloroform, and can be redissolved an indefinite number of times in acetone. G. Curme[5] in 1921 reviewed the researches which have formed the foundation for an olefine gas industry, especially as to the sources and uses of ethylene and propylene in combination.

H. Davies[6] has described the dyeing of Lustron and Celanese acetate silk, the former showing a greater affinity for basic dyes. The W. Davey fluorescent screen sensitive

1. J. Cox, E. P. 221552; abst. C. A. 1925, **19**, 879; J. S. C. I. 1924, **43**, 982-B.
2. F. Crane, U. S. P. 1513802; abst. Chem. Zentr. 1925, I, 1137.
3. L. Cretcher and W. Pittenger, J. A. C. S. 1924, **46**, 1503; abst. Chem. Zentr. 1924, II, 820.
4. C. Cross, J. Soc. Dyers and Col. 1920, **36**, 19; abst. Ann. Rep. S. C. I. 1920, **5**, 137.
5. Chem. Met. Eng. 1921, **25**, 907, 957, 999, 1049.
6. H. Davies, Proc. Am. Assoc. Textile Chem. Colorists, 1924, 179; Am. Dyestuff Rept. **13**, 753; abst. C. A. 1925, **19**, 401.

to X-ray and ultraviolet radiations[1], is prepared with a cellulose acetate lacquer combining primarily low-boiling solvents, it having been found that a film gives superior results as an intensifying screen and with superior mechanical strength when the solvent is either entirely eliminated or reduced to the point that the fluorescent material and binder is too stiff to pour at room temperature. W. Davis and J. Eyre[2] have investigated the discontinuity of the hydration process in cellulosic materials, primarily from a mathematical viewpoint. After sizing[3], artificial silk is dried by passage over or in contact with adjustable steam-chests having between them adjustable glass rods for varying the position of the silk relative to the chests. M. Deschiens detailed the industrial uses of acetated cellulose[4] with especial application to airplane dope manufacture[5], and the production of acetic acid from calcium carbide for esterification purposes[6].

When alkalicellulose is treated with chloracetic acid[7] in the presence of alkali hydroxides, a clear viscous solution is formed which yields transparent films upon evaporation resembling glue or gelatin and which inflame with difficulty. The free cellulose-acetic acid is a white, fibrous substance, insoluble in water but soluble in alkaline solutions, and forms insoluble salts with lead, copper and aluminum oxides. The alkali salts of cellulose acetic acid and cellulose propionic acid may be used as gelatin substitutes.

1. W. Davey, U. S. P. 1480896.
2. W. Davis and J. Eyre, Proc. Roy. Soc., 1923, 512.
3. J. Dean, E. P. 221944; abst. J. S. C. I. 1924, **43**, 905-B.
4. M. Deschiens, Chim. et Ind. 1920, **3**, 591; abst. C. A. 1920, **14**, 2705; Chem. Met. Eng. 1920, **23**, 533; Chem. Tech. Uebers, 1921, **45**, 559; Chem. Zentr. 1920, IV, 753. Compare Rev. Prod. Chim. 1920, **23**, 177; abst. Chem. Zentr. 1920, IV, 320; Kunst. 1920, **10**, 180. Chem. Age (N. Y.), 1921, **29**, 370; abst. Chim. et Ind. 1922, **8**, 425; Rev. Prod. Chim. 1921, **24**, 716.
5. *Ibid.* Chim. et Ind. 1921, **5**, 239; abst. C. A. 1921, **15**, 2627. Cuir 1923, **12**, 58; abst. C. A. 1923, **17**, 1731.
6. *Ibid.* Rev. prod. chim. 1921, **24**, 3; abst. C. A. 1921, **15**, 1409. See also Chem. Trade J. 1920, **67**, 603; abst. C. A. 1921, **15**, 764.
7. Deutsche Celluloid Fabr., D. R. P. 332203; abst. J. S. C. I. 1921, **40**, 344-A; Phot. Abst. 1921, **3**, 84.

Acetylene freed from catalyst poisons is converted to acetaldehyde by the aid of steam[1], and of oxides or mixtures of oxides as catalysts at higher temperatures. By this treatment either the carbon precipitated on the catalyst by the reaction is burned up, or else the metallic oxide partly reduced to a lower stage of oxidation is rejuvenated into the higher oxide form. A stencil sheet[2], of the kind in which characters are formed thereon my impact with type, is prepared from a sheet of Yoshino paper impregnated with a cellulose acetate solution to which zinc oxide has been added. The sheet may be hand-coated by drawing it over the surface of the cellulose ester solution, and removing the excess by drawing the coated side over a wire or straight edge. W. Dickie[3] has designed an apparatus for coating bare wire with a viscous, cellulose acetate insulating dope in an even and uniform manner.

A new elastic material—cellon-caoutchouc—was described in 1921, combining the valuable properties of both[4], hydrogenation products of naphthalene and phenol being admixed with acetylcellulose by means of the mutual solvent cyclohexanol (hexalin). It may be used for all purposes where it is desirable to eliminate the brittle character of celluloid without introducing the resiliency of caoutchouc. In a series of three papers published in 1921 by R. Ditmar[5], the uses of tetralin and hexalin in the production of cellulose acetate varnishes is described. As a protective coloring airplane lacquer or wing dope[6], has been patented a

1. Deutsche Gold & Silber-Scheideanstalt vorm. Rössler, F. P. 518087; abst. Rev. Prod. Chim. 1921, **24**, 641; Chem. Zentr. 1921, IV, 355. D. R. P. 334357; abst. Chem. Zentr. 1921, II, 1019. Dan. P. 27963. See also F. P. 518574; abst. Chem. Zentr. 1921, IV, 513.
2. A. B. Dick Co., E. P. 195977; abst. C. A. 1923, **17**, 3758.
3. U. S. P. 1485254.
4. R. Ditmar, Chem. Zeit., 1921, **45**, 819; abst. J. S. C. I. 1921, **40**, 709-A; Chem. Tech. Uebers, 1923, **47**, 6.
5. Gummi-Ztg. 1921, **36**, 39; abst. C. A. 1920, **14**, 357, 1227, 1901, 3129; 1922, **16**, 361; Zts. ang. Chem. 1921, **34**, 474; Chim. et Ind. 1922, **8**, 640; Kunst. 1921, **11**, 169; Chem. Ztg. 1921, **45**, 819.
6. W. Doerflinger, U. S. P. 1345354.

battleship gray solution of acetylcellulose, stannic oxide, and a small amount of spirit-soluble nigrosin.

A plastic composition results when cellulose acetate is dissolved in a mixture of propyl alcohol 45, ethylene chlorbromide 55, benzyl acetate 5, with volatile solvents[1]; and a convenient container for a tear gas (bromacetone)[2] is cellulose acetate, which is insoluble in bromacetone. In the manufacture of staple fiber from a composite strand or yarn of cellulose acetate[3], it is afterwards collected in skein form, to obviate the invariably open nature of the staple fiber, the strands before cutting up into short lengths being treated with a soluble aluminum salt to diminish their inflammability.

C. Dreyfus has found[4] that the addition of acaroid resin to solutions of cellulose acetate confers valuable waterproofing and tautening effects on the varnish, suitable proportions being cellulose acetate 1, acaroid resin 1-2, acetone 2.5-15. A fire-proof lacquer results[5] upon dissolving cellulose acetate 7-12, in a mixture of methyl acetate 30-70, denatured alcohol 10-30, benzine 10-30, triacetin 2-6 and triphenyl phosphate 1-3. In 1920, benzenemonomethylsulfonamide was patented as a plastic-inducing agent for acetylated cellulose[6]. In order to dispense with or reduce the usual period of seasoning of cellulose ester plastics[7], the mass

1. H. Dow, U. S. P. 1339552.
2. *Ibid.* U. S. P. 1411422.
3. W. Dreaper, E. P. 175746.
4. E. P. 222168; abst. J. S. C. I. 1924, **43**, 977-B.
5. G. Dreyfus, F. P. 521476; abst. Kunst. 1921, **11**, 190; Chem. Zentr. 1921, IV, 1189; Mon. Sci. 1923, (5), **13**, 5; Caout. et Gutta. 1922, **19**, 11194.
6. H. Dreyfus, 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. U. S. P. 1501206; abst. C. A. 1924, **18**, 2809; J. S. C. I. 1924, **43**, 743-B. F. P. 521370; abst. Caout. et Guta. 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.
7. *Ibid.* E. P. 179208; abst. C. A. 1922, **16**, 3370; J. S. C. I. 1922, **41**, 542-A; Chem. Zentr. 1922, IV, 646; Caout. et Gutta. 1923, **20**, 11687; Chem. Tech. Uebers, 1922, **46**, 311. F. P. 542740; abst. Caout. et Gutta. 1923, **20**, 11686; Chem. Zentr. 1923, II, 1066; Chem. Ztg. 1922, **46**, 892. U. S. P. 1528291; abst. C. A. 1925, **19**, 1497; J. S. C. I. 1925, **44**, 312-B.

of cellulose acetate and plastifier is heated nearly to the melting point of the former during the malaxating operations, and then directly cast or pressed into the finished article.

Triphenyl phosphate ceases to be a cellulose acetate solvent at temperatures below 150°, but by the addition of xylenemonomethyl (or monoethyl, or dimethyl) sulfonamide, or monomethyl (or dimethyl) amide of 1.3-dimethylbenzenesulfonate, a compound solvent results of satisfactory dissolving power at low temperatures[1]. In forming acetate plastics[2], xylenemonomethyl (or ethyl) sulfonamide as plasticizer is mixed with such a large amount of methyl or ethyl alcohol or benzene that the plasticizing action is restrained during the mixing operation, but after the mixing is completed, the volatile solvent is evaporated to permit increased action of the solvent of high boiling point on the cellulose acetate so that the latter is progressively dissolved. New results are said to be obtained in acetylcellulose plastics by employing mixtures of *o*- and *p*-dimethyl (or methylethyl, or diethyl) sulfonamide[3], or *o*-toluene-dimethyl (or diethyl) sulfonamide alone. In spinning acetate silk by the dry method of projecting solutions into heated air[4], the rate of solidification is controlled by adding limited quantities of high-boiling solvents to the acetate solution, thereby enabling it to be drawn out into extremely fine filaments (low denier) before congealing. Example, cellulose acetate is dissolved in acetone 400 with 25-50 of diacetone alcohol, acetone alcohol (acetylcarbinol), acetylacetone or cyclopentanone.

1. H. Dreyfus, U. S. P. 1353384.
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. 1508928; abst. C. A. 1924, **18**, 3719; J. S. C. I. 1924, **43**, 864-B. Compare E. P. 114304; U. S. P. 1383385.
4. *Ibid.* E. P. 182166; abst. J. S. C. I. 1922, **41**, 570-A, 627-A; Chem. Zentr. 1922, IV, 907; Chem. Ztg. Rep. 1922, **46**, 352; Caout. et Gutta. 1923, **20**, 11688. U. S. P. 1566384; abst. C. A. 1926, **20**, 511; J. S. C. I. 1926, **45**, 122-B. Can. P. 281189.

Cellulose acetate with ketohexamethylenes (cyclohexanone, methylcyclohexanone) forms an excellent basis for films and celluloid substitutes[1], by virtue of the avidity with which the cellulose ester is dissolved. Cyclobutanone, dimethylcyclobutanone and diethylcyclobutanone act similarly[2]. In order to produce acetylated cellulose of high viscosity[3], cellulose is esterized in the presence of a large quantity (six or more times the weight of cellulose) of glacial acetic acid, acetic anhydride and the usual catalysts being employed. Example, cotton 100, is introduced into a mixture cooled below 0° of glacial acetic acid 800, sulfuric acid 15-20 and acetic anhydride 200-250, the temperature being allowed to rise to 25-30° during 2-6 hrs., until solution of the cotton is complete. In using such an acetate for filament formation[4], especially by the dry or evaporative process, there is said to be marked augmentation in tensile strength of the filaments in the wet condition.

The H. Dreyfus method of acetic anhydride manufacture involves heating sodium acetate with sodium pyrosulfate[5], sodium sulfate being a by-product. Or, by reacting with sulfur trioxide upon an inorganic salt (sodium or calcium chloride or sulfate) whereby addition products are formed which transform sodium or calcium acetate into acetic anhydride[6]. He has illustrated an apparatus for the progressive evaporation of solvent in acetate silk forma-

1. H. Dreyfus, U. S. P. 1395401; abst. J. S. C. I. 1921, **40**, 886-A; Phot. Abst. 1922, **2**, 14; Mon. Sci. 1922, (5), **12**, 69. Belg. P. 285860, 285868.

2. *Ibid.* E. P. 184671; abst. J. S. C. I. 1922, **41**, 693-A; Phot. Abst. 1922, **2**, 137. U. S. P. 1440006; abst. C. A. 1923, **17**, 1141; J. S. C. I. 1923, **42**, 600-A; Chem. Ztg. 1923, **47**, 269. Ital. P. 233801.

3. *Ibid.* E. P. 207562; abst. C. A. 1924, **18**, 1571; J. S. C. I. 1924, **43**, 129-B; Chem. Zentr. 1924, I, 1464. Australian P. 12325. India P. 7998, 1922; 9234, 1923; Refers to India P. 7074, 6956, 6957, 6958, 6959. Ital. P. 190207. Swiss P. 105945. F. P. 565654. Ital. P. 220640. E. P. 2026, 1907; 14271, 24382, 1910; 20977, 1911; 20852, 1912; 6463, 14101, 1915; 100009; 101555. U. S. P. 1217722. Can. P. 245307. Belg. P. 310377.

4. *Ibid.* E. P. 217287. Cf. E. P. 207562, 210108.

5. *Ibid.* U. S. P. 1430304. F. P. 478951.

6. *Ibid.* U. S. P. 1368789; abst. Mon. Sci. 1922, (5), **12**, 3. See also F. P. 448342. F. P. Addn. 17674 to 448342. U. S. P. 1283115.

tion[1]. In the fabrication of acetylcellulose plastics and film products[2], xylenealkylsulfonamides, xylylmonomethyl (or dimethyl, or monoethyl) sulfonamides, with volatile solvents and urea as antacid has been described. In the acetation of cellulose[3], sodium acid sulfate (sodium bisulfate) may take the place of sulfuric acid—for no very obvious reason. Other inorganic bases have been recommended for this purpose[4].

P. Drinker[5], who had charge of the doping of airplanes for the American Forces in France during the past war, contributed in 1921 an illuminating article on the commercial development of cellulose acetate and its employment in aeronautics, a bibliography being appended. An artificial textile fabric is made from filaments of cellulose acetate in which bubbles of air or inert gas have been entangled[6], fabrics so prepared being very light, fluffy, opaque and soft to the touch. The introduction of bubbles of air is effected by forming an emulsion of the acetate solution and directly incorporating air therein by means of injectors. A slow-burning celluloid has been evolved[7], comprising adding 20-35% of cellulose propionate to ordinary celluloid, the propionate having an advantage over cellulose acetate in being soluble in ethyl acetate. Solutions of cellulose in thiocyanate have been described[8], susceptible of use in the manufacture of vulcanized rubber.

1. H. Dreyfus, F. P. 531816. Belg. P. 310428. F. P. Addn. 36751 to 531816; abst. C. A. 1931, **25**, 1084.
2. *Ibid.* F. P. 498726; abst. Chem. Ztg. 1920, **44**, 133.
3. *Ibid.* Swiss P. 94022; abst. Chem. Zentr. 1922, IV, 1062. Belg. P. 286146. Swiss P. 93814; abst. Chem. Zentr. 1922, IV, 1113.
4. *Ibid.* Belg. P. 302653. See Belg. P. 312222.
5. P. Drinker, J. I. E. C. 1921, **13**, 831; abst. C. A. 1921, **15**, 3910; Chim. et Ind. 1922, **7**, 121; Kunst. 1921, **11**, 189; Rev. prod. Chim. 1921, **24**, 716. Kunst. 1922, **12**, 18; Chem. Tech. Uebers, 1922, **46**, 266. Paper, 1921, **28**, 29.
6. L. Drut, E. P. 143253; abst. C. A. 1920, **14**, 2862. D. R. P. 346830.
7. A. Dubosc and A. Luttringer, Bull. soc. ind. Rouen, 1920, **48**, 91; abst. C. A. 1921, **15**, 171.
8. A. Dubosc, Rev. gen. mat. color. **28**, 91; abst. Chem. Zentr. 1924, II, 130.

J. Duclaux[1] believes acetylcellulose when in colloidal solution does not yield solutions of the same viscosity each time because the esters consist of mixtures of varying degrees of esterization, and in order to remedy this lack of uniformity makes use of methods of purification as evolved by colloid chemistry, as fractional precipitation or diffusion, or filtration or dialysis through an ultra-filter. Such a process, it would appear, would be unduly expensive for commercial exploitation. In order to insure uniformity of evaporation and the production of highly transparent and non-blushing acetylcellulose films[2], use is made of solvents of the ester which are water-soluble and but slightly volatile, formamide, acetamide, chloral and chloral hydrate meeting these specifications, used in conjunction with lower boiling solvents.

In the formation of membranes for ultra-filtration and dialysis[3], cellulose acetate is precipitated in a porous or jelly form by adding water to an acetic acid solution of the ester. The membrane is then treated with alcohol or acetone to remove the water, and can then be used for filtration purposes. Greater strength is attained by forming this membrane on cloth[4]. A process for acetone purification has been worked out[5] by treatment with carbon bisulfide which unites with the acetone, giving a mixture which boils at 39°. With the exception of methylal and methyl alcohol, none of the other impurities in acetone combine with bisulfide.

1. J. Duclaux, F. P. 511393; abst. Chim. et Ind. 1921, **6**, 650; Chem. Ztg. 1921, **45**, 377; Phot. Abst. 1921, **4**, 130.

2. *Ibid.* E. P. 184197; abst. J. S. C. I. 1922, **41**, 693-A, 748-A; Chem. Met. Eng. 1922, **27**, 1186. F. P. 530440; abst. Chem. Ztg. 1921, **45**, 1077.

3. *Ibid.* E. P. 203713; abst. J. S. C. I. 1924, **43**, 972-B; Caout. et Gutta. 1924, **21**, 12204.

4. *Ibid.* E. P. 203714; abst. J. S. C. I. 1924, **43**, 658-B; Caout. et Gutta. 1924, **21**, 12204.

5. J. Duclaux and A. Lanzenberg, Bull. soc. chim. 1920, **27**, 779.

Heretofore caps for the closures of bottles have been made of cellulose acetate in film form[1], but for most satisfactory application it is advisable to keep them in a moist condition until used. A. Dulitz remedies this disadvantage so that the sealing caps may be transported in a dry condition, by the addition thereto of certain hygroscopic, non-incompatible bodies as acetin. O. Dunham[2] has described the manufacture of a transparent, thin, light-weight box non-susceptible to atmospheric changes by casting a cellulose acetate form by means of an apparatus patented himself. Flexible cellulose acetate products are obtained by incorporating therewith a mixture of *o*- and *p*-hydroxybenzyl alcohol[3].

A lacquer for shoe heels comprises cellulose acetate 12, acetone 1152, benzene 14, benzyl alcohol 3, industrial spirit 7, and either dichlorhydrin, dichlorethylene or triacetin 10 parts. To form a filler composition for application to wooden heels prior to the lacquer, lithopone 48 is added to the above composition[4]. The V. Edwards reinforced glass[5] is made in the usual manner by sandwiching a sheet of acetate plastic between two sheets of glass under heat and pressure, but to obviate the discoloration of the finished glass due primarily to the action of actinic or ultra-violet rays, a special glass is used of such a nature that it will not transmit the ultra-violet rays. Such a glass may be made by adding small amounts of arsenic trioxide, cerium nitrate, nickel sulfate or ferrous sulfate to a soda glass flux during manufacture of the sheet.

1. A. Dulitz, E. P. 176367; abst. C. A. 1922, **16**, 2395. U. S. P. 1520054; abst. C. A. 1925, **19**, 729. U. S. Reissue 16042; abst. C. A. 1925, **19**, 1776. D. R. P. 364397. U. S. P. 1520940; abst. C. A. 1925, **19**, 729.
2. O. Dunham, U. S. P. 1488634.
3. J. Dupont, Caout. et Gutta. 1920, **17**, 10662; abst. Kunst. 1921, **11**, 78.
4. F. Edbrook, E. P. 202154; abst. C. A. 1924, **18**, 335. U. S. P. 1607516; abst. C. A. 1927, **21**, 333; J. S. C. I. 1927, **46**, 85-B. Can. P. 238217.
5. U. S. P. 1467030.

In the manufacture of staining solutions and lacquers from soft lignite[1], the latter is extracted with acetone acidified with HCl, and this extract added to a cellulose acetate lacquer. For preparing layers of acetylcellulose for coating materials[2], the ester is dissolved in solvents including those which dissolve only when heated so that very viscous solutions are obtained. Open fabrics can be coated with smooth layers that do not sink into the fabric, suitable surfaces being impressed thereon by rolls, if desired. In preparing hard celluloids, acetylcellulose with either dichlorhydrin, acetylmethylaniline (manol) or naphthyl acetate[3] are admixed without volatile solvent until a homogeneous mass results, then the minimum of solvent added to cause plasticization, and the volatile solvent removed by kneading. A. Eichengruen[4] in 1921 indicated the commercial uses of Cellon and Cellon lacquers, and described various methods for producing lacquers and varnishes therefrom[5].

B. Eldred[6], on account of their ready solubility in water, prefers ethylene, propylene and butylene chlorhydrins as solvents, his preferred formula for a lacquer being acetylcellulose 10, propylene chlorhydrin 100. In the production of formic acid[7], an alkali formate (sodium or

1. C. Ehrenberg, H. Wiederhold, C. Krug, M. Holsboer, K. Fischer and Studienges, D. R. P. 422739; abst. J. S. C. I. 1926, **45**, 414-B.

2. A. Eichengrün, U. S. P. 1357447; abst. C. A. 1921, **15**, 319; J. S. C. I. 1921, **40**, 211-A; Paper, 1921, **27**, #21, 27; Caout. et Gutta. 1921, **18**, 11074. D. R. P. 287745. The U. S. Appl. was applied for Apr. 11, 1910, and renewed Apr. 2, 1920 (Serials 554809, 370898).

3. *Ibid.* U. S. P. 1420028; abst. C. A. 1922, **16**, 2780. D. R. P. 296205.

4. Verh. Vereins Beförd. Gewerbefl. 1921, 78; abst. Chem. Tech. Ueber. 1921, **45**, 99.

5. *Ibid.* Kunst. 1924, **14**, 92; abst. Chem. Zentr. 1924, II, 100.

6. B. Eldred, 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.

7. Elektrochemische Werke, H. Bosshardt and D. Strauss, Holl. P. 6647; abst. Chem. Ztg. 1922, **46**, 343; Chem. Zentr. 1922, II, 873; Swiss P. 92980; abst. Chem. Zentr. 1922, IV, 709. Swiss P. 94602 Addn. to 92980; abst. Chem. Zentr. 1923, II, 335; Chem. Ztg. 1922, **46**, 304.

calcium) is kneaded to a paste with pulverized sodium acid sulfate and a small amount of formic acid, and heated, formic acid distilling *in vacuo*. Improvements in electric insulation were published in 1921 in which insulating tape impregnated with acetylcellulose solution[1] is wrapped around the article to be insulated. To augment the adherence, the impregnated tape is moistened with solvent after application. In the removal of wash waters from precipitated cellulose esters[2], a series of diminishing acidity washings has been described, the latter washings having a proportion of alcohol therein which is saturated with cellulose acetate from a previous operation.

A mixture of the monacetic esters obtained by esterifying gases removed in the cracking of petroleum has been described as valuable cellulose acetate solvents, the mixture comprising ethyl, propyl and butyl acetates, with the propyl ester predominating[3]. A paint and varnish remover has been described[4] in which the votality of the solvents is retarded by introducing cellulose acetate into the composition as a thickening agent. In order to obtain ketone bodies from cracked gasolene[5], the olefine hydrocarbons are treated with sulfuric acid of 1.8 sp. gr., the resulting acid sulfate extract separated, and then electrolytically oxidized to produce a mixed ketonic material adapted for use as an acetylcellulose solvent. Sodium hypochlorite is used to decompose the alkylsulfuric acid[6].

G. Ellis[7], the discoverer of the S. R. A. (sulfonated ricinoleic acid) colors suitable for dyeing cellulose acetate

1. Elektro-Material, E. P. 143280; abst. C. A. 1920, **14**, 2844.
2. Elektro-Osmose A. G., D. R. P. 358679; abst. Chem. Ztg. 1922, **46**, 643; Chem. Zentr. 1922, IV, 1118.
3. C. Ellis, U. S. P. 1365049; abst. C. A. 1921, **15**, 865.
4. *Ibid.* U. S. P. 1499101.
5. C. Ellis and A. Wells, U. S. P. 1365053; abst. C. A. 1921, **15**, 944.
6. *Ibid.* U. S. P. 1450493.
7. G. Ellis, J. Soc. Dyers Col. 1924, **40**, 285; abst. J. S. C. I. 1924, **43**, 864-B. S. R. A. colors are 10% solutions of azo, anthraquinone and other dyestuffs in a fatty solvent as Turkey red oil or oleic acid, and yield clear, stable solutions for dyeing when diluted

by colloidal solubilisation or dispersion gave the details for the application of these colors in an article published in 1924. Cellulose acetate threads or fabrics are dyed, stencilled or printed with the dyes of the aryl- or substituted aryl-benzo- or naphtho-quinone monoimide series generally comprised within the term indophenols[1], blue and violet shades being obtained. When acetylcellulose filaments are pretreated with carbocyclic compounds containing salt forming groups before dyeing[2], yellow shades are produced by *m*-nitrobenzeneazodiphenylamine and naphthenic acid, and a blue dyeing obtained from 1-methylamino-4-*p*-tolylaminoanthraquinone. In coating an article with a cellulose acetate solution, the fire-retarding nature may be considerably increased by adding to the lacquer ammonium magnesium (or manganese) phosphate (or arsenate)[3]. A method for benzene recovery said to have been in use for some time in Cellite factories[4] is the Bayer method as developed by F. Runkl, of absorbing benzene from gas by means of charcoal, the absorption being nearly absolute until one part of charcoal has absorbed 0.4 of light oils.

A method for detecting and estimating free sulfuric acid and sulfacetates in acetylcellulose has been worked out[5], the free sulfuric acid being determined by extracting with water and titration with barium hydroxide solution, and the sulfacetates by heating with water in an autoclave

with water. Most of the S. R. A. colors have no affinity for vegetable fibers. The shades on cellulose acetate are of good fastness. Although a dye liquor containing S. R. A. colors is essentially a colloidal solution, the addition of assistants as sodium chloride and sulfate is advised.

1. G. Ellis and British Celanese, Ltd., E. P. 220505; abst. C. A. 1925, **19**, 736. Belg. P. 311611. U. S. P. 1545819; abst. C. A. 1925, **19**, 2880; J. S. C. I. 1925, **44**, 709-B.

2. *Ibid.* E. P. 224925; abst. C. A. 1925, **19**, 1952; J. S. C. I. 1925, **44**, 39-B. Belg. P. 311612, 311613. U. S. P. 1618414; abst. C. A. 1927, **21**, 1361. Compare E. P. 219349.

3. J. Emhardt, U. S. P. 1393355; abst. C. A. 1922, **16**, 502.

4. A. Engelhardt, Gas und Wasserfach, 1921, **64**, 205; J. usines a gaz 1921, **45**, 170; abst. C. A. 1921, **15**, 2540. Cf. D. R. P. 310092; abst. C. A. 1921, **15**, 1031.

5. M. Entat and E. Vulquin, Ann. Chim. Analyt., 1922, **4**, 131; abst. J. S. C. I. 1922, **41**, 541-A; Ann. Rep. S. C. I. 1922, **7**, 138.

at 125°, and titrating as before. It has been proposed to separate cork from wood, jute and leather by acetylating the former[1]. In 1923 R. Escales and H. Levy[2] published a comprehensive resume of cellulose and starch acetates with 77 bibliographic references, and G. Esselen[3] an account of the manufacture of cellulose acetate solvents, in which he postulates a theory of affinity of the ester for hydroxyl groups, to account for the solvent effect of non-solvents in presence of alcohol[4]. He has calculated the internal pressure of the chlorinated methanes and ethanes which dissolve acetylcellulose[5], and shows that the solvent action obtained is in accord with the relative values of the internal pressures.

A cellulose butyrate soluble at ordinary temperatures in mixtures of benzene and alcohol is prepared by subjecting cellulose (cotton roving or paper pulp) to preliminary impregnation with sulfuric and butyric acids[6], and then acylating with butyric anhydride and butyric acid at 40-50, until a test sample dissolves in chloroform. The pretreatment may be with sulfuric and acetic acids, when a cellulose butyrate containing a proportion of combined acetic acid is produced (acetobutyrate)[7]. To facilitate the penetration of dyestuffs[8], cellulose acetate fibers may previous to dyeing, be swollen by weak solvents.

1. Technologic Paper No. 154, Bureau of Standards, p. 14.
2. R. Escales and H. Levy, 1923, **13**, 25.
3. G. Esselen, J. I. E. C. 1920, **12**, 801; abst. Ann. Rep. S. C. I. 1920, **5**, 324; C. A. 1920, **14**, 2705.
4. *Ibid.* Paper, 1921, **28**, 20.
5. *Ibid.* Caout. et Gutta. 1922, **19**, 11335; Kunst. 1921, **11**, 189.
6. G. Esselen and H. Mork, U. S. P. 1425580; abst. C. A. 1922, **16**, 3393; J. S. C. I. 1922, **41**, 748-A; Mon. Sci. 1923, (5), **13**, 15; Chem. Tech. Uebers, 1923, **47**, 64. E. P. 167143; Chem. Zentr. 1921, IV, 1140.
7. *Ibid.* U. S. P. 1425581; abst. C. A. 1922, **16**, 3394; J. S. C. I. 1922, **41**, 936-A; Mon. Sci. 1923, (5), **13**, 15; Chem. Tech. Uebers, 1923, **47**, 64.
8. Etablissements Mercier et Fessy, F. P. Appl. 8976; abst. Chim. et Ind. 1922, **8**, 441.

The Exceloid Co.[1] first coat articles with shellac as a filler, then with one or more coats of a nitrocellulose solution, followed by immersion in a solution of cellulose acetate in acetone and benzyl alcohol, each coat being allowed to dry and harden before the next is applied. J. Faber in 1917 applied for a patent for producing cellulose acetate tubes of superior strength[2]. In obtaining concentrated acetic acid from more dilute solutions[3], substances are added (acetone oils, b. pt. 100-130°) which with water form systems having a lower boiling point than any component of the system.

A solution for dyeing acetate silk is prepared by dissolving an unsulfonated dye base of the triphenylmethane, anthraquinone or other series[4], in glycerol, epichlorhydrin or ethylenechlorhydrin, and diluting with water to obtain the base in a finely divided state. Applicable are methyl violet 6B base, China green base or Alizarin geranol base dissolved in ethylenechlorhydrin. If an aqueous bath containing pyridine is used[5], China green or other basic dyes give satisfactory shades. The pyridine is removed from the dyed acetate by formic or acetic acids. Or[6], the acetylcellulose may be dyed in the presence of a hydrogenated pyridine (piperidine), or a urea or urea derivative base (guanidine, creatinine). In dyeing acetate fibers[7], a salt

1. Exceloid Co., Ltd., and B. Baker, E. P. 209633; abst. C. A. 1924, **18**, 1758.

2. D. R. P. Anm. F. 42207; abst. Chem. Ztg. 1922, **46**, 556.

3. Fabr. de Soie Artificielle de Tubize and J. Duclaux, E. P. 213914; abst. C. A. 1924, **18**, 2523; J. S. C. I. 1925, **44**, 227-B. Belg. P. 316475. U. S. P. 1660418; abst. J. S. C. I. 1928, **47**, 255-B.

4. Farbenfabriken vorm. F. Bayer & Co., E. P. 214246; abst. C. A. 1924, **18**, 2610; Chem. Age (London), 1924, **10**, 653.

5. *Ibid.* E. P. 215373; abst. C. A. 1924, **18**, 2967; J. S. C. I. 1925, **44**, 281-B. U. S. P. 1517581; abst. J. S. C. I. 1925, **44**, 69-B; C. A. 1925, **19**, 404.

6. *Ibid.* E. P. 215783 Addn. to 215373; abst. C. A. 1924, **18**, 3481; J. S. C. I. 1925, **44**, 801-B. See U. S. P. 1517581.

7. Farbenfabriken vorm. Friedr. Bayer & Co., P. Rabe and W. Schepss, E. P. 216838; abst. C. A. 1925, **19**, 183; J. S. C. I. 1925, **44**, 627-B; Chem. Zentr. 1924, II, 2789. U. S. P. 1645450; abst. C. A. 1928, **22**, 171; J. S. C. I. 1927, **46**, 875-B. Compare E. P. 179384. D. R. P. 355533.

of an oxyacid of nitrogen or chlorine is added to the dyebath in order to obtain deeper shades without using protective colloids, e.g., aniline nitrate with Chrysoidine G or Crystal violet P with sodium nitrate. Chlorates or nitrates of ammonium, sodium, magnesium, calcium, zinc, monomethylamine, dimethylamine, guanidine, pyridine, piperidine may be used, especially in conjunction with Methylene blue, Rhoduline red B, Safranine, Auramine or Bismark brown.

Acetylcellulose artificial filaments of high strength are said to result when cellulose acetate 20, acetone 78, pyridine 4 is spun into a calcium chloride setting bath of 23% strength at 45°. Instead of pyridine, chlorethyl alcohol, chlorbenzene, ethyl acetate, or aniline may be used[1]. Azo dyes are produced by coupling a diazotized dinitroanilinesulfonic or -carboxylic acid with an aromatic amine which does not contain a sulfo group but which may be substituted in the amino group[2], the products dyeing cellulose acetate deep red, bordeaux, blue and bluish violet shades. Acetylcellulose may be dissolved in a mixture of zinc chloride and a thiocyanate[3].

To produce a stripping film[4] over baryta-coated stock, is caused to flow a slightly hardened gelatin solution, a cellulose acetate layer, and then a pyroxylin solution followed by a gelatin solution in acetic acid. To render the acetate layer more easily stripped, acetin or triphenyl phosphate may be added. New cellulose derivatives have been described[5] obtained by the action of ethylene oxide or homo-

1. Farbenfabriken vorm. F. Bayer & Co., E. P. 219333; abst. C. A. 1925, **19**, 580; J. S. C. I. 1925, **44**, 843-B. Cites D. R. P. 274260.
2. *Ibid.* E. P. 225862; abst. C. A. 1925, **19**, 1632.
3. *Ibid.* D. R. P. 281374; abst. Chem. Zentr. 1915, I, 235. See also D. R. P. 322586.
4. *Ibid.* D. R. P. 357011; abst. C. A. 1923, **17**, 2397; J. S. C. I. 1922, **41**, 917-A. D. R. P. 357720; abst. C. A. 1923, **17**, 2397. Farbenfabr. vorm. F. Bayer & Co. and A. von Biehler, D. R. P. 358285, Addn. to 357011; abst. C. A. 1923, **17**, 2397; Phot. Abst. 1923, **3**, 15.
5. Farbenfabr. vorm. F. Bayer & Co. and E. Hubert, D. R. P. 363192; abst. Kunst. 1923, **13**, 35; Chem. Tech. Uebers, 1923, **47**, 6, 77; Chem. Ztg. 1922, **46**, 962. Farbenfabr. vorm. F. Bayer & Co., O. Leuchs and E. Hubert, D. R. P. 368413, Addn. to 363192; abst. Chem. Tech. Uebers, 1923, **47**, 77; Chem. Ztg. 1922, **46**, 1141.

logues on cellulose in the presence of at catalyst. The products formed have increased reacting power, dissolve or swell greatly in water, being probably cellulose glycol ethers. They may be acetylated, and are useful for lacquers and plastic masses.

A film for use as a transparency comprises an opalescent cellulose acetate support and a hardened gelatin backing which prevents curling and is susceptible of being colored if required[1]. Plastic masses having high permanent plasticity, pliability, elasticity and transparency[2] are prepared from acetylated cellulose and the condensation product obtained by the reaction between equimolecular quantities of formaldehyde and ethyl acetoacetate. In the formation of impregnating media[3], cellulose acetate containing less than 50% combined acetic acid is dissolved in mixtures of water and ethylenechlorhydrin, to which other solvents may be added. Clear, non-inflammable films may be obtained from the evaporation of the ester dissolved in ethylenechlorhydrin 30-40%, water 70-60%.

To prevent curling of photographic film comprising a cellulose support[4], the back of the latter is given an alcoholic bath with a dilute acetylcellulose solution containing mono- or di-acetin. A mixture of water 60, monochlorhydrin 40 forms an excellent lacquer[5] provided the cellulose acetate contains less than 50% acetic acid in combintion, but the solvent mixture will hardly attack that containing more. Plastic masses with cellulose esters as cellulose acetate result by incorporation of esters of unsatu-

1. Farbenfabr. vorm. F. Bayer & Co. and A. von Biehler, D. R. P. 374596.
2. Farbenfabr. vorm. F. Bayer & Co., L. Taub and L. Rosenthal, D. R. P. 379343; abst. J. S. C. I. 1923, **42**, 1172-A.
3. Farbenfabr. vorm. F. Bayer & Co., D. R. P. 383699; abst. J. S. C. I. 1923, **42**, 265-B.
4. *Ibid.* D. R. P. 384839.
5. Farbenfabr. vorm. F. Bayer & Co. and L. Rosenthal, D. R. P. 406426, Addn. to 383699; abst. J. S. C. I. 1925, **44**, 217-B. E. P. 228518; abst. Chem. Zentr. 1925, I, 908, 2732.

rated fatty acids of natural drying oils with mono- or polysaccharides, the esters being obtained by the action of fatty acid chlorides upon the polysaccharides in presence of agents which combine with HCl, as pyridine or quinoline. Suitable esters include glucose linoleate, dextrose linoleate, hydrocellulose linoleate and sucrose hexlinoleate[1]. As a cellulose acetate plastifiant, cyclohexanol phthalate[2] has been recommended, it being claimed that colloiding can be carried out at a much lower temperature than usual. Ethylenediphenol has a similar action both on acetylcellulose and on nitrocellulose[3]. As resin-substitutes for combining with cellulose esters[4] there has been recommended benzyl-*m*-phenylenediamine, diaminodiphenylamine, naphthylenediamine, benzidin, resorcinol, pyrogallol, aminophenol and aminonaphthol.

Cellulose esters are treated with the product obtained through the condensation of aldehydes upon ethyleneglycolaryl ethers, or ethylenethiohydrin. In the first[5], the products are a complete substitute for castor oil in imparting a softening effect, and in the second[6] celluloid-like masses result of excellent tenacity. Thioglycol phthalate[7] combines both plasticity and softness when combined with cellulose acetate. Ethylidenediphenol phosphate, diethylidenephenol thiosulfonate[8]; ethyleneglycolphenyl ether (phe-

1. Farbenfabr. vorm. F. Bayer & Co., L. Rosenthal and W. Lenhard, D. R. P. 411900; abst. J. S. C. I. 1925, **44**, 642-B.
2. *Ibid.* D. R. P. 367106; abst. Kunst. 1923, **13**, 34; Chem. Zentr. 1923, II, 591; Chem. Ztg. 1922, **46**, 1094.
3. *Ibid.* D. R. P. 367560; abst. J. S. C. I. 1923, **42**, 397-A; Kunst. 1923, **13**, 34; Chem. Ztg. 1922, **46**, 1094.
4. D. R. P. 366114; abst. Chem. Zentr. 1923, II, 756.
5. *Ibid.* D. R. P. 369445, Addn. to 366115; abst. Chem. Ztg. 1923, **47**, 51; Kunst. 1923, **13**, 69.
6. Farbw. vorm Meister, Lucius & Brüning ,A. Steindorff and F. Biehler, D. R. P. 369446, Addn. to 366115; abst. Kunst. 1923, **13**, 70; Chem. Ztg. 1923, **47**, 51.
7. Farbw. vorm. Meister, Lucius & Brüning and F. Biehler, D. R. P. 369447, Addn. to 366115; abst. Kunst. 1923, **13**, 70; Chem. Ztg. 1923, **47**, 51.
8. *Ibid.* D. R. P. 369535, Addn. to 367560; abst. Chem. Ztg. 1923, **47**, 51; Kunst. 1923, **13**, 70.

nylglycol ether)[1]; ethyleneglycol monocresylbenzoate[2], dibenzoyldiphenylethane[3], 1- or 2-tetrahydronaphthalinsulfamid, 1- or 2-tetrahydronaphthalinsulfo-oxethylamid[4] are other cellulose ester plasticizing bodies whose advantages have been extolled. Dimethoxydiphenylmethane and dibenzyldioxydiphenylethane belong to this category of camphor substitutes for use with acetylcellulose[5].

In the preparation of acetic anhydride[6] by heating acetic acid with acetyl chloride or thionyl chloride, the escaping HCl is passed first through a fractionating column, then through a cooled reflux condenser, the yield being quantitative. Or[7], the gases in the towers may be scrubbed with liquids (nitrobenzene, chlorbenzene, *o*-dichlorbenzene) which readily absorb acetyl chloride but not HCl. Cycloacetals have been described as acetylcellulose solvents[8], prepared from aldehydes and *a*- and *b*-glycols, as ethylene ethylidene ether (b. pt. 80-82°), ethylene butylidene ether, 1.3-butyleneglycol acetal and the product from formaldehyde and 1.3-butyleneglycol (b. pt. 115-120°).

Formic acid esters are formed when carbon monoxide in the presence of water is allowed to act on alcohols at raised temperatures, with or without increased pressure and catalysts[9], and acetaldehyde from acetylene by the use

1. D. R. P. 372545, Addn. to 369445; abst. Kunst. 1923, **13**, 70; Chem. Ztg. 1923, **47**, 218.
2. Farbw. vorm. Meister, Lucius & Brüning A. Steindorff and G. Balle, D. R. P. 372546, Addn. to 366115; abst. Kunst. 1923, **13**, 70; Chem. Ztg. 1923, **47**, 218.
3. D. R. P. 369560.
4. D. R. P. 368362.
5. Farbw. vorm. Meister, Lucius & Brüning and F. Biehler, D. R. P. 369536, Addn. to 367560; abst. Chem. Ztg. 1923, **47**, 51; Kunst. 1923, **13**, 69.
6. Farbw. vorm. Meister, Lucius & Brüning, D. R. P. 396696; abst. J. S. C. I. 1924, **43**, 890-B.
7. Farbw. vorm. Meister, Lucius & Brüning and F. Henle, D. R. P. 411519; abst. J. S. C. I. 1925, **44**, 693-B; Chem. Zentr. 1925, II, 92.
8. Farbw. vorm. Meister, Lucius & Brüning, R. Leopold and A. Michael, D. R. P. 419223; abst. J. S. C. I. 1926, **45**, 248-B.
9. Farbw. vorm. Meister, Lucius & Brüning, O. Ernst and K. Sponsel, D. R. P. 422500; abst. J. S. C. I. 1926, **45**, 513-B.

of a catalyst perpetually rejuvenated[1]. It is claimed that acetylcellulose may be toughened for film and filament formation by adding to its solutions up to 5% nitrocellulose[2]. Occupational poisoning with tetrachlorethane with cases was[3] published in 1924.

H. Fenton and A. Berry[4] have investigated the possibilities of substitutes for acetone as a cellulose acetate solvent in the airplane industry, and find no objection to the use of esters or weak acids insofar as effect on the tensile strength of the fabric is concerned. These authors find a direct relationship between the dielectric constant and dissolving action of a solvent. An apparatus has been patented[5] for molding plastic cellulose acetate, a predetermined amount of the mass being forced by means of a plunger into the molds which are arranged on a rotatable table. A special arrangement brings forward the measuring vessels which contain the plastic charge and returns the empties, so that rapid automatic molding can be realized. A review of the various methods of preparing plastics[6] was published in 1921.

For the manufacture of formic, acetic and hydrofluoric acids[7], they are generated in drum-shaped vessels provided with stirring apparatus which by its own rotation or by that of the drum, lifts up cylindrical rollers. A. von Fischer finds[8] that the suitability of cellulose acetate for

1. Farbw. vorm. Meister, Lucius & Brüning, Dan. P. 27724. Holl. Appl. 15132; abst. Chem. Ztg. 1922, **46**, 304.
2. A. Fausten, U. S. P. 1512751; abst. Chem. Zentr. 1925, I, 1034. D. R. P. 427181; abst. Chem. Zentr. 1926, II, 136.
3. A. Feil, Chim. et Ind. Special No. 1924, 763; abst. C. A. 1924, **18**, 3238.
4. Proc. Cambr. Phil. Soc. 1920, **20**, 16; abst. J. S. C. I. 1920, **39**, 624-A; Ann. Rep. S. C. I. 1920, **5**, 323; Kunst. 1921, **11**, 165; Caout. et Gutta. 1922, **19**, 11381.
5. Firma Phoenix, D. R. P. 421407; abst. Plastics, 1926, **2**, 99.
6. E. Fischer, Kunst. 1921, **11**, 33; abst. C. A. 1921, **15**, 2157; Chem. Zentr. 1921, IV, 1020.
7. H. Fischer, D. R. P. 452138; abst. J. S. C. I. 1929, **48**, 16-B.
8. Kolloid-Zeits., 1921, **29**, 260; abst. C. A. 1922, **16**, 490; J. S. C. I. 1921, **40**, 883-A; Ann. Rep. S. C. I. 1922, **7**, 138; J. C. S. 1921, **120**, i, 848; Bull. Soc. Chim. 1922, **34**, 1185; Phot .Abst. 1922, **2**, 13.

the production of plastic materials cannot be decided from the absolute value of the viscosity of its solutions, but curves plotted from the results of viscosity determinations on solutions of mixtures of alcohol 96% denatured with 0.5% camphor, and acetone give a reliable criteria. A good cellulose acetate always shows a minimum viscosity in an acetone-alcohol mixture containing 80% by volume of acetone, but the converse is not always true. Minimum viscosity in a mixture of 90% acetone invariably indicates poor quality.

Knitted fabrics, more especially hosiery[1], may be produced of variegated colors in a single dyeing if a portion of the fabric has been treated with a cellulose acetate solution prior to the dyeing operation. As a gelatinizer for cellulose esters[2], triacetin, butyrin, tributyrin or mono- or di-butyrin have been advocated. In the manufacture of gramophone records[3] a combination of acetated cellulose and acaroid resin with *p*-toluenesulfonanilide, diethyldiphenylurea, phenyl urethan, phenyl oxamate or cyclohexanone as plasticizing agents has received patent protection.

To produce poly-ply veneer that is not prone to deformation by atmospheric changes[4], the wood cells are preferably previously opened and all fermentable material removed therefrom, then coated with one or a plurality of cellulose acetate coatings,the plies being united by heat and pressure until all volatile solvent has been dissipated. According to K. Freudenberg[5], yields of 35-36% cellobiose octa-acetate can be obtained by keeping the temperatures low during the early stages of reaction on the cellulose, which is not in conformity with the conceptions of cellulose of Hess[6]. As a material for the preparation of ultra-

1. H. Fleisher, U. S. P. 1444786.
2. Forschungs & Verwertungs-Genossenschaft Synex, Swiss P. 95377; abst. Chem. Zentr. 1923, II, 653.
3. W. Forse, F. Jones and G. Walters, U. S. P. 1468609.
4. V. Forssman, U. S. P. 1465937; abst. C. A. 1923, **17**, 3769.
5. Ber. 1921, **54**, 767; abst. C. A. 1921, **15**, 2721; Paper, 1921, **29**, #2, 26; Kunst. 1922, **12**, 20; Chim. et Ind. 1921, **6**, 773.
6. J. S. C. I. 1920, **39**, 512-A; Paper, 1920, **27**, 13.

filters[1], the physical properties of cellulose acetate have been investigated, excellent filters resulting from films prepared from cellulose acetate 3-10% dissolved in 96% acetone 10, chloroform 9.

A. Fuchs[2] has described the various coating materials on airplanes and of the components used to confer waterproof, plastic, fireproof and contractile properties. Cellulose acetate is said to be made in Japan[3] by placing 20 parts cellulose at below 25° into a mixture of 100 each acetic anhydride and acetic acid, 2-3 of sulfuric acid and 15 glycerol. The object of the glycerol is not clear unless it be for partial hydration purposes due to the hydroxyls present therein, when it should be added after the primary esterification has been completed. The properties and uses of ethylene glycol were given *in extenso*[4] in 1924. R. Furness[5] has described the manufacture of artificial silk by the acetate process and discussed the use of metallic thiocyanates as solvents for acetylcellulose. A photostatic copy of the (then) confidential Report 183 was issued in 1920 by H. Gardner to the U. S. Navy Department on tests of cloth and coatings for airplanes[6].

In applying coated fabrics to objects[7], the fabric is first impregnated with a cellulose acetate solution in a uniform manner, and this attached to the object with a lacquer of the type, cellulose acetate 21, phenol 10, ethyl alcohol 69%. The di- and tri-esters of stearic, palmitic and lauric acids with cellulose may be made by treating a modified cellulose with the fatty acid-chloride in benzene or toluene

1. R. Fricke and P. Klempt, Kolloid-Z., 1923, **33**, 164; abst. C. A. 1923, **17**, 3811; J. S. C. I. 1923, **42**, 1104-A.
2. Chim. et Ind. 1920, **3**, 167; abst. J. S. C. I. 1920, **39**, 292-A; Chem. Zentr. 1920, IV, 753; Ann. Rep. S. C. I. 1920, **5**, 323.
3. S. Fujise and K. Seisakusho, Jap. P. 36545; abst. C. A. 1921, **15**, 1812; Caout. et Gutta. 1922, **19**, 11379.
4. H. Fuller, J. I. E. C. 1924, **16**, 624; abst. C. A. 1924, **18**, 2221.
5. Chem. Age (London), 1922, **7**, 522; abst. C. A. 1923, **17**, 342.
6. H. Gardner, Navy Department, Aircraft Tech. Note No. 183 of 1920.
7. H. Gault, U. S. P. 1394890; abst. C. A. 1922, **16**, 502.

in an excess of pyridine[1]. The cellulose esters produced are not inflammable, are soluble in benzene, chloroform, tetrachlorethane and pyridine. Soft transparent films result upon evaporation of their solutions. The same esters of starch have also been described[2], starch dilaurate, for instance, being soluble in benzene, aromatic hydrocarbons and chloroform, insoluble in water, alcohol and acetone.

Soluble cellulose esters of the higher saturated fatty acids have been described by H. Gault and P. Ehrmann, and H. Gault and M. Urban[3]. Hydrocellulose undecylenate and triundecylenate have been prepared, soluble in benzene and chloroform, insoluble in water, alcohol and acetone. In the dyeing and printing of acetylcellulose[4], the latter is first treated with an aromatic sulfonic acid (benzene, or naphthalenesulfonic acids) to open the filaments, then dyeing in the customary way. Or the acetate silk may be treated for a long time with cold potassium permanganate solution[5], washed, treated with sodium bisulfite and hydrochloric acid until the brown tone disappears, then colored with basic dyes.

In the union of two or more layers of dissimilar plastic materials which are difficult to stick together[6], as acetylcellulose and rubber, a suitable intermediate layer is provided to which the layers to be connected firmly adhere, such being straw meal, wood meal, barium sulfate, talc, china clay and comminuted fibrous materials. "Rubber

1. H. Gault and P. Ehrmann, Comp. Rend. 1923, **177**, 124; abst. C. A. 1923, **17**, 3249; J. S. C. I. 1923, **42**, 826-A; J. C. S. 1923, **124**, i, 757.

2. H. Gault, Compt. Rend. 1923, **177**, 592; abst. C. A. 1924, **18**, 80; J. C. S. 1923, **124**, i, 1064.

3. Compt. Rend. 1924, **179**, 333; abst. C. A. 1924, **18**, 3714; J. C. S. 1924, **126**, i, 1047; J. S. C. I. 1924, **43**, 742-B.

4. J. Geigy, Can. P. 244018. E. P. 213593; abst. C. A. 1924, **18**, 2433; J. S. C. I. 1925, **44**, 708-B; Rayon J. 1926, **1**, #1, 55. U. S. P. 1613228; abst. C. A. 1927, **21**, 655; J. S. C. I. 1927, **46**, 139-B.

5. Gillet et Fils, F. P. 570264; abst. J. S. C. I. 1930, **49**, 280-B; Rayon J. 1926, **1**, #1, 55.

6. Ges. für Verwertung Chemischer Producte, E. P. 145544; abst. C. A. 1920, **14**, 3537.

celluloid" has been described[1], comprising a mixture of rubber and acetylcellulose by means of the solvents tetralin or hexalin which are harmonious to both.

Propylene chloride or similar compound obtained by saturating an unsaturated hydrocarbon with chlorine, is further chlorinated in the presence of sulfur dioxide, sulfur chlorides or sulfuryl chloride[2], trichlorhydrin being obtained. The G. Goerner cellulose acetate lacquer owes its claim to novelty in the employment of methylene chloride as the predominating solvent ingredient[3], and another type lacquer formula to the employment of furfural, a cellulose acetate 10, methyl acetate or acetone 100, furfural (furfuryl alcohol) 10. Ethylene chloride is obtained by treating ethylene (prepared by passing alcohol vapor over hot aluminum oxide) with chlorine in the presence of a catalyst (iron, copper or antimony chlorides) the ethylene being used in large excess and a temperature of from 30-120° maintained[4].

Cellulose or cellulose compounds when treated with alkalis and carbon oxysulfide (COS) give rise to viscous solutions which may be worked up into films and plastic masses[5]. *Iso*propyl alcohol as produced in the petroleum industry in the cracking process with its uses, especially as a cellulose acetate solvent[6] was reviewed by D. Grant and C. Johns in 1922. E. Graves has described an improved dye cop or package for dyeing cellulose acetate threads or textiles[7], and S. Graves[8] a cellulose ester composition in which the inflammability of the ester is mitigated by

1. I. Ginsberg, Rubber Age, 1921, **10**, 165; abst. C. A. 1922, **16**, 361.
2. Glysyn Corp., E. P. 168676; abst. C. A. 1923, **17**, 772.
3. U. S. P. 1384188; abst. C. A. 1921, **15**, 3746; J. S. C. I. 1921, **40**, 655-A.
4. T. Goldschmidt, A. G. and O. Matter, E. P. 147908; abst. Chem. Tech. Uebers, 1921, **45**, 103. D. R. P. 298931; abst. Chem. Tech. Uebers, 1922, **46**, 82.
5. K. Gottlob, Aust. P. 88350; abst. Chem. Ztg. 1922, **46**, 506; Chem. Zentr. 1922, IV, 1062.
6. Am. J. Pharm., 1922, **94**, 418; abst. C. A. 1922, **16**, 2944.
7. U. S. P. 1348167.
8. U. S. P. 1382077.

incorporation of corn starch. It is claimed that when applied to a fabric or surface, the composition will not break or exfoliate.

In making acetic acid by reaction of an inorganic acid on an acetate[1], sufficient water is added to the reaction mixture to permit complete liberation of the acetate component, and the distillate from the reaction is collected as a concentrate, followed by a dilute fraction. Methyl-sulfonic acids derived from amino- or monoalkylamino-azo compounds[2], dissociate slowly in hot aqueous solutions which are slightly acid or alkaline, and the free (colored) amino- or alkylamino-azo bases liberated are readily absorbed by cellulose acetate silk immersed in the solution. By the combination of diazotized *p*-nitraniline and sodium anilinemethyl-omega-sulfonate, a dye is obtained particularly adapted to coloring cellulose acetate, after combination with aldehyde and bisulfite[3]. A. Green and K. Saunders[4] have given a description of the "ionamines," which are the omega-sulfonic acids of amino-dyestuffs, especially applicable to acetylcellulose silk dyeing. Ionamine A, B, H, and I are the usual four compounds which when developed with resorcinol, *b*-naphthol or *b*-hydroxynaphthoic acid give (with A) reddish-brown, reddish-purple, navy-blue to black; with B, reddish-orange, scarlet, crimson; with H, reddish-brown, reddish-purple, purple; and with I, purple-brown, purple, bright blue. Ionamines prepared from secondary

1. Grasselli Chem. Co., E. P. 221256; abst. C. A. 1925, **19**, 832; J. S. C. I. 1924, **43**, 891-B. U. S. P. 1463209; abst. J. S. C. I. 1923, **42**, 998-A. Can. P. 241465, 241466. Belg. P. 310961.

2. A. Green, K. Saunders and British Dyestuffs Corp., Ltd., E. P. 200873; abst. C. A. 1924, **18**, 475; J. S. C. I. 1923, **42**, 749-A, 926-A. U. S. P. 1483797; abst. C. A. 1924, **18**, 1206; J. S. C. I. 1924, **43**, 29-B.

3. A. Green and K. Saunders, U. S. P. 1483798; abst. C. A. 1924, **18**, 1206.

4. J. Soc. Dyers and Col. 1923, **39**, 10; abst. C. A. 1923, **17**, 3920; J. S. C. I. 1923, **42**, 138-A.

aminoazo compounds have greater penetrative power than those obtained from the primary[1].

A process for treating milk and milk products has been patented[2], in which a cellulose acetate membrane is used for dialysis in separating components in the milk. The transformation of cellulose by aerobic decomposition[3] has been reported upon by J. Groenewege, and J. Grolea[4] published in 1923, his formula for the preparation of an airplane body lacquer from acetylcellulose in triphenyl phosphate, dibutyl tartrate and volatile solvents. Another varnish for the same purpose[5], employs an amount of acetone insufficient of itself to produce the low viscosity, adding thereto a hygroscopic chloride (zinc, calcium, magnesium, tin chlorides) in amount sufficient to induce the low viscosity desired. The properties and methods of manufacture of cellulose distearate and dilaurate were described[6] in 1921.

Aldol may be prepared from acetaldehyde[7] by first removing any acetic acid therefrom, then condensing the aldehyde to aldol by a catalyzer of alkaline reaction (alkaline earth cyanides, oxides and hydroxides). Trichlorethylene may be prepared from tetrachlorethane[8] by injection of ammonia gas at 60-70° into the latter under pressure. In preparing acetic acid from oxidizing acetaldehyde[9], formation of peracetic acid is prevented (and hence possibility of explosions diminished) by passing the oxi-

1. A. Green and K. Saunders, J. Soc. Dyers and Col. 1924, **40**, 138; abst. J. S. C. I. 1924, **43**, 504-B.
2. G. Grindrod, U. S. P. 1503892.
3. J. Groenewege, Mededeel. Algem. Proofstate. Landbeuw, 1921, 8; abst. Chem. Tech. Uebers, 1922, **46**, 130.
4. Ital. P. 168401.
5. S. Groves and T. Ward, U. S. P. 1400430.
6. A. Grün and F. Wittka, Z. angew. Chem., 1921, **34**, 645; abst. J. S. C. I. 1922, **41**, 94-A; Bull. Soc. Chim. 1922, **34**, 1249; Caout. et Gutta. 1922, **19**, 11333, 11459; J. C. S. 1922, **122**, i, 114.
7. N. Grünstein, U. S. P. 1437139.
8. A. Guyot, U. S. P. 1343716; abst. Chem. Met. Eng. 1920, **23**, 301.
9. *Ibid.* U. S. P. 1409098; abst. J. S. C. I. 1922, **41**, 309-A; E. P. 130651; abst. J. S. C. I. 1919, **38**, 739-A.

dized vapors through a heated chamber at 100° to decompose the peracetic acid.

It is claimed that satisfactory results may be obtained (upon which point we are dubious) by using suitable purified wood pulp for acetylation purposes, so long as the pulp is free from alkali. When completely anhydrous glacial acetic acid is used, no esterification occurs, rather 1-2% water must be present[1]. When wood pulp is used as the cellulose material[2], hydrazine and hydroxylamine are said to be efficient accelerators in the acylation process. In the preparation of paper for use as a dielectric for electrical condensers[3], thin tissue paper is coated with a cellulose acetate solution, allowed to dry, and then wound or otherwise attached to the wire or object to be coated, incipient plasticity being induced by the addition of a small amount of volatile solvent. In 1921 S. Halen[4] reviewed our knowledge of the starch acetates, and discussed the acetylcellulose patent literature[5].

Acetate silk has a strong affinity for aromatic compounds containing the hydroxyl or amido group and therefore is dyed by aminoazobenzene and *p*-nitraniline, which is then developed[6]. The azonin and dispersol dyes are particularly adapted for acetate silk. *Celloxane,* which contains a large proportion of zinc nitrate, gives deeper shades with basic dyes on acetylcellulose than can be obtained without its use. The cellulose acetate may be dyed with 2.4-dinitrodiphenylamine compounds containing no sulfo group, e.g., with 2.4-dinitrophenylamine and its 2′- or 4′-hydroxy-,

1. E. Hägglund, Kunst. 1923, **13**, 20.
2. E. Hägglund, N. Löfman and E. Färber, Cellulosechemie, 1922, **3**, 13; abst. C. A. 1922, **16**, 1664; J. S. C. I. 1922, **41**, 247-A; Ann. Rep. S. C. I. 1922, **7**, 137; Paper, 1922, **30**, #14, 28; J. C. S. 1922, **122**, i, 323; Bull. Soc. Chim. 1922, **32**, 2092; Caout. et Gutta. 1922, **19**, 11459, 11569; Chem. Zentr. 1922, II, 897.
3. F. Haigh, E. P. 138226.
4. Kunst. 1921, **11**, 121; abst. C. A. 1922, **16**, 657; Chim. et Ind. 1922, **7**, 548.
5. S. Halen, Kunst. 1922, **12**, 73; abst. C. A. 1922, **16**, 2600.
6. A. Hall, Text. Col. 1924, **46**, 153; abst. C. A. 1924, **18**, 1202.

4′-amino-, 4′-acetylamino-, and *N*-methyl-dinitrodiphenylamine[1].

W. Harrison in 1920 gave an historical resume with copious references[2] of cellulose nitrates, formates and acetates, with methods for treatment of fibers obtained therefrom. The structure of cellobiose (cellose) has been investigated by W. Haworth and E. Hirst[3], and experimental evidence adduced in support of its constitutional formula as glucose-*b*-glucoside. W. Henderson in 1924 published details of the manufacture and properties of cellulose acetate, primarily from the viewpoint of their technical aspects[4], and A. Henning[5] the advantages of a fire extinguisher of methyl bromide and trichlorethylene or dichlorethylene. In a study of the constitution of cellulose, S. Hentikka[6] finds that cellobiose, by prolonged treatment with calcium hydroxide solution gives calcium *iso*saccharinate, from which *iso*saccharin is obtainable.

The M. Hepner acoustics diaphragm as for microphones[7] is made from thin mica attached in place by cellulose acetate as the agglutinant. In the preparation of cellulose acetate plastics which are equivalent to celluloid[8], and which require but a comparatively short time for seasoning, the ester and plastifying material are compacted by heat and pressure and then ground into a very fine powder. By now molding into the shape required, little or no distortion occurs after the lapse of time.

From experiments with Roentgen rays[9], it is concluded that cellulose acetate is amorphous and consists of

1. A. Hall and Silver Springs Bleaching and Dyeing Co., Ltd., E. P. 222001; abst. C. A. 1925, **19**, 1059.
2. Color Trade J. 1920, **6**, #3, 91.
3. J. C. S. 1921, **119**, 193; abst. Paper Trade J. 1922, **74**, 55.
4. Chem. Met. Eng. 1924, **30**, 449.
5. E. P. 172573; abst. Chem. Met. Eng. 1922, **26**, 800.
6. Ann. Acad. Sci. Fennicae, 1922, (A), **9**, 3; abst. Chem. Zentr. 1923, I, 296; J. C. S. 1923, **124**, i, 756.
7. U. S. P. 1435843; abst. C. A. 1923, **17**, 454.
8. R. Herrmann, U. S. P. 1510779.
9. R. Herzog and W. Jancke, Umschau, 1921, **25**, 53; abst. J. S. C. I. 1921, **40**, 342-A; Chem. Zentr. 1921, II, 573.

a mixture in which the ester has undergone considerable degradation. When examined under X-rays[1], the spectrographic diagram of cellulose acetate silk is of a crystalline structure symmetrically disposed. Evidence has been adduced from X-ray diagrams and other sources[2], that during acetylation of cellulose, pseudomorphic crystals are formed. The synthesis of cellulose has been given in comprehensive discussion by K. Hess[3], from which it appears[4] that the saponification products of acetylcellulose are to be regarded as chemically intact cellulose. It has been possible to obtain splendid large crystals of acetylcellulose, which swell in chloroform just as the amorphous substance does.

Lignin obtained from resin-free wood meal obtained by treatment with 41.2% HCl when acetylated in the presence of pyridine[5], gave an ester of maximum acetyl value 32.5% of combined acetic acid. Cellulose esters which approximate very closely to the formula $C_6H_8O_3(O.CO_2Me)_2$, are formed by the action of an excess of methyl chlorformate on hydrocellulose dissolved in cold, aqueous 8% sodium hydroxide. These carbonic esters of cellulose form white, amorphous granular material, soluble in pyridine, chloroform or acetic acid and readily hydrolyzed[6]. Cellulose methylcarbonate is attacked to some extent by water and rapidly decomposed by alkalis, regenerating hydrocellulose. The thermal decomposition of formic acid has been determined[7].

1. R. Herzog and H. Gonell, Kolloid-Z., 1924, **35**, 201; abst. J. S. C. I. 1925, **44**, 6-B.
2. R. Herzog and G. Londberg, Ber. 1924, **57**, 329; Caout. et Gutta. 1924, **21**, 12438.
3. Z. angew. Chem. 1920, **34**, 49; abst. C. A. 1921, **15**, 2720; Chem. Zentr. 1921, II, 707.
4. K. Hess, Z. angew. Chem. 1924, **37**, 792.
5. E. Heuser and W. Ackermann. Cellulosechemie, 1924, **5**, 13; abst. J. C. S. 1924, **126**, i, 619.
6. E. Heuser and F. Schneider, Ber. 1924, **57**, 1389; abst. C. A. 1925, **19**, 251; J. S. C. I. 1924, **43**, 904-B.
7. C. Hinshelwood, H. Hartley and B. Topley, Proc. Roy. Soc., 1922, A **100**, 575; abst. J. S. C. I. 1922, **41**, 268-A.

E. Hirst acetylated esparto cellulose[1] and obtained almost quantitative yields of ester without loss of the pentose residue, dissolving in acid methyl alcohol in sealed tubes at 130°, yielding methylglucoside and methylpentoside. The fire hazards of cellulose nitrate and acetate X-ray and other films, especially upon storage[2], have been pointed out by M. Hodgson. The Holzveredelung[3] first transform wood cellulose into hydrocellulose and then acetylate this in the usual way to produce an ester of very low viscosity when dissolved in the usual solvents. It is claimed[4] that the chlorination of acetylene is rendered controllable and does not result in polymerized products, by conducting it in the presence of water vapor at 400-500°.

Acetaldehyde may be produced from ethyl alcohol by passing the latter and air over contact substances containing silver in the form of gauze[5]. Compared with the use of silver deposited on asbestos, the yield of aldehyde is raised from 70.4 to 93.6% and the life of the catalyst prolonged. Concentrated acetic acid may be recovered from dilute solutions by evaporating the solution[6], passing the vapors over an adsorbent (carbon) and recovering acetic acid from the charged adsorbent. A cardboard container suitable for packing soaps or alkaline pasty substances[7] consists of coating the container inside and out with a lacquer of cellulose acetate. In the manufacture of artificial silk from cellulose acetate and pyridine[8], the material is run into two superposed baths (hot and cold aqueous baths). Comparatively thick filaments pass first into the hotter bath

1. Rept. Brit. Assoc. Advancement. Sci. 1922, 358; abst. C. A. 1923, **17**, 3417.
2. M. Hodgson, Amer. J. Roent., 1924, 557.
3. Belg. P. 307358.
4. Holzverkohlungs-Ind. A. G., E. P. 174635; abst. Chem. Eng. 1922, **26**, 991; Chem. Ztg. 1923, **47**, 474.
5. Holzverkohlungs-Ind. A. G., D. R. P. 422729; abst. J. S. C. I. 1926, **45**, 611-B. Ital. P. 268996.
6. *Ibid.* D. R. P. 472399; abst. C. A. 1929, **23**, 2449.
7. G. Howlett, U. S. P. 1355976; abst. C. A. 1921, **15**, 154.
8. E. Hubert, U. S. P. 1517627; abst. C. A. 1925, **19**, 404.

where they are drawn, and thence into the bath of lower temperature.

Diphenylmethane dyestuffs are condensed with phenylmethylpyrazolone, *b*-naphthol, or nitromethane in aqueous solution and the leuco-products subsequently oxidized. For example, a dyestuff capable of yielding fluorescent shades fast to light on cellulose acetate silk[1] is obtained by condensing Thiopyronine with phenylmethylpyrazolone in an aqueous solution of caustic soda. Under similar conditions golden yellow fluorescent and red fluorescent dyestuffs are obtained from Acridine orange and phenylmethylpyrazolone and from Thiopyronine and nitromethane. Two color effects are obtainable on acetate silk by dyeing the acetate portion by means of a basic dye containing amino-, alkyl-, or arylamino-groups which have been liberated by treatment of the dyesalt with sodium carbonate[2], and then dyeing the cellulose portion another shade by means of a direct dye. Acetate silk may also be dyed in shades fast to washing by means of slightly water-soluble, feebly basic nitroarylamines or their derivatives[3]. Orange-yellow, greenish-yellow and yellow dyes are 8-nitro-2-naphthylamine, 3-nitro-4-aminobenzophenone, 4-nitro-2-aminodiphenylamine, and the condensation product of 3-chlor-6-nitraniline and formaldehyde.

Cellulose acetate is also dyed with azo colors derived from aminoaldehydes[4]. *p*-Aminobenzaldehyde, diazotized and coupled with salicylic acid gives yellow; 1.7-aminonaphthol, maroon; with *b*-naphthol and phenylhydrazine, brown. *m*-Aminobenzaldehyde, diazotized and coupled with dimethylaniline, golden-orange; with diphenylamine, golden-yellow. Where ammonium salts (not thiocyanate) are

1. G. Hugel, F. P. 589745; abst. J. S. C. I. 1926, **45**, 149-B.
2. A. Hunter, E. P. 191120; abst. C. A. 1923, **17**, 3103; J. S. C. I. 1923, **42**, 78-A, 180-A.
3. I. G. Farbenind. A. G., K. Meyer and H. Hopff, D. R. P. 428176; abst. J. S. C. I. 1926, **45**, 785-B.
4. I. G. Farbenind. A. G., R. Metzger and C. Schuster, D. R. P. 433349; abst. J. S. C. I. 1927, **46**, 277-B.

added to the dye-bath[1], strong dyeings on acetate silk are obtained without acidification, with basic, acid, and some substantive dyes. In the manufacture of varnishes[2], cellulose acetate containing more than 50% combined acetic acid is dissolved in a mixture of ethylenechlorhydrin or monochlorhydrin with water, the total water content, inclusive of that in the cellulose acetate, not exceeding 50% of the chlorhydrin present.

Acetate silk may be dyed in an aqueous bath with insoluble or sparingly soluble dyes (excluding color bases)[3], with the addition of soap and organic compounds (amyl alcohol, glycerol, glycerol monochlorhydrin, cyclohexanol, phenol, *p*-toluenesulfon-amide or -anilide) which form easily dissociated salt-like alkali derivatives. Or[4], the acetate silk may be dyed with basic dyes with addition of not more than 5 gm. of a soluble thiocyanate per liter of dye-bath together with the requisite water-soluble colloid, when dyeings fast to rubbing will be obtained. Monoazo dyes from diphenylamine-monosulfonic acid coupled with unsulfonated diazo compounds of the benzene or naphthalene series may be used as colorants[5], *m*-nitroaniline and diphenylamine-sulfonic acid giving a golden-yellow.

Carboxylated azo dyes (other than salicylic acid derivatives) have been patented[6]. Examples, *p*-aminophenoxy-acetic acid and *b*-naphthol, red-orange; *p*-aminobenzoic acid and *m*-phenylaminediamine, orange; *a*-naphthylamine with *p*-hydroxybenzoic acid, gold-yellow; *p*-nitraniline with 4-hydroxy-*a*-naphthoic acid, brown-red. In order to increase

1. I. G. Farbenind. A. G., E. Müller and A. Schaeffer, D. R. P. 438378; abst. J. S. C. I. 1927, **46**, 964-B.
2. I. G. Farbenind. A. G. and L. Rosenthal, D. R. P. 439009 Addn. to 383699; abst. J. S. C. I. 1927, **46**, 661-B.
3. I. G. Farbenind. A. G., A. Aurednicek, E. Keiner and R. Krech, D. R. P. 439111; abst. J. S. C. I. 1927, **46**, 964-B.
4. I. G. Farbenind. A. G., H. Kesseler and E. Döring, D. R. P. 444961; abst. J. S. C. I. 1928, **47**, 229-B.
5. I. G. Farbenind. A. G., H. Eichwede, E. Fischer and C. Müller, D. R. P. 441325; abst. J. S. C. I. 1927, **46**, 905-B.
6. I. G. Farbenind. A. G. and R. Metzger, D. R. P. 457957

the penetrativeness of dyestuffs for acetate silk[1], especially basic dyes like Diamond fuchsin, the addition of pyridine or piperidine to the dyebath is recommended.

To increase the stability of lacquers of cellulose acetate dissolved in monochlorhydrin[2], small amounts of aniline, pyridine or quinoline are added. Starch esters of higher fatty acids (palmitate, stearate, undecylenate) are prepared by treating unmodified starch with the chloride of the acid in the presence of a tertiary base and a diluent (chloroform, benzene, toluene)[3]. Filaments obtained by spinning acetylcellulose into salt solutions containing a solvent or swelling agent[4], are improved by superposing on the precipitating bath a liquid as paraffin oil, which does not mix with the bath and which is a non-solvent of the cellulose ester.

Acetylcellulose is dyed by treatment with insoluble or difficultly soluble dyes in the presence of true sulfonic acids or their salts having fat-splitting, tanning or saponaceous properties, as naphthenesulfonic acids, synthetic tans or sulfite cellulose lye[5]. In the preparation of tetrachlorethane and trichlorethylene from acetylene and chlorine[6], the following points were determined: antimony pentachloride as catalyzer is best; optimum temperature for chlorine absorption is 80-100°; difficulties are decrease of absorption power of antimony pentachloride which rapidly is reduced to the trichloride, and danger of explosions. In preparing glycolchlorhydrin[7], chlorine is passed into water containing copper chloride or other copper compound as catalyst. Ethylene is then passed into the solution and these opera-

1. I. G. Farbenind. A. G., D. R. P. 445979, Addn. to 439004; abst. Die Kunstseide, 1927, #8, 421.
2. *Ibid.* D. R. P. 472311; abst. C. A. 1929, **23**, 2585.
3. *Ibid.* D. R. P. 484242; abst. C. A. 1930, **24**, 962.
4. I. G. Farbenind. A. G., E. Hubert, O. Leuchs and L. Lock, D. R. P. 477066; abst. C. A. 1929, **23**, 4070.
5. I. G. Farbenind. A. G. and R. Metzger, D. R. P. 480298; abst. C. A. 1930, **24**, 6033.
6. S. Igi, J. Chem. Ind. (Japan), 1920, **23**, 1217; abst. C. A. 1921, **15**, 2273; Bull. Soc. Chim. 1921, **30**, 1495.
7. J. Irvine and W. Haworth, U. S. P. 1496675; abst. C. A. 1924, **18**, 2345.

tions repeated until a relatively strong solution of chlorhydrin results.

Methyl, ethyl, propyl and butyl formates have been patented as desirable cellulose acetate solvents[1]. The J. Jarvis composition[2] comprises cellulose acetate 75, naphthalene 25, acetone 60, and he has claimed[3] that the addition of 2% acetone cinchonine or cinchonine sulfate to cellulose acetate solutions imparts increased strength and tenacity to the product. Cinchonine salts are relatively expensive. He has described an apparatus for carrying out the manufacture of acetate films as above described[4]. An uninflammable film is made by combining nitrocellulose and acetylcellulose[5], chloral, chloral hydrate, cinchonine or cinchonine sulfate. The B. Jellinek cellulose acetate process[6] is for the production of an ester especially adapted for film formation.

Fabrics for balloons and dirigibles are prepared by first impregnating the fabric with gelatin, over which is placed one or more coats of a cellulose ester[7]. Esters as solvents for acetylcellulose[8] are obtained by reacting at elevated temperatures upon methyl chloride and sodium halide as iodide, thus forming methyl iodide.

P. Karrer[9] has described a new degradation of cellulose, being the conversion of amylose by acetyl bromide into

1. B. Jaillard, F. P. 487350; F. P. Addn. 22415 to 487350; abst. Caout. et Gutta. 1923, **20**, 11783; Chem. Zentr. 1922, II, 487.
2. J. Jarvis, U. S. P. 1343135; abst. C. A. 1920, **14**, 2418; J. S. C. I. 1920, **39**, 541-A; Paper, 1921, **27**, #21, 26; Chem. Ztg. 1920, **44**, 810. Cites U. S. P. 199908.
3. *Ibid.* U. S. P. 1349156; abst. C. A. 1920, **14**, 3154; J. S. C. I. 1920, **39**, 653-A; Ann. Rep. S. C. I. 1920, **5**, 324.
4. *Ibid.* U. S. P. 1351652; abst. C. A. 1920, **14**, 3320; J. S. C. I. 1920, **39**, 686-A.
5. *Ibid.* U. S. P. 1354401; abst. C. A. 1921, **15**, 172; J. S. C. I. 1920, **39**, 719-A; Ann. Rep. S. C. I. 1920, **5**, 325.
6. B. Jellinek, Aust. P. 80625; abst. Chem. Ztg. 1920, **44**, 429.
7. A. Johnston, U. S. P. 1407197; abst. J. S. C. I. 1922, **41**, 248-A. E. P. 124520; abst. J. S. C. I. 1919, **38**, 357-A.
8. S. Karpen & Bros., Can. P. 244388. E. P. 220721; abst. J. S. C. I. 1924, **43**, 850-B. U. S. P. 1459971; abst. J. S. C. I. 1923, **42**, 952-A.
9. Ber. 1922, **55**, (B), 153; abst. J. C. S. 1922, **122**, i, 231; Bull. Soc. Chim. 1922, **32**, 1039.

acetylbrommaltose. When cork is purified it yields a triacetate giving 72% glucose upon hydrolysis. The preparation and properties of levoglucosan tripalmitate and tristearate and cellulose hexapalamitate were described[1]. Lichenin may be acetated into a triacetate of similar rotary power of cellulose acetate[2]. Methods of manufacture and properties of cellulose hexastearate, starch hexapalmitate and hexacetate, and inulin tripalmitate and tristearate have also been published[3].

Dichlorethylene is produced by bringing vapors of tetrachlorethane and steam at ordinary atmospheric pressure in contact with a metal (aluminum, zinc, iron, magnesium) capable of combining with chlorine[4]. An airplane fabric of low burning quality is obtained by combining a cellulose ester with boric acid and magnesium chloride (both of which are soluble in volatile solvents) in the form of a lacquer[5]. The cellulose ester composition of J. Kessler[6] owes its plasticity to the presence of an acetin (free from the hygroscopic mono-acetin) in conjunction with cellulose acetate. As camphor substitutes for use with acetylcellulose[7] have been described the methyl, ethyl, butyl, phenyl and naphthyl esters of formyl-, acetyl-, propionyl- or benzoyl-salicylic acid, or -naphthoic acid; methyl acetylsalicylate (methyl aspirin) being especially useful. A mixture of diacetin and triacetin[8] is alleged to be better than com-

1. P. Karrer, J. Peyer and Z. Zega, Helv. Chim. Acta, 1922, **5**, 853; abst. C. A. 1923, **17**, 988; Caout. et Gutta. 1923, **20**, 12023.
2. P. Karrer and B. Joos, Biochem. Z. 1923, **136**, 537; abst. J. C. S. 1923, **124**, i, 541.
3. P. Karrer and Z. Zega, Helv. Chim. Acta, 1923, **6**, 822; abst. C. A. 1924, **18**, 80.
4. F. Kaufler and A. Wacker Ges. Ind., U. S. P. 1419969; abst. Chem. Met. Eng. 1922, **27**, 611; J. S. C. I. 1922, **41**, 648-A. E. P. 156080; abst. J. S. C. I. 1921, **40**, 411-A.
5. F. Kawashima, U. S. P. 1469839; abst. C. A. 1923, **17**, 3909.
6. 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. Cites U. S. P. 410208, 598648. E. P. 13131, 1900.
7. *Ibid.* U. S. P. 1408095; abst. Caout. et Gutta. 1922, **19**, 11653.
8. *Ibid.* U. S. P. 1456782; abst. C. A. 1923, **17**, 2505; J. S. C. I. 1923, **42**, 712-A.

mercial acetin for inducing plasticity and flexibility to acetylcellulose solutions. In recovering cellulose acetate from its solutions[1], it is forced through small orifices into a precipitating liquid, the idea being that in "breaking" the solution up in this manner, more efficient coagulation and a higher degree of purification may be accomplished.

The J. Kessler process of cellulose acetylation[2] bases its claim to basicity upon forcing the acetylizing solution into the cellulose under pressure, the saturated cellulose retaining the precise amount of esterizing fluid which it is desired the cellulose shall retain, and then subjecting the impregnated cellulose to acetylation in the usual manner.

Articles exposing an extensive surface of rubber are first covered with an albuminoid layer[3], which can be tanned if desired, and a layer of acetylcellulose applied to this. The coating is said to strongly adhere, rendering the products so coated resistant to moisture and atmospheric oxidation. Acetate fibers may be dyed in an alkaline thiosulfate (hyposulfite) vat with amino- or nitro-anthraquinones or their alkyl or halogen derivatives ,e.g., 1- or 2-amino-, 1.5-dinitro-, 1.5-diamino-, 1-amino-2-methyl-, 1-methylamino-, 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[4]. P. King[5] in 1922 gave a review outlining the technical applications of acetylcellulose, especially in the filament industry.

In the preparation of acetylcellulose soluble in acetone[6],

1. J. Kessler and V. Sease, U. S. P. 1456781; abst. C. A. 1923, **17**, 2505; J. S. C. I. 1923, **42**, 712-A.
2. U. S. P. 1466401; abst. C. A. 1923, **17**, 3789; J. S. C. I. 1923, **42**, 1065-A; Chem. Age, 1923, **31**, 464.
3. Ketschendorfer Kunstlederfabrik A. G., D. R. P. 390094; abst. J. S. C. I. 1924, **43**, 528-B.
4. W. Kilby and Morton Sundour Fabrics, Ltd., E. P. 214112; abst. C. A. 1924, **18**, 2610; J. S. C. I. 1924, **43**, 508-B. Cf. E. P. 211720; abst. J. S. C. I. 1924, **43**, 375-B.
5. J. Textile Inst., 1922, **13**, 145; abst. C. A. 1922, **16**, 4353.
6. G. Kita, K. Asami, J. Kato and R. Tomihisa, Z. Angew. Chem. 1924, **37**, 414; abst. J. S. C. I. 1924, **43**, 668-B; C. A. 1924, **18**, 2961; J. C. S. 1924, **126**, i, 945.

dry cotton paper, acetic acid and acetic anhydride are mixed and cooled with ice water, a small amount of sulfuric acid being added as catalyst. The mixture is transferred to a thermostat and the reaction temperature carefully controlled. Hydration is effected by a mixture of equal weights of glacial acetic acid and water. If the hydration temperature is too high the viscosity of the product does not increase and the copper value increases with the time of hydration, while the reverse is the case with a suitably low temperature. The influence of temperature is more marked during acetylation than during hydration. Acetylation at a relatively high temperature (e.g. 25°) gives an inferior acetone-soluble acetate even if hydration is effected at a low temperature, while the temperature of hydration has comparatively little influence with a product of low-temperature acetylation. The most suitable temperature depends on the quantity of sulfuric acid added as catalyst, a smaller quantity of the latter being required at higher temperatures, though with too small a quantity a good acetate is not obtainable. If the quantity of catalyst and the time of acetylation are suitably limited good results may be obtained even at higher temperatures. There is no advantage in neutralising the sulfuric acid on hydration.

E. Knoevenagel has pointed out that cellulose acetates which do not swell in water and alcohol, swell considerably with modification of their physical properties, in a mixture of these liquids[1]. The swollen material may readily be saponified by treatment with 0.5 *N* KOH solution at room temperature, an accurate method of acetyl determination being based on this observation. The effect of various organic liquids and binary mixtures has been studied with special reference to the physical conditions obtaining, and the degree and character of swelling consequent on treatment with these substances. The systems nitrobenzene-al-

1. E. Knoevenagel, Koll. Chem. Beihefte, 1921, **13**, 194; 1922, **16**, 180; abst. J. S. C. I. 1921, **40**, 382-A; Ann. Rep. S. C. I. 1922, **7**, 137.

cohol[1], and alcohol with benzene, nitrobenzene or carbon tetrachloride[2] have been specifically studied, as well as various proportions of nitrobenzene-ethyl alcohol[3]. Parallel thermal studies have also been made[4], the thermal constant being the same for alcohol, alcohol-benzene and nitrobenzene as swelling media, *viz.*, 0.114 cals. mol. Chloroform-soluble cellulose acetate swelled in 50% ethyl alcohol increased in weight 38.1% after 48 hours. After standing 6 months under water at room temperature[5], the value was 36.2.

By action of benzoyl chloride in basic solution on alkali-cellulose[6], a compound $C_6H_2O_7(O.CO.C_6H_5)_3$ was obtained, completely soluble in chloroform—a cellulose benzoate or hydrocellulose benzoate. It is claimed that cellulose acetate does not swell in pure water or in absolute alcohol, but readily does so in mixtures of alcohol, acetone and acetic acid[7]. In each case, there is a definite mixture where the swelling is at a maximum. Under identical conditions, swollen acetylcellulose dyes many times quicker than the unswollen. Alcohols, benzene and water in varying amounts, are taken up by cellulose acetate in constant amounts[8], and experiments with aqueous solutions of aniline, phenol, methyl tartrate and ethyl tartrate of low concentrations,

1. E. Knoevenagel and A. Bregenzer, Koll. Chem. Beihefte, 1921, **14**, 1; abst. J. C. S. 1921, **120**, i, 771.
2. *Ibid.* Koll. Chem. Beihefte, 1921, **13**, 242; abst. J. C. S. 1921, **120**, i, 709; Kunst. 1922, **12**, 21.
3. *Ibid.* Koll. Chem. Beihefte, 1921, **13**, 262; abst. J. C. S. 1921, **120**, i, 710; Kunst. 1922, **12**, 21.
4. E. Knoevenagel, Koll. Chem. Beihefte, 1922, **17**, 51; abst. C. A. 1923, **17**, 1568.
5. *Ibid.* Koll. Chem. Beihefte, 1923, **18**, 39; abst. J. C. S. 1923, **124**, i, 757.
6. E. Knoevenagel and H. Busch, Zellulosechemie, 1922, p. 52; Caout. et Gutta. 1923, **20**, 11751.
7. E. Knoevenagel and O. Eberstadt, Koll. Chem. Beihefte, 1921, **13**, 194; abst. J. S. C. I. 1921, **40**, 382-A.
8. E. Knoevenagel, J. Hogrefe and F. Mertens, Koll. Chem. Beihefte, 1922, **16**, 180; abst. C. A. 1923, **17**, 1362; J. C. S. 1923, **124**, i, 17.

proved that a partition occurs after 24 hours in keeping with Henty's law[1].

By the use of suitable catalysts[2], chloroform-soluble cellulose acetates can be converted into acetone-soluble esters, which occasionally show lower copper numbers than do the original acetates, which is not in harmony with the hypothesis that the conversion of less soluble into the more soluble acetates is accompanied by hydrolysis. Knoll & Co.[3] hydrolyze acetone-insoluble acetylcellulose with metal sulfates and bisulfates in the presence of a relatively small proportion of water. It is not necessary that the acetylcellulose be in solution[4]. By the slow addition of water it is possible to convert the excess acetic anhydride into organic acid and yet without much decomposition of the cellulose molecules, to obtain acetone-soluble acetylcellulose successfully[5]. The hydrolysis may be carried on by the use of glacial acetic acid alone, provided the mass is heated to 100°[6], or with 90% formic acid at the above temperature[7]. Where a bisulfate is used as catalyst in the esterization[8], hydrolysis proceeds with unusual uniformity.

In the concentration of formic acid[9], it is distilled in the presence of neutral formates, the concentrated formic acid being above 70% strength in a single distillation. If cellulose 100 is maintained in contact 3-4 hours at 25° with a mixture of glacial acetic acid 610, sulfuric acid absolute 5,

1. E. Knoevenagel and R. Motz, Koll. Chem. Beihefte, 1921, **13**, 233; abst. J. C. S. 1921, **120**, i, 709; Kunst. 1922, **12**, 21.
2. E. Knoevenagel and K. Koenig, Cellulosechemie, 1922, **3**, 113; abst. C. A. 1923, **17**, 875; J. S. C. I. 1923, **42**, 140-A; J. Text. Inst. 1923, **14**, 42-A; Caout. et Gutta. 1923, **20**, 11991.
3. D. R. P. 297504; abst. Chem. Zentr. 1917, I, 1038. See Ital. P. 182982.
4. Knoll & Co., D. R. P. 305348, Addn. to 297504; 303530; abst. Chem. Zentr. 1918, I, 977.
5. *Ibid.* D. R. P. 305884, Addn. to 297504, 303530, 305348; abst. Chem. Zentr. 1918, II, 236.
6. *Ibid.* D. R. P. 306131; abst. Chem. Zentr. 1918, II, 325. D. R. P. 347817; Addn. to 297504; abst. J. S. C. I. 1922, **41**, 410-A.
7. *Ibid.* D. R. P. 346672; abst. Chem. Zentr. 1922, II, 487.
8. *Ibid.* D. R. P. 384726.
9. R. Koepp & Co. and E. Eloed, D. R. P. 416072, Addn. to 391300; abst. J. S. C. I. 1925, **44**, 971-B. Swiss P. 131825.

acetic anhydride 50, the cellulose rapidly disintegrates and passes into solution. By then adding acetic anhydride 250 and maintaining a temperature of 40° for 1-2 hours, a cellulose acetate insoluble in chloroform results[1]. A preparation for sealing bottles to prevent evaporation and consequent losses, consists of dissolved cellulose acetate high in flexilizers[2]. The toxicity of gaseous carbon bisulfide, ether, chloroform and tetrachlorethane has been dealt with by E. Kohn[3].

Sterno, a solidified liquid fuel[4] comprising nitrocellulose coagulated by a precipitant, may be improved by the use of a cellulose acetate solution as the coagulant, that form of hydrolyzed acetylcellulose known as Sericose, having been found most satisfactory. Theroz is a similar "canned heat." Dioxydiethylsulfide (dihydroxydiethylsulfide) esters of formic, acetic, benzoic or phthalic acid, thiodiglycol or its sulfate[5] have been patented as softening agents in film manufacture.

Cellulose acetate sheets may be decorated by means of atomization (spray process)[6], this being carried out preferably in a partial vacuum and with cooling of the material to prevent its decomposition. In the coating of wires with cellulose acetate solution[7], the wire under tension is conducted through the coating substance, and then through a tube the diameter of which is adjusted to remove the

1. J. Koetschet, M. Beudet and Soc. Chim. des Usines du Rhone, U. S. P. 1389250; abst. C. A. 1922, **16**, 162; J. S. C. I. 1922, **41**, 855-A; Mon. Sci. 1922, (5), **12**, 69; Phot. Abst. 1922, **2**, 95. E. P. 146092; Addn. to 13696, 1914; abst. C. A. 1920, **14**, 3529; J. S. C. I. 1921, **40**, 765-A; Phot. Abst. 1921, **4**, 130; Chem. Met. Eng. 1920, **23**, 1132; Paper, 1921, **28**, 111. Belg. P. 291920. Swiss P. 96140; Addn. to 68996; abst. Kunst. 1923, **13**, 35; Chem. Ztg. 1922, **46**, 730. Cites U. S. P. 1258913.
2. R. Koehler, Farben-Ztg. 1924, **30**, 690; abst. C. A. 1925, **19**, 1034.
3. Kunst. 1924, **14**, 101.
4. H. Kranich, U. S. P. 1503835.
5. G. Kränzlein and M. Corell, U. S. P. 1422869; abst. C. A. 1922, **16**, 3094.
6. V. van der Laan, D. R. P. 415823; Addn. to 407213; abst. Plastics, 1925, **1**, #3, 73.
7. J. Lahousse, U. S. P. 1498738.

amount of excess solution required. In this manner it is possible to deposit upon the wire a predetermined weight of cellulose ester. The general uses of acetylcellulose[1] were set forth by A. Lang in 1921.

E. Langfeldt[2] has devised a paint efficacious for preventing rusting of ship's bottoms by a combination of coal-tar 130, cellulose acetate 15, acetone or tetrachlorethane 285. The coal-tar seems too high in proportion to the amount of cellulose acetate recommended. A. Laska[3] has described the manufacture of phenylcresyl-, phenylxylyl-, cresylxylyl-phosphate as cellulose ester plastifying bodies. L. Lawrie[4] in 1924, contributed various methods of dyeing acetate silk with its behavior towards the chemicals used in the dyehouse[5], and including the Ionamines[6], soluble bisulfite compounds of insoluble azo dyestuffs[7], carboxyl derivatives of various dyestuffs[8], colloidal suspensions of dyestuffs[9], and the use of Celloxane[10].

The recuperation of solvents from acetate dope in the airplane industry has been dilated upon by Lebrun[11]. The combination of cellulose acetate and coumarone resin in appropriate solvents[12], produces an excellent lacquer, especially for application to surfaces of wood. W. Leigh-Barnett[13] reviewed the various cellulose acetate manufac-

1. Chem. Ztg., 1921, **45**, 76; Chem. Tech. Uebers, 1922, **46**, 202.
2. U. S. P. 1397103; abst. C. A. 1922, **16**, 653.
3. A. Laska and H. Prillwitz, U. S. P. 1425392, 1425393.
4. Chem. Age (London), 1924, 12.
5. L. Lawrie, J. Soc. Dyers Col. 1924, **40**, 69; abst. C. A. 1924, **18**, 1575; J. S. C. I. 1924, **43**, 331-B; Faser. 1924, **6**, 37.
6. 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.
7. E. P. 204280; abst. C. A. 1924, **18**, 909; D. R. P. 420017; abst. J. S. C. I. 1926, **45**, 317-B. Belg. P. 309771.
8. E. P. 202157; abst. J. S. C. I. 1923, **42**, 972-A.
9. E. P. 179384; abst. C. A. 1922, **16**, 3402; J. S. C. I. 1922, **41**, 543-A; Chem. Ztg. 1922, **46**, 919; Chem. Tech. Uebers, 1922, **46**, 318.
10. E. P. 182830; abst. C. A. 1922, **16**, 4356; J. S. C. I. 1922, **41**, 616-A, 666-A.
11. Caout. et Gutta. 1921, **18**, 11156.
12. F. Lehmann, F. P. 471104; abst. J. S. C. I. 1915, **34**, 187. F. P. 469925; abst. J. S. C. I. 1915, **34**, 25.
13. J. S. C. I. 1921, **40**, 8-T; reprinted Kunst. 1921, **11**, 35.

turing processes in 1921, and described some esters formed by the action of chloracyl chloride upon cellulose[1]. Cellulose acetonitrates (nitroacetylcelluloses) are formed when cellulose is nitrated in the usual manner, and then acetylated with a mixture of acetic anhydride 2 parts, acetic acid 1 and phosphoric acid as catalyst[2]. The product is soluble in formic acid and benzene-phenol, insoluble in acetone, ether-alcohol, glacial acetic acid or nitrobenzene. Threads made of this solution[3] are precipitated in a formic acid or benzene-phenol bath. The H. Levey process of cellulose acetate manufacture[4] involves a pretreatment of the cellulose with a chloracetic acid, after which esterization takes place in the presence of zinc chloride and acetic anhydride. He has described cellulose phthalate[5] obtained by modifying cellulose by treatment with chlorinated acetic acid as before, then treated with a mixture of phthalic anhydride and zinc chloride. The ester is practically insoluble in all solvents.

In order to remove all extraneous matter from cellulose acetate solutions intended for artificial filament formation, L. Levy[6] filters the partly hydrolyzed acetate before precipitation, using for filament manufacture solutions of 25-30% dissolved acetylcellulose[7]. Instead of employing acetic acid as the solvent in the acetylating bath[8], acetone is used instead, this procedure being claimed as especially

1. J. S. C. I. 1921, **40**, 253-T; reprinted Kunst. 1922, **12**, 26.
2. Le Verre Souple, F. P. 529173; abst. Chem. Zentr. 1922, II, 595.
3. *Ibid.* F. P. 529175; abst. Chem. Zentr. 1922, II, 595.
4. H. Levey, U. S. P. 1330543; abst. J. S. C. I. 1920, **39**, 744-A; Paper, 1921, **28**, 33; Chem. Ztg. 1920, **44**, 481; Kunst. 1920, **10**, 166; Chim. et Ind. 1922, **7**, 346.
5. J. I. E. C. 1920, **12**, 743; abst. C. A. 1920, **14**, 2705; J. S. C. I. 1920, **39**, 624-A; Paper, 1921, **28**, #4, 34; Ann. Rep. S. C. I. 1920, **5**, 324; Kunst. 1921, **11**, 20; Chim. et Ind. 1921, **5**, 575.
6. E. P. 213631; abst. C. A. 1924, **18**, 2428; J. S. C. I. 1924, **43**, 507-B.
7. L. Levy, E. P. 217003; abst. C. A. 1925, **19**, 398; J. S. C. I. 1924, **43**, 706-B.
8. *Ibid.* E. P. 226309; abst. C. A. 1925, **19**, 2131; J. S. C. I. 1925, **44**, 126-B.

advantageous where the acetylcellulose is to be converted into filaments.

S. Lewis[1] in the quantitative determination of the fluorescent powers of cellulose and its derivatives, found that unmistakable fluorescent curves are given by hydrocellulose, oxycellulose and cellulose acetate. In reducing the inflammability of cellulose derivatives as the acetate[2], a combination of calcium sulfate and triphenyl phosphate is employed. The G. Leysieffer composition[3] involves the preparation of hard, elastic masses from acetylcellulose without the addition of fillers, by using acetate previously softened with water and incorporating it with a plastifier (triacetin). Ethyl alcohol may be prepared[4], by passing over a contact body acetaldehyde, excess of hydrogen, up to 0.3% oxygen, diethyl ether not being formed. In the preparation of solid condensation products of acetylene[5], 5-15% nitrogen is added to the acetylene by means of catalysts to prevent coking and discoloration.

In the concentration of dilute (10%) solutions of acetic acid[6], the mixture is treated with a quantity of anhydrous ammonium alum 5% in excess of that required to combine with the water present, and the crystalline mass extracted in a battery on the counter-current system with a saturated solution of ammonium alum, or[7] by anhydrous sodium sulfate. In order to produce a cellulose acetate in fibrous condition (i.e. which does not pass into solution in the ester-

1. J. Soc. Dyers Col. 1924, **40**, 29, 111. See also J. Soc. Dyers Col. 1918, **34**, 167; 1921, **37**, 20; 1922, **38**, 99; abst. C. A. 1920, **14**, 3318; 1922, **16**, 2807; 1924, **18**, 1243, 2960.
2. G. Leysieffer, E. P. 206770; abst. J. S. C. I. 1924, **43**, 52-B. Ital. P. 243842.
3. E. P. 156752. D. R. P. 470579; abst. C. A. 1929, **23**, 1750. Ital. P. 237073.
4. T. Lichtenhahn, U. S. P. 1403794; abst. Chem. Met. Eng. 1922, **26**, 799. Cites U. S. P. 1311824.
5. *Ibid.* Can. P. 238888; abst. C. A. 1924, **18**, 1300.
6. F. Lichtenthaeler, U. S. P. 1492717; abst. J. S. C. I. 1924, **43**, 671-B.
7. *Ibid.* U. S. P. 1492718; abst. J. S. C. I. 1924, **43**, 671-B.

izing process) W. Lindsay[1] impregnates cellulose with benzene and alcohol and then acetylates with a mixture of acetic anhydride and benzene. He prepares non-inflammable celluloid compounds[2] by combining cellulose acetate with triphenyl phosphate and dichlorhydrin; or the former may be replaced by trichlorphenol or diphenylamine. Borneol[3] dissolved in methyl or ethyl alcohol is also an efficient acetylcellulose plastifiant. He has described the formation of decorative bodies (handles, toilet articles) of laminated acetate plastic[4].

A process for the production of cellulose butyrate has been patented[5], in which cellulose is esterified in the presence of butyric acid, butyric anhydride and sulfuric acid as catalyst. The ester is soluble in the usual acetylcellulose solvents, and claimed to dissolve in hot solvent naphtha. A cellulose acetobutyrate results when the cellulose is first treated in a preliminary impregnating bath with acetic acid and sulfuric acid[6], followed by butyration as above stated. Depending upon the ratio of acetic to butyric acids combined with the cellulose, the mixed ester dissolves somewhat in hot benzene. Plastic compositions, lacquers and dopes have been described[7] employing the butyrates. These products were tried out during the past war by the U. S. Bureau of Aircraft Production, but not used. The bleach-

1. U. S. P. 1338661; abst. C. A. 1920, **14**, 1897; J. S. C. I. 1920, **39**, 445-A; Ann. Rep. S. C. I. 1920, **5**, 136; Chim. et Ind. 1922, **7**, 762.

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

3. 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.

4. *Ibid.* U. S. P. 1506014.

5. A. D. Little, Inc., G. Esselen and H. Mork, E. P. 161564; abst. C. A. 1921, **15**, 2547; Phot. Abst. 1922, **2**, 137; J. S. C. I. 1922, **41**, 855-A; Chem. Ztg. 1922, **46**, 1094. U. S. P. 1425580; abst. J. S. C. I. 1922, **41**, 748-A.

6. *Ibid.* E. P. 167143; abst. C. A. 1922, **16**, 1152; J. S. C. I. 1922, **41**, 748-A; Chem. Eng. & Works Chem., 1921, **11**, 252; Chem. Ztg. 1922, **46**, 1051. F. P. 532145; Chem. Ztg. 1922, **46**, 10.

7. *Ibid.* E. P. 182820; abst. C. A. 1922, **16**, 4346; J. S. C. I. 1922, **41**, 894-A; Ann. Rep. S. C. I. 1922, **7**, 138; Caout. et Gutta. 1923, **20**, 11688. F. P. 532146; abst. Chem. Ztg. 1922, **46**, 10.

ing, dyeing and finishing of acetate silk was detailed by A. Little[1] in 1924.

In preparing acetoacetic acid solutions[2], methyl acetoacetate is hydrolyzed in a solution containing more than the theoretical amount of NaOH, methyl alcohol being removed by an air stream. B. Loewe has described a novel artificial silk[3] prepared by combining acetate silk with a central thread or core of real silk, the density being almost the same as natural silk. Differential dyeings may be made upon such a thread with beautiful effects. Lignosulfoacids of cellulose sulfite liquors, so called lignoprotein[4], may be combined with cellulose acetate by means of mutual organic solvents to produce compounds having decided plastic properties, the difficulty being to economically remove the color from the lignoprotein.

The F. Lovejoy photographic film[5] is formed of a relatively tough base layer of cellulose acetate composition, with an over layer of nitrocellulose on which the photographically sensitive coating is placed. A. Luttringer[6] has described the higher fatty acid esters of cellulose (mono-, di-, and tri-stearate, palmitate, laurate, ricinoleate), their methods of preparation and solubilities.

Trichlorethylene is prepared by de-chlorinating tetrachlorethane with the aid of soda and lime, the causticization being carried out at 100° or a trifle higher[7]. A. Mailhe and F. de Godon[8] have described advances in the preparation of acetic acid by the "dry" method. An artificial mass

1. A. Little, Am. Dyestuff Rep. 1924, **13**, 5; abst. C. A. 1924, **18**, 906.
2. G. Ljunggren, Biochem. Z. 1924, **145**, 422; abst. C. A. 1925, **19**, 470; J. C. S. 1924, **126**, i, 706.
3. E. P. 213908; abst. C. A. 1924, **18**, 2610; J. S. C. I. 1924, **43**, 742-B; D. R. P. 476005; abst. C. A. 1929, **23**, 3808. India P. 10235, 1924.
4. R. Loeffler, U. S. P. 1464949.
5. F. Lovejoy, U. S. P. 1518409; abst. C. A. 1925, **19**, 446; J. S. C. I. 1925, **44**, 152-B.
6. A. Luttringer, Caout. et Gutta. 1923, **20**, 11960.
7. J. MacMillan, U. S. P. 1397134; abst. Chem. Tech. Uebers, 1922, **46**, 3.
8. Bull. Soc. Chim. 1920, **27**, 330; abst. C. A. 1920, **14**, 2488; Caout. et Gutta. 1922, **19**, 11424. Belg. P. 287312.

from tar oils and formaldehyde which combines with acetylcellulose to produce rubber-like products[1], is obtainable when an organic halogen compound (carbon tetrachloride, acetyl bromide, ethyl chloride, benzyl bromide, bromoform, chloral, ethyl iodide) is added through a reflex condenser to a boiling mixture of tar-oil (cresol) and formaldehyde.

E. Mardles has investigated the scattering of light by organosols and gels of cellulose acetate[2], and finds that when a cone of light from an electric lamp is passed horizontally just below the surface of a sol or gel in a nephelometer tube, scattered light passes up the tube, a quantitative measurement of this light indicating the Tyndall number, the amount of light scattered by a chosen sample of castor oil at 20° being taken as unity. In an unstirred system, the Tyndall number increases rapidly with the concentration up to a maximum of 0.006 for cellulose acetate in benzyl alcohol, further increase causing a decrease in the number. He has determined the relative solvent power of single and mixed liquids for cellulose acetates, nitroacetates and chloracetates[3], by investigating the temperature at which precipitation occurs on cooling. In general, the solvent power and degree of dispersion of the cellulose esters are highest under conditions which admit of the greatest molecular attraction between the dispersed phase and the dispersing medium. A very comprehensive investigation. The correlation of solvent power and viscosity[4], and the elasticity of organogels of cellulose acetate[5] have also been determined, as well as the simple viscosity of dissolved acetylcellulose[6].

1. R. Mannesmann, Swiss P. 85870; abst. Kunst. 1921, **11**, 47.
2. E. Mardles, Trans. Faraday Soc., preprint 1922; abst. C. A. 1923, **17**, 909.
3. J. S. C. I. 1923, **42**, 127-A; abst. J. C. S. 1923, **124**, i, 443.
4. E. Mardles, J. S. C. I. 1923, **42**, 207-T.
5. *Ibid.* Trans. Faraday Soc., (Advance proof), Jan. 15, 1923; abst. J. S. C. I. 1923, **42**, 178-A; C. A. 1923, **17**, 2663. (Advance proof), May 14, 1923; abst. J. S. C. I. 1923, **42**, 649-A; Caout. et Gutta. 1923, **20**, 12024.
6. *Ibid.* J. C. S. 1923, **123**, 1951; abst. C. A. 1923, **17**, 3788; J. S. C. I. 1923, **42**, 970-A; J. C. S. 1923, **124**, i, 900. J. C. S. 1924, **125**, 2244. See I. Masson and R. McCall, J. C. S. 1920, **117**, 819.

A description was published in 1924 of the various technical methods of synthesizing monochloracetic acid[1]. Fabrics are woven from incompletely mercerized cotton yarn and acetylcellulose yarn and the composite fabric is then subjected to the action of a mercerizing bath maintained at a sufficiently low temperature (15° or lower) to inhibit reaction on the acetylcellulose. Differential dyeings are then possible[2]. By means of high-boiling plastifiants[3], finely divided cellulose and cellulose acetate may be combined to form molded articles, or phenol or cresol fused with an arylated or alkylated sulfamide may be used as a gelatinant[4].

In the preparation of non-scatterable glass[5], a core of acetated cellulose is imprisoned between two sheets of glass which have had a thin layer of gelatin coated on their inner sides to increase adhesion. The gelatin may be in a layer or film, or may be in the form of a hot solution flowed on the glass[6] (a fine patentable distinction). M. Mashino[7] prepares acetic anhydride by heating sulfur monochloride and sodium acetate under agitation, using powdered antimony as catalyst. Acetaldehyde results in a continous manner[8] in the usual way, but using a greatly diluted acid containing mercury salts as catalyst. Low temperatures and pressures as little as possible above atmospheric con-

1. J. Marqués, Quimica e industria, **1**, 59; Chem. Zentr. 1924, II, 2159; abst. C. A. 1925, **19**, 3082.

2. W. Marshall, U. S. P. 1511741; abst. C. A. 1925, **19**, 183. E. P. 210484; abst. J. S. C. I. 1924, **43**, 290-B; C. A. 1924, **18**, 1757.

3. C. Martin, F. P. 519822; abst. Chim. et Ind. 1922, **7**, 762; Chem. Zentr. 1921, IV, 499. Belg. P. 288151.

4. *Ibid.* F. P. 573701; abst. Plastics, 1925, **1**, 73. Belg. P. 313229.

5. L. Mascart, U. S. P. 1342267.

6. *Ibid.* U. S. P. 1342268.

7. M. Mashino, J. Chem. Ind., Japan, 1921, **24**, 1023; abst. J. S. C. I. 1921, **40**, 826-A.

8. H. Matheson, U. S. P. 1384842; abst. C. A. 1921, **15**, 3850.

ditions are used[1], no aldehyde resin being formed. Acetic acid results from passing the aldehyde and air under 120 lb. per square inch in the presence of manganese acetate as catalyst[2]. If the acetaldehyde is cooled to about 0° and 10% caustic soda in water-alcohol added with stirring[3], an almost quantitative yield of acetaldol takes place.

As a serviceable acetylcellulose plastic[4], ethylidene diacetate 30%, tricresyl phosphate 20%, alcohol 70% added to cellulose acetate has received patent recognition. In the production of ethylidene esters[5], mercury oxide is dissolved in acetic acid, sulfur trioxide added to combine with water to form an acid which precipitates the diacetate as an anhydrous mercury salt, acetylene being passed through the mixture to produce ethylidene diacetate. In chlorinating acetylene[6], A. Maze passes acetylene into a solution of alkali hydroxide or carbonate saturated with chlorine to form dichlorethylene and tetrachlorethane.

An anastatic photographic film has been described by A. McDaniel[7], in which a nitrocellulose film carrying a sensitized coating has superposed on it a cellulose acetate compound containing calcium chloride or other hygroscopic substance to prevent "static" markings. Mehren[8] has discussed the patent literature relating to solvents for cellulose

1. H. Matheson, U. S. Reissue 15434 to 1384842; abst. C. A. 1922, **16**, 3665.

2. *Ibid.* U. S. P. 1410207; abst. J. S. C. I. 1922, **41**, 347-A. E. P. 132558; abst. J. S. C. I. 1919, **38**, 846-A. U. S. P. 1676454; abst. C. A. 1928, **22**, 3170. J. S. C. I. 1928, **47**, 666-B. Can. P. 247519; abst. C. A. 1925, **19**, 2346.

3. *Ibid.* U. S. P. 1450984.

4. *Ibid.* U. S. P. 1488608; abst. C. A. 1924, **18**, 1908; Chem. Age. 1924, **32**, 206. Can. P. 198972.

5. H. Matheson and F. Skirrow, Can. P. 237664; abst. C. A. 1924, **18**, 988.

6. U. S. P. 1425669; abst. C. A. 1922, **16**, 3314.

7. U. S. P. 1431894; abst. C. A. 1922, **16**, 4152; J. S. C. I. 1922, **41**, 917-A; Phot. Abst. 1923, **3**, 15. Cites U. S. P. 584862, 1232702. E. P. 7501, 1892; 13088, 1913. D. R. P. 69231.

8. Kunst. 1922, **12**, 99; abst. C. A. 1922, **16**, 3548; Chem. Zentr. 1922, IV, 799.

esters. C. Meigs[1] has described an artificial silk obtained by dissolving a mixture of cotton and cellulose acetate in ammoniacal copper hydroxide (which, of course, saponifies the cellulose acetate), the solution being then spun into sulfuric acid as the precipitant.

In the manufacture of cellulose from wood by the sodium sulfate process, a liquid resin is produced called "talloel," which forms a precipitate by settlement after the reaction mass has been leached. This talloel may be hydrogenated in the presence of nickel to liquids of an acid nature which have a dissolving effect upon acetated cellulose[2]. Hydrogenation may be applied to the distillate[3]. Acetic acid may be simultaneously purified and decolorized by treatment with reducing agents as nascent hydrogen, hydrogen sulfide, sulfur dioxide, hydriodic acid[4] or stannous chloride[5].

The G. Miles plastic[6] comprises cellulose acetate combined with the fatty acids (caproic, caprylic, capric) obtained from cocoanut oil, in the presence of a volatile solvent. He produces a moldable composition by combining acetylcellulose with about 3% glycerol[7]. Silica gel is claimed to be a better catalyst than either thorium or titanium oxides for esterification in the vapor phase[8]. When a mixture of alcohol and acetic acid vapor is slowly passed

1. C. Meigs, U. S. P. 1471699; abst. C. A. 1924, **18**, 173.
2. M. Melamid, E. P. 143187; abst. Kunst. 1921, **11**, 6. E. P. 169962.
3. *Ibid.* E. P. 170562, Addn. to 169962.
4. K. Meyer, Zts. ang. Chem. 1923, **36**, 169; abst. C. A. 1923, **17**, 2106.
5. A. Milani, F. P. 532826; abst. Chem. Ztg. 1922, **46**, 239; Chem. Zentr. 1923, II, 908.
6. G. Miles, U. S. P. 1357335; abst. C. A. 1921, **15**, 314; J. S. C. I. 1921, **40**, 7-A; Paper, 1921, **27**, #21, 27; Kunst. 1921, **11**, 167; Chem. Tech. Ueber. 1921, **45**, 99; Caout. et Gutta. 1921, **18**, 11074. E. P. 146212; abst. C. A. 1920, **14**, 3528; Chem. Met. Eng. 1920, **23**, 1036; Phot. Abst. 1921, **4**, 130; Paper, 1921, **28**, #3, 35.
7. *Ibid.* U. S. P. 1394752; abst. C. A. 1922, **16**, 494; J. S. C. I. 1921, **40**, 886-A; Phot. Abst. 1922, **2**, 14; Mon. Sci. 1922, (5), **12**, 69.
8. C. Milligan, J. Chappell and E. Reid, J. Phys. Chem. 1924, **28**, 872; abst. J. S. C. I. 1924, **43**, 847-B.

over silica gel at 150° a 90% yield of ethyl acetate is obtained.

Water-resistant properties are imparted to cellulose by exposing to the action of thionyl chloride, either with or without the addition of indifferent solvents (chloroform, carbon tetrachloride)[1]. Acetic anhydride may be prepared by treatment of sodium acetate with a mixture of nitric oxide and nitrogen tetroxide[2], results being quantitative. Plastic mixtures suitable for kneading or rolling under high pressure[3] are formed of yeast, glyceryl esters (formate, acetate, butyrate, phthalate, camphanate) and acetyl starch, sugar or cellulose, a typical mixture being dry yeast 10-40, triacetin 50, acetylcellulose 100.

In order to produce a cellulose acetate having a predetermined dyeing speed[4], various batches are blended in proportions in the presence of a solvent. If the "dyeing speed" is too slow, it may be increased by a partial saponification of the ester in one or more batches before blending[5], *then* combining selected lots[6]. E. Mueller in 1924 reviewed the German patent literature on the dyeing of acetate silk[7]. R. Mueller[8] uses wood pulp in flocculent form to produce a fibrous acetylcellulose, and has described an apparatus for carrying the process into effect.

According to W. Nauck[9], wood cellulose must be very finely subdivided for proper acetylation. Being denser than

1. F. Moeller, E. P. 145610; abst. J. S. C. I. 1921, **40**, 842-A. E. P. 145611, Addn. to 145610; abst. J. S. C. I. 1921, **40**, 843-A. E. P. 184462; abst. J. S. C. I. 1924, **43**, 12-B. U. S. P. 1499025.
2. M. Moest and E. Schirm, U. S. P. 1337253.
3. W. Mooser-Schiess, U. S. P. 1367886; abst. C. A. 1921, **15**, 1061.
4. H. Mork and C. Coffin, U. S. P. 1421288; abst. C. A. 1922, **16**, 2989; Mon. Sci. 1923, (5), **13**, 15. See U. S. P. 854374.
5. *Ibid.* U. S. P. 1421289; abst. C. A. 1922, **16**, 2989.
6. *Ibid.* U. S. P. 1421290; abst. C. A. 1922, **16**, 2989.
7. Faser. 1924, **6**, 15; abst. C. A. 1924, **18**, 1752. See D. R. P. 198008, 350921.
8. D. R. P. 400190, Addn. to 387685; abst. Chem. Zentr. 1925, I, 1664. F. P. 519840; abst. Rev. prod. Chim. 1921, **24**, 713.
9. Cellulosechemie, 1921, **2**, #5, 61; abst. C. A. 1921, **15**, 2721; Phot. Abst. 1922, **2**, 52; Kodak Abstr. Bull. 1922, **8**, 66; Kunst. 1921, **11**, 164.

cotton cellulose, wood has a smaller specific surface, takes longer to acetylate, forms a more viscous dope, and gives a tougher film. The hydrated cellulose acetate of W. Nebel[1] is prepared by disintegrating cellulose in a dilute hydrochloric acid solution in acetic acid, then acetylating in the usual manner with zinc chloride as catalyst. The ester formed is soluble in acetone, diacetone alcohol, methylethyl ketone and benzaldehyde; insoluble in chloroform, ethyl alcohol and amyl acetate. A liquid mixture adapted for waterproofing collars and cuffs is prepared from acetone 100, cellulose triacetate 6, triphenyl phosphate 3, castor oil 0.25-0.50, zinc oxide and lithopone 3, with 0.5 barium sulfate[2].

Airplane fabrics may be made fire-resistant[3] by coating with cellulose acetate solution in which finely powdered sodium sulfate, alum or borax have been ground. A fire retardant comprises cellulose acetate dissolved in liquid sulfur dioxide[4], which causes the ester to pass into solution, even in the cold. Liquid anhydrous ammonia acts similarly[5]. The S. Ogden compositions[6] consists of asbestos impregnated with acetated cellulose. Acetic acid may be purified by distillation with 2% of its weight of chromium trioxide[7], the first 5% being rejected.

In order to produce nacreous or chatoyant effects with cellulose acetate solutions[8], finely divided goldfish scales, pulverized mother-of-pearl, ground cat's eye or moonstone particles are incorporated therewith, and the volatile sol-

1. U. S. P. 1478137; abst. C. A. 1924, **18**, 752; J. S. C. I. 1924, **43**, 129-B.
2. A. Neusella, U. S. P. 1453764; abst. C. A. 1923, **17**, 2367.
3. G. Nikolas, U. S. P. 1429295; abst. C. A. 1922, **16**, 4070.
4. Nitrogen Corp. and J. Clancy, E. P. 189416; abst. J. S. C. I. 1923, **42**, 1171-A. Ital. P. 212139.
5. *Ibid.* 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.
6. Can. P. 223046.
7. K. Orton and A. Bradfield, J. C. S. 1924, **125**, 960; abst. C. A. 1924, **18**, 2127; J. S. C. I. 1924, **43**, 535-B; J. C. S. 1924, **126**, i, 607.
8. J. Paisseau, E. P. 207144.

vent evaporated. Ammonium, sodium, potassium or calcium thiocyanates, all latent solvents of acetone-soluble acetyl-cellulose[1], are used therewith to produce acetate filaments, the thiocyanate being used in the precipitating bath and afterwards removed by washing. Or[2], the acetate solution may be extruded into a setting bath containing a proportion of acetone, sufficient to induce the degree of swelling of the acetate filaments desired. P. Pavlov[3] has studied the adsorption of acetic acid by charcoal and E. Peytral[4] the thermal decomposition of acetic anhydride at high temperatures.

The surface of dielectric material as cellulose acetate[5] is coated with an aqueous silver nitrate solution which is converted into chloride with salt solution, and thence to the metal with zinc rollers in a sulfuric acid bath. Nitro- or acetyl-cellulose may be greatly reduced in viscosity by heating the same to about 120° in an autoclave for several hours[6]. L. Pittinger has described the preparation and properties of mono*iso*propyl-, monopropyl-, mono*iso*butyl-, monobutyl- and monoamyl-glycol ether, possible cellulose acetate softeners[7].

H. Platt has given directions for dyeing Celanese (cellulose acetate)[8], and H. Plauson[9] the manufacture of colloid powders (without previously dissolving the material as cellulose acetate) by subjecting to intensive mechanical

1. C. Palmer and W. Dickie, U. S. P. 1465994; abst. C. A. 1923, **17**, 3919.
2. *Ibid.* U .S. P. 1467493; abst. C. A. 1923, **17**, 3789.
3. Kolloid Zts. 1924, **35**, 225; abst. J. S. C. I. 1924, **43**, 1010.
4. Bull. Soc. Chim. 1922, **31**, 113; abst. J. S. C. I. 1922, **41**, 196-A; J. C. S. 1922, **122**, i, 219. Bull. Soc. Chim. 1924, **35**, 969; abst. C. A. 1925, **19**, 38. See also J. C. S. 1918, **114**, i, 1; 1920, **118**, i, 217; 1921, **120**, i, 156.
5. E. Pfiffner, D. R. P. 407888; abst. J. S. C. I. 1925, **44**, 364-B.
6. A. Phillips, U. S. P. 1411669; abst. J. S. C. I. 1922, **41**, 393-A; Chem. Ztg. 1922, **46**, 797; Chem. Tech. Uebers, 1922, **46**, 309. E. P. 177536; abst. J. S. C. I. 1923, **42**, 1126-A. F. P. 549265; abst. Caout. et Gutta. 1924, **21**, 12092; Chim. et Ind. 1923, **10**, 1130.
7. J. A. C. S. 1924, **46**, 1503; abst. J. C. S. 1924, **126**, i, 826.
8. Proc. Am. Assoc. Textile Chem. Colorists, 1924, 99; Am. Dyestuff Rept. 1924, **13**, 255; abst. C. A. 1924, **18**, 1752.
9. U. S. P. 1392849; abst. C. A. 1922, **16**, 452.

disintegration followed by separation of the liquid dispersion medium. The products obtained from acetone-soluble cellulose acetate with a 3.5% solution in acetone in xylene, may be used for varnishes or artificial leather manufacture. Artificial wood results from combining acetylcellulose with a filler and a resin condensed from an aldehyde and a ketone by an alkaline condensing agent[1].

Vinyl acetate and ethylidene diacetate may be prepared by heating acetylene with dry hydrochloric acid gas in the presence of a diluent gas (nitrogen, carbon monoxide)[2]. The essence of the H. Plauson acetaldehyde manufacturing method[3] is passing acetylene containing water through a porous conductive anode containing mercury phosphate, the current being supplied to the anode at a potential of at least 1.5 volts. He diminishes the amount of acetic acid required to prepare acetylcellulose[4] by submitting cellulose to the action of the acetylating agent in the vapor phase, it being possible to obtain fibrous products in which the outer portion of the filament has been acetylated and the inner portion unchanged.

Acetate silk may be dyed full shades fast to light[5], it is claimed, by immersion in colloidal suspensions of insoluble pigments (lamp-black, ultramarine, cobalt oxide, ochre, cinnabar, antimony sulfide), it being necessary that pigment particles not exceed 0.1 micron in size. Acetaldehyde may be prepared by hydrating acetylene with steam under pressure at a fairly high temperature, the reaction being facilitated by an acid as nitric[6]. As superior to the acetins

1. H. Plauson, U. S. P. 1397144.
2. H. Plauson, U. S. P. 1425130.
3. *Ibid.* F. P. 532908; abst. Chem. Ztg. 1922, **46**, 239. F. P. 532909; abst. Chem. Ztg. 1922, **46**, 239. F. P. 532913; abst. Chem. Ztg. 1922, **46**, 212. Belg. P. 295035, 295036. Can. P. 237832.
4. *Ibid.* E. P. 200160; abst. Caout. et Gutta. 1924, **21**, 12167. See E. P. 25893, 1911.
5. *Ibid.* E. P. 211178; abst. J. S. C. I. 1924, **43**, 332-B. Cites E. P. 155836; abst. J. S. C. I. 1922, **41**, 357-A.
6. H. Plauson and J. Vielle, E. P. 156152; abst. Chem. Met. Eng. 1921, **24**, 938.

as acetylcellulose gelatinants, mono-, di- and tri-butyrin have been patented[1].

When formaldehyde, or substances which split off formaldehyde[2] are added to swollen or gelatinized cellulose acetate, indurated masses result which can be worked up into molded structures and films. Glycol, glyceryl and benzyl benzoates, all high boilers[3], are said to be excellent solvents and extensifiers for acetylcellulose. A table of boiling points and compositions of vapor for different concentrations of acetic acid has been published[4]. Cellulose acetate is prepared for dyeing with the usual dye solutions by treatment with a dilute sodium hydroxide solution containing NaCl in order to insure uniform penetration of the color[5].

In order to obviate rise in temperature due to combination of water with acetic anhydride in the esterization of cellulose[6], M. Putnam acetylates in the usual manner, then hydrolyzes the product by adding to it a mixture of previously hydrolyzed cellulose acetate and excess of the hydrolyzing solution. He has patented as a desirable acetylcellulose dissolvant[7], ethylene chlorhydrin 5-25, ethyl alcohol

1. W. Plinatus, F. P. 581651; abst. Chem. Zentr. 1926, I, 2522. E. P. 246272; abst. C. A. 1927, **21**, 496; J. S. C. I. 1926 ,**45**, 315-B.
2. F. Pollak, Aust. P. 87713, 87720; abst. Chem. Zentr. 1922, IV, 907. See D. R. P. 210519, 238348, 254385. F. P. 412797.
3. A. Pouteaux, F. P. 541643; abst. Chem. Zentr. 1923, II, 642.
4. G. Povarnin and V. Markov, J. Russ. Phys. Chem. Soc. 1924, **55**, 381; abst. C. A. 1925, **19**, 2438.
5. E. Prince and Soc. Chim. des Usines du Rhone, 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. E. P. 150989; abst. J. S. C. I. 1921, **40**, 692-A; Textilber. 1921, **3**, 20; Chem. Ztg. 1922, **46**, 10. Swiss P. 90096; abst. Chem. Ztg. 1921, **45**, 617. Swiss P. 100109. Cites U. S. P. 1061771.
6. U. S. P. 1396878; abst. C. A. 1922, **16**, 646; J. S. C. I. 1922, **41**, 10-A; Chem. Ztg. 1922, **46**, 59.
7. M. Putnam and W. Kirst, U. S. P. 1406224; abst. Chem. Met. Eng. 1922, **26**, 799; Phot. Abst. 1922, **2**, 95; Kodak Abstr. Bull. 1922, **8**, 206; J. S. C. I. 1922, **41**, 248-A; Chem. Tech. Uebers, 1922, **46**, 130; Caout. et Gutta. 1922, **19**, 11653.

15-45, benzene 60-25. J. Ramsbottom[1] discussed the application of airplane dopes of acetylcellulose in 1924, and the factors of humidity, tautness, tension and extensibility of fabrics acetate coated and pigmented, and B. Rassow[2] has reviewed the properties of the formylcelluloses.

Diethyl tartrate 12, with cellulose acetate 10, produces a desirable plastic useful for film formation[3]. Transparent or opaque coatings with cellulose acetate are obtainable by coating an object with a solution of the ester in a volatile solvent, then treating with water or acidified solution to precipitate the ester on the article to be covered[4]. In 1923 appeared an article on the solvent properties of acetone for acetylcellulose and other bodies[5]. To prepare cellulose acetate filaments or fabrics for dyeing[6], they are subjected to a limited alkaline treatment in an aqueous bath containing sodium acetate.

The C. Robinson composite board is prepared from a multi-ply paper stock in which the individual plies are agglutinated with an acetylcellulose solution in a volatile solvent with a relatively small amount of softener[7], the compound board[8] being rendered more fire-resistant by incorporation of fire-retardants in the acetylcellulose solution. As a substitute for celluloid and vulcanite[9], phenol-alde-

1. Journ. of the Royal Aeronautical Society, May, 1924, 273; Jour. Soc. Automotive Engineers, 1924, (Aug.) 16; Trans. Faraday Soc. 1924, **20**, 245; abst. C. A. 1924, **18**, 2608. Trans. Faraday Soc., 1924, **20**, 295; abst. J. S. C. I. 1925, **44**, 238-B.
2. Chem. Zts. 1922, **46**, 886; abst. Ann. Rep. S. C. I. 1922, **7**, 138.
3. F. Redlich, D. R. P. 304224; abst. Chem. Zentr. 1920, II, 38.
4. J. Reitstoetter, D. R. P. 375274; abst. J. S. C. I. 1923, **42**, 898-A.
5. R. Remler, Ind. Eng. Chem., 1923, July, 717; abst. India Rubber W. 1923, **69**, 28.
6. L. Richardson, U. S. P. 1442631; abst. Chem. Met. Eng. 1923, **28**, 735; C. A. 1923, **17**, 1154. See Rheinische Westfallische Sprengstoff A. G. F. P. Appl. 16073, 1921; 8515, 1922. E. P. Appl. 16823.
7. C. Robinson, U. S. P. 1334637.
8. *Ibid.* U. S. P. 1344962.
9. W. Robinson-Bindley and A. Weller, U. S. P. 1331127; abst. Chem. Ztg. 1920, **44**, 481. E. P. 145128; abst. Chem. Ztg. 1920, **44**, 617.

hyde condensation products are incorporated in a cellulose lacquer, and the solution sprayed or brushed on the object to be coated, or the volatile solvents evaporated until a semi-solid, moldable mass results.

K. Roka[1] passes acetylene 1 and chlorine 2 simultaneously through a 40 mm. clay pipe 60 cm. long with superheated steam at 500° at a velocity of 15 liters acetylene per hour, di- and tri-chlorethylene being formed. According to H. Ross[2] airplane fabrics are best waterproofed and tautened by applying thereto cellulose acetate 10, triphenyl phosphate 3-4, and then a top coat of cellulose acetate 10, triphenyl phosphate 6-7. Propylenechlorhydrin may also be added[3]. Details of volatile solvent recovery by the Bregeat process were published[4] in 1921.

In the manufacture of hollow, artificial textile articles[5], there is incorporated with a cellulose acetate solution a carbonate, which will evolve a gas upon extrusion into the acid precipitating bath. Dry kelp contains about 90% alginic acid (algin). A. Rowland has described the use of metallic alginates (sodium, aluminum, zinc) as additions to acetylcellulose solutions for coating airplanes[6]. L. Rutstein[7] gave a summary of our knowledge of the manufacture of artificial silk in 1920.

A. St. John[8] uses "a mixed phenyl-cresyl phosphate containing one or more molecules of cresol and of phenol" as an acetylcellulose plastifiant, monocresyldiphenyl phosphate being specified. In the D. Sakom method of acetaldehyde preparation[9], a stream of acetylene entering the

1. U. S. P. 1418882.
2. Can. P. 200433.
3. H. Ross and Pratt & Lambert, U. S. P. 1440178; abst. C. A. 1923, **17**, 1157; J. S. C. I. 1923, **42**, 712-A. Can. P. 198265.
4. M. Roulleux and R. Dort, Chem. Met. Eng. 1921, **24**, 916; abst. C. A. 1921, **15**, 2521.
5. J. Rousset, U. S. P. 1427330.
6. A. Rowland, U. S. P. 1395016.
7. L. Rutstein, Chem. Age (N. Y.), 1920, **29**, 297; abst. Chim. et Ind. 1921, **6**, 817.
8. A. St. John, U. S. P. 1462306.
9. D. R. P. 389403; abst. J. S. C. I. 1924, **43**, 449-B.

lower end of a reaction vessel is treated with a countercurrent of a finely divided stream of a solution of sulfuric or arsenic acids containing mercuric oxide, acetaldehyde being led off from the top of the reaction vessel. W. Sanderson[1] has detailed the methods for dyeing acetate silk with directions for the use of about 60 dyes.

In producing a plate made ready for printing[2], a sheet of transparent cellulose acetate is covered on both sides with sensitized gelatin, then exposed to light through a negative and developed in the usual manner. The relief formed on the side adjacent to the negative forms the printing surface and the obverse side the make-ready. Absolute protection against fire in airplane fabrics is said to result by coating with a cellulose acetate solution to which dry ammonium sulfate and sodium stannate has been added, the double decomposition between the two salts resulting in the formation of ammonia and hydrated stannic oxide (stannic acid)[3]. The fabric may be "opened up" by pretreatment with hydrofluoric acid[4]. In producing trichlorhydrin or trichlorpropane[5], dichlorpropylene is treated with chlorine in the presence of iodine chloride, phosphorous or aluminum chloride. A. Schamelhout[6] has published a monograph on acetone, proposed for introduction into the Belgian National Formulary.

A non-inflammable celluloid substitute has been described[7], composed of a homogeneous mixture of acetyl-

1. J. Soc. Dyers Col. 1922, **38**, 162; abst. C. A. 1923, **17**, 211; Am. Dyestuff Rep. 1922, **11**, 6; Chem. Tech. Uebers, 1923, **47**, 47.
2. E. Sauer, E. P. 151405; abst. C. A. 1921, **15**, 477; Chem. Ztg. 1922, **46**, 271.
3. C. Saunders, G. Stanley and C. Bennett, U. S. P. 1358250.
4. *Ibid.* U. S. P. 1399026.
5. H. Saunders and L. Sutherland, U. S. P. 1362355; abst. Chem. Tech. Uebers, 1921, **45**, 103.
6. J. pharm. Belg. 1919, **1**, 890; 1920, **2**, 205; abst. C. A. 1920, **14**, 1870.
7. F. Schaurich, Kunst. 1920, **10**, 207; abst. Kodak Abstr. Bull. 1921, **7**, 112; Phot. Abst. 1921, **2**, 42.

cellulose with casein. W. Scheele[1] prepares cellulose for acetylation by treating with a mixed solution of hydrogen dioxide and sodium peroxide, washing free from alkali, drying and acetylating in the usual manner. This cellulose acetate when dried and mixed with an equal weight of finely ground Manila copal and methylethyl ketone used as solvent[2] becomes suitable for film formation. The incorporation of camphor in the composition augments the plasticity.

In preparing negative papers that are to be dry stripped[3], the paper is first subbed with rubber or rosin size and then coated with plastic cellulose acetate, which after stripping, reinforces the (finally coated) gelatino-bromide film. In the manufacture of formic acid[4], the kneading together of formate and acid and the distillation of the formic acid are combined in a single operation under vacuum. Waste cellulose acetate scrap is brought into a homogeneous form by means of a limited amount of solvent[5] and then subjecting it to high pressure at 90-100°. From this uniform mass, articles are fabricated. W. Schrauth[6] has given the physical and chemical properties of hexalin and heptalin and their formate and acetate, as valuable additions to cellulose esters in the lacquer industry.

E. Schulke[7] produces wool-like yarns from cellulose esters by injecting the filaments into a precipitating tank, twisting, drying, and the dry filament bundle passed through

1. W. Scheele, U. S. P. 1379699; abst. C. A. 1921, **15**, 3395; Chem. Zentr. 1921, IV, 585; Chem. Tech. Uebers, 1921, **45**, 310; Mon. Sci. 1922, (5) **12**, 5.
2. *Ibid.* U. S. P. 1408035; abst. J. S. C. I. 1922, **41**, 290-A; Mon. Sci. 1923, (5), **13**, 15; Caout. et Gutta. 1922, **19**, 11653; Chem. Ztg. 1922, **46**, 635. Cites U. S. P. 744413.
3. K. Schinzel, Phot. Korr. 1921, (May), 112.
4. A. Schloss, D. R. P. 445644; abst. J. S. C. I. 1928, **47**, 596-B; Chem. Zentr. 1927, II, 864.
5. F. Schmidt, E. P. 205463; abst. J. S. C. I. 1924, **43**, 507-B; Chem. Zentr. 1924, I, 715.
6. Farben. Ztg., **26**, 647; abst. Chem. Tech. Uebers, 1922, **46**, 59.
7. E. P. 167458. D. R. P. 342223; abst. Chem. Tech. Uebers, 1922, **46**, 97. D. R. P. 342536; abst. Chem. Tech. Uebers, 1922, **46**, 97.

a system of rough-surfaced rollers whereby they are stretched, torn and carded, the carded filaments being finally twisted into yarn. The A. Schulze optical projection-screen is prepared by roughening a screen of acetylcellulose[1], as by a sand blast, then applying petroleum jelly to both surfaces or only to the surface turned towards the spectators, a dark aspect of the screen being produced while increasing the transparency.

Solubility determinations of cellulose acetate in lithium, sodium, calcium and barium bromide and iodide; calcium nitrate or thiocyanate, potassium mercuric iodide, and zinc chloride at 15° and at 100° have been made, solutions prepared at the higher temperatures being more viscous. There is no action of the salt solutions on the acetyl group[2]. A mold for casting cements has been described[3] comprising cellulose acetate. An acetylcellulose solvent combination has been patented[4], comprising acetone and ethyl acetate with either diacetone alcohol or mesityl oxide. Methyl or ethyl phthalate may be added. The type solvent recommended is acetone 65, ethyl acetate 25, mesityl oxide 3, diacetone alcohol 7 and triacetin and triphenyl phosphate each 1.4, where acetate cinematographic films are to be cast[5]. Chlorpropyl acetate has been added to the list of cellulose ester solvents[6], boiling at 145°, practically insoluble in water and relatively stable. Propylene chlorhydrin boiling at 127° is a direct acetylcellulose solvent[7]. A waterproofing

1. A. Schulze, U. S. P. 1381022.
2. K. Schweiger, Z. physiol. Chem. 1921, **117**, 61; abst: C.A. 1922, **16**, 2599; Ann. Rep. S. C. I. 1922, **7**, 137; J. S. C. I. 1922, **41**, 323-A; J. C. S. 1922, **122**, i, 324; Caout. et Gutta. 1922, **19**, 11460; Bull. Soc. Chim. 1923, **34**, 453. See also R. Herzog and F. Beck, Z. physiol. Chem. 1920, **111**, 287; abst. J. S. C. I. 1921, **40**, 254-A. P. von Weimarn, Kolloid. Zeits, 1921, **29**, 197; abst. J. S. C. I. 1921, **40**, 842-A.
3. S. Seailles, E. P. 217605; abst. C. A. 1925, **19**, 387.
4. V. Sease, U. S. P. 1434634; abst. C. A. 1923, **17**, 467; J. S. C. I. 1923, **42**, 50-A; Chem. Ztg. 1923, **47**, 93; Caout. et Gutta. 1923, **20**, 11931.
5. *Ibid.* U. S. P. 1488294; abst. C. A. 1924, **18**, 1750; J. S. C. I. 1924, **43**, 464-B.
6. M. Seaton, U. S. P. 1397986; abst. Phot. Abst. 1922, **2**, 54; Kodak Abstr. Bull. 1922, **8**, 73.
7. *Ibid.* U. S. P. 1480016.

composition of caoutchouc 2, cellulose acetate 6, tetrachlorethane 60 has been brought forward. They are preferably dissolved separately and then mixed[1].

Five patents were issued to P. Seel during this period 1920-1924 in the cellulose ester art, embracing a composition with liquid chloro-substituted naphthalenes or anthracenes[2], transparent, flexible film of camphor and these chlorine derivatives[3]; a composition of acetylcellulose and ethyl propionate[4]; combinations of fusel oil with triphenyl phosphate[5]; and a method for the manufacture of cellulose acetate[6]. In acetylating cellulose, a circulation of air is maintained through the liquid reaction mixture containing acetic acid, the acid vapor being separated from the air by condensation. Circulation of air is continued until the reaction mixture becomes a powdery mass, after which further reaction mixture is stirred into the mass and the above treatment continued. Catalytic preparation of ethyl-, propyl-, *iso*propyl, butyl, *iso*butyl- and *iso*amyl-ether has been described[7], together with their physical properties.

In the manufacture of synthetic acetic acid[8], the introduction of an alkaline earth during the distillation step is said to increase the yield. In preparing copying foils for photo-mechanical transfer purposes[9], in place of the usual tissue paper, plastic acetylcellulose is used as the carrier, bearer or foundation for the copying foil. Radio-

1. J. See, U. S. P. 1431845; abst. C. A. 1922, **16**, 4308.
2. U. S. P. 1342601; abst. C. A. 1920, **14**, 2418; J. S. C. I. 1920, **39**, 541-A; Chem. Ztg. 1920, **44**, 645.
3. U. S. P. 1342602; abst. C. A. 1920, **14**, 2418.
4. U. S. P. 1342603; abst. C. A. 1920, **14**, 2418; Chem. Ztg. 1920, **44**, 645.
5. U. S. P. 1379596; abst. C. A. 1921, **15**, 3255.
6. U. S. P. 1494816; abst. C. A. 1924, **18**, 2249; J. S. C. I. 1924, **43**, 669-B.
7. J. Senderens, Compt. rend. 1924, **178**, 1412; abst. C. A. 1925, **19**, 2194. See also Compt. rend. 1923, **177**, 1183; abst. C. A. 1924, **18**, 823.
8. A. Serret, F. P. 525337; abst. Chim. et Ind. 1922, **7**, 740. Chem. Zentr. 1922, IV, 43.
9. E. Seyfferth, U. S. P. 1499844; abst. C. A. 1924, **18**, 2810. E. P. 196008, 196324, Addn. of 196008. Can. P. 227269. See also E. P. 18189, 1910; 27258, 1910.

active substances are incorporated with cellulose acetate highly plastified and sheets or objects made therefrom[1], the products being sufficiently supple to readily bend to the shape of the body. These radio-active molds are readily cleaned without loss of radio-active material, and can be made to yield a predetermined quantity of emanation per unit area.

Vinyl esters are producable by bringing together acetylene and a carboxylic acid in presence of a catalyst, and continually removing the vinyl ester as formed[2]. Acid substances may be removed from cellulose acetate bodies having a large surface in proportion to their mass, as film[3], by washing them with a strong solution of a salt. Lead suboxide is prepared by oxidizing pieces of lead with air in a ball mill with steel balls which abrade the oxide from the surface of the lead as the action proceeds. An anti-corrosive and anti-fouling paint may be formed by mixing this powder with cellulose acetate[4].

A mixture of *o*- and *p*-oxybenzyl alcohol obtained by condensing formaldehyde, paraldehyde or trioxymethylene with phenol in presence of alkali with the subsequent addition of an acid as acetic[5], when added to acetylcellulose compositions, induces flexibility and durability to films produced therefrom. As an insulating material for electrical purposes[6], natural bitumen is combined with cellulose acetate by means of a mutual solvent as tetrachlorethane. In the manufacture of propellent explosives of the type which give little smoke and no flame[7] (flameless powder), cellu-

1. E. Seyfferth and Rheinisch-Westfälische Sprengstoff A.-G., E. P. 196518; abst. J. S. C. I. 1923, **42**, 430-A, 712-A.
2. Shawinigan Laboratories, Ltd., Can. P. 237841. Norw. P. 32676, 35854.
3. S. Sheppard, U. S. P. 1357733; abst. C. A. 1921, **15**, 314; J. S. C. I. 1921, **40**, 7-A; Kunst. 1922, **12**, 23.
4. G. Shimadzu, E. P. 215222; abst. C. A. 1924, **18**, 2968.
5. Soc. Anon. des Etablissments J. Dupont, E. P. 168838.
6. Siemens-Schuckertwerke, G. m. b. H., E. P. 156527.
7. O. Silberrad, U. S. P. 1349983.

lose acetate is incorporated with the nitrocellulose to reduce the flame on combustion.

Acetate silk is dyed in yellow to red shades of excellent fastness by diphenylamine derivatives[1] produced by condensing 2.4-dinitrochlorbenzene with aromatic amines containing no sulfonic groups, as 2.4-dinitro-diphenylamine, -2′-hydroxydiphenylamine, -4′-hydroxydiphenylamine, -4′-aminodiphenylamine, -4′-carboxydiphenylamine, -4′-acetylaminodiphenylamine, -*N*-methyldiphenylamine, used in aqueous suspension or colloidal emulsion. In the production of acetic anhydride from ethylidene diacetate[2], the latter acidified with 10% acetic acid is treated with sulfur dioxide as catalyst, and the anhydride recovered by distillation.

A cellulose acetate film without camphor or other solid solvent[3] is coated by ruling thereon with fish glue solutions containing suitable dyestuffs, the glue solubilized by formaldehyde vapor, the intermediate space of the acetate film being then stained by means of a solution of a dye in aniline or nitrobenzene. Formulas are given. L. Smith[4] has described the properties of the *b*-monochlorhydrin from glycerol. Sulfurized phenol compounds may be used for mordanting acetate silk[5], best results being obtained by treating the acetate in a bath of mordant, NaOH and sodium phosphate. In the preparation of acetaldehyde from acetylene[6], the process is rendered practically continuous

1. Silver Springs Bleaching & Dyeing Co., Ltd., and A. Hall, E. P. 222001; abst. J. S. C. I. 1924, **43**, 939-B.

2. F. Skirrow, U. S. P. 1429650; abst. Chem. Tech. Uebers, 1923, **47**, 30. Cites U. S. P. 1152098, 1192816.

3. J. Smith, U. S. P. 1390252.

4. Zts. Physik Chem. 1920, **94**, 723; abst. C. A. 1920, **14**, 2630; Chem. Tech. Ueber, 1921, **45**, 25.

5. Soc. Alsacienne de Prod. Chim., E. P. 224218, Addn. to 215012; abst. C. A. 1925, **19**, 1202; J. S. C. I. 1925, **44** ,588-B.

6. Soc. anon. de Produits Chim. Etablissements Maletra, E. P. 140784; abst. C. A. 1920, **14**, 2203; J. C. S. 1921, **120**, i, 706; Chem. Met. Eng. 1920, **23**, 253. L. Trevoux, U. S. P. 1428668; abst. C. A. 1922, **16**, 3665; J. S. C. I. 1922, **41**, 838-A. E. P. 165085, Addn. to 140784; abst. C. A. 1922, **16**, 566; J. S. C. I. 1922, **41**, 838-A. U. S. P. 1436550.

where mercuric sulfate is used, if ferric oxide is periodically added to the bath.

Cellulose acetate may be prepared for dyeing by treatment with disodium phosphate (Na_2H) and NaOH, the loss in weight of acetate by this treatment being 6%. Trisodium phosphate may also be used[1]. A bath of sodium sulfate and trisodium phosphate acts similarly[2]. Acetylcellulose fabrics may be un-sized by treatment in a hot bath containing a neutral soap and potassium chloride, sulfate or phosphate (K_2H)[3]. Acetic acid or anhydride results from heating ethylidene diacetate under reduced pressure in the presence of sulfuric acid as contact substance[4], the acetic anhydride thus formed being separated from paracetaldehyde by distillation[5]. A process has been described for the preparation of chlorinated cellulose (cellulose chloride) in which chlorine is chemically combined with cellulose[6]. A process for acetylcellulose manufacture utilizing chlorinated cellulose has been worked out[7], it being claimed that only 2 parts acetic anhydride and 1.5 parts glacial acetic acid are required to esterify to the triacetate stage.

When paraldehyde is treated electrolytically in presence of sulfuric acid, acetic acid and ethyl acetate are

1. Soc. Chim. des Usines du Rhone and E. Sisley, E. P. 183806; abst. C. A. 1923, **17**, 213; J. S. C. I. 1923, **42**, 652-A; Chem. Ztg. 1923, **47**, 578. U. S. P. 1440501; abst. C. A. 1923, **17**, 1154; J. S. C. I. 1923, **42**, 180-A; Chem. Met. Eng. 1923, **28**, 225. Belg. P. 291921. Ital. P. 211190. Swiss P. 90096. See H. Mork, F. P. 416752.

2. Soc. Chim. des Usines du Rhone, E. P. 192994, Addn. to 150989; abst. C. A. 1923, **17**, 3612; J. S. C. I. 1923, **42**, 749-A, 926-A. F. P. 512649; abst. Chim. et Ind. 1921, **6**, 650. D. R. P. Anm. S-52355; abst. Kunst. 1922, **12**, 24. D. R. P. 505610; abst. C. A. 1931, **25**, 591. Belg. P. 291902.

3. *Ibid.* E. P. 206113; abst. C. A. 1924, **18**, 1206; J. S. C. I. 1924, **43**, 250-B. D. R. P. 395829; abst. J. S. C. I. 1925, **44**, 38-B.

4. *Ibid.* D. R. P. 346236; abst. C. A. 1923, **17**, 1247. D. R. P. 322746; abst. Chem. Zentr. 1920, IV, 437. Belg. P. 292201.

5. *Ibid.* Belg. P. 292200.

6. Societe de Recherches et d'Applications Cellulose et Papiers, F. P. 525594; abst. Chem. Zentr. 1921, IV, 1342; Chim. et Ind. 1922, **7**, 1184.

7. *Ibid.* F. P. 525738; abst. Phot. Abst. 1922, **2**, 54; Rev. franc. Phot. 1922, **3**, Suppl., 24; Chim. et Ind. 1922, **8**, 654.

formed[1]. The cathode is of carbon and the anode of platinum, about 10% of sulfuric acid being used. Acetic acid forms, and in presence of sulfuric acid combines with any alcohol produced, ethyl acetate resulting. Cellulose esters of the higher fatty acids as palmitic (cellulose di-palmitate) are produced by esterifying with palmityl chloride in the presence of pyridine or quinoline. These esters are soluble in benzene, and yield transparent pellicles upon evaporation of solvent[2]. Starch palmitate is similarly prepared[3]. Instead of starting with cellulose or starch, partially acetylated or nitrated cellulose may be used. As an example, if dinitrocellulose is heated with lauryl chloride in toluene, "Lauro-dinitrocellulose" (better cellulose lauryl-dinitrate) results, less flammable than trinitrocellulose and dissolving generally in the same solvents[4]. Partially acetated cellulose gives lauro-diacetylcellulose (cellulose acetolaurate or lauroacetate).

In the waterproofing and strengthening of threads and fabrics[5], such as cellulose acetate which has a diminished tensile strength in the wetted condition, the threads are subjected to gaseous formaldehyde followed by treatment with a phenol, or with oil of turpentine followed by ozonized air. In airplane fabric coating compositions, acetylcellulose with diethyl *iso*phthalate or ethyl cinnamate is advocated to produce a superior degree of tautness[6]. If a transpar-

1. Soc. des Acieries et Forges de Firminy, F. P. 516461; abst. Mon. Sci. 1922, (5), **12**, 49, 61.

2. Soc. de Stearinerie et Savonnerie de Lyon and P. Berthon, E. P. 201510; abst. C. A. 1924, **18**, 469; J. S. C. I. 1924, **43**, 128-B; Caout. et Gutta. 1924, **21**, 12204. F. P. 571730. U. S. P. 1553924; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 877-B.

3. *Ibid.* E. P. 208685; abst. C. A. 1924, **18**, 1584; J. S. C. I. 1924, **43**, 191-B. U. S. P. 1651366; abst. C. A. 1928, **22**, 881; Plastics, 1928, **4**, 262.

4. *Ibid.* E. P. 219926; abst. C. A. 1925, **19**, 729; J. S. C. I. 1925, 37-B. F. P. 581160; abst. Plastics, 1925, **1**, 73. U. S. P. 1651990, 1651991; abst. C. A. 1928, **22**, 868; Plastics, 1928, **4**, 688.

5. Societe la Soie Artificielle de la Voulte, E. P. 158851.

6. Societe Nauton Freres et de Marsac and T. Tesse, E. P. 126989; abst. C. A. 1919, **13**, 2460. F. P. 499993; abst. Chim. et Ind. 1921, **5**, 333. See also E. P. 124763.

ent airplane dope is desired[1], the acetylcellulose is dissolved in methyl acetate, and high boilers as benzyl alcohol, ethyl acetoacetate, eugenol or *iso*eugenol added. To prepare acetylcellulose of greater receptivity to dyestuffs[2], a previous soaking in tribasic sodium phosphate is recommended.

Copper oxide or nickel oxide made by precipitation of the nitrate with ammonia and igniting is said to be peculiarly efficient in changing ethyl alcohol to acetaldehyde[3]. Esters as ethyl, propyl, glycol, or glyceryl lactates, oxalates, tartrates, citrates, chloracetates, maleates, malates and succinates are producible by esterifying the alcohol and acid in the presence of a catalyst and a third liquid miscible with the alcohol but substantially immiscible with water (benzene, toluene, carbon tetrachloride, hexane)[4]. Furfural may be used as a direct acetylcellulose solvent[5], or with other organic solvents (ethyl acetate, methyl alcohol, ethyl chloride, benzene, toluene) in which the cellulose ester is not completely soluble, without a diminution in its solvent power.

In simulating celluloid, ivory, amber, tortoise shell and ebony[6], wood is first coated with glue, dried, smoothed and then combined with cellulose ester solution in high boilers and slowly dried to avoid the formation of pinholes and blisters. As a plastic composition for films or filaments[7], cellulose acetate 10, triacetin and triphenyl phosphate 1 each

1. Societe Nauton Freres et de Marsac and T. Tesse, E. P. 158521. F. P. 508975; abst. Caout. et Gutta. 1921, **18**, 10894.

2. Societe pour la Fabrication de la Soie "Rhodiaseta," Swiss P. 100708. E. P. 218913; abst. C. A. 1925, **19**, 580.

3. J. Steffens, U. S. P. 1400247.

4. J. Steffens, U. S. P. 1421604; abst. Chem. Tech. Uebers, 1923, **47**, 4. U. S. P. 1421605; abst. Chem. Tech. Uebers, 1923, **47**, 4.

5. F. Steimmig, D. R. P. 307075; abst. J. S. C. I. 1920, **39**, 153-A.

6. H. Steiner, U. S. P. 1396075.

7. W. Stevenson, U. S. P. 1458505. E. P. 138379; abst. C. A. 1920, **14**, 1879. See E. P. 130029.

has been patented. The artificial silk of J. Stevenson[1] is made by forcing an acetone solution of acetylcellulose through a spinnerette orifice into a decomposing solution of sodium sulfate. Benzyl, tribenzyl, chlorbenzyl, hydroxybenzyl, tolyl or chlortolyl phosphates[2] are claimed as more efficient than triphenyl or tricresyl phosphates as acetylcellulose plastifiers.

In the manufacture of acetic anhydride from sodium acetate and sulfur dichloride[3], the reaction is carried out under 20° under a pressure 5 lbs. above atmospheric. After completion of the reaction, the acetic anhydride is vacuum distilled. The anhydride may be purified from sulfur compounds present as a normal impurity[4], by treatment with a chlorate, bromate or manganese oxide. Acetic acid obtained from an acetylation process may be recovered by extraction with a solvent insoluble or nearly so in water and a considerably higher boiling point than acetic acid, i.e. cresols, guaiacol, hexahydrocresols or wood tar[5]. In improving asbestos paper, and especially asbestos paper used in making cigarettes[6], potassium nitrate dissolved or admixed with cellulose acetate in solution is used to coat the asbestos so the burned portion of the wrapper will not be dark in color. Ethyl butyrate has been granted patent protection as a cellulose acetate solvent[7]. E. Swindells[8]

1. U. S. P. 1478926; abst. C. A. 1924, **18**, 756; J. S. C. I. 1924, **43**, 129-B. E. P. 198392; abst. J. S. C. I. 1923, **42**, 711-A; C. A. 1923, **17**, 3794. Can. P. 224374. India P. 9129, 1923. Holl. P. 15246. F. P. 574626; abst. Chem. Zentr. 1925, I, 919. See F. P. 473126. D. R. P. 274260. E. P. 130029.
2. F. Stockelbach, U. S. P. 1370853; abst. Mon. Sci. 1922, (5), **12**, 5.
3. C. Strosacker, U. S. P. 1403920; abst. J. S. C. I. 1922, **41**, 198-A; Chem. Tech. Uebers, 1922, **46**, 138. Compare D. R. P. 132605, 222236, 241898.
4. C. Strosacker and C. Schwegler, U. S. P. 1467074.
5. H. Suida, E. P. 218271, 218272; abst. C. A. 1925, **19**, 523; J. S. C. I. 1925, **44**, 899-B. U. S. P. 1624810, 1624811; abst. C. A. 1927, **21**, 1819; J. S. C. I. 1927, **46**, 380-B.
6. N. Sulzberger, U. S. P. 1518944; abst. C. A. 1925, **19**, 577.
7. A. Sulzer, U. S. P. 1398949; abst. Mon. Sci. 1922, (5), **12**, 68.
8. Color Trade J. May 1924, 163.

has described methods of applying the "ionamines," a group of dyestuffs that will print direct on acetylcellulose.

R. Tamba has described an amylose disulfate[1], obtained by the action on starch of a mixture of chlorsulfonic acid and chloroform in dry pyridine, and H. Tenen[2] the technical applications of acetate varnishes and lacquers. In the T. Tesse process for diminishing the visibility of objects[3], airplanes are camouflaged for night flying by the doping of the wings and body with solutions of cellulose acetate containing pigments (lampblack, Paris blue, ochres, alizarin lakes). Ethyl acetoacetate, methyl acetate, acetone, eugenol and *iso*eugenol are used as solvents. He advises the application of three coats to airplane fabrics[4], the intermediate coat being formed of cellulose acetate solution containing zinc oxide and carvol, carvacrol or similar solvents boiling above 200°, and being so supple that the coating is soft. The outer or top coat contains but little plasticizing body[5].

The adipic acid esters of cyclohexanol, cyclohexyl and *o*-methylcyclohexyl[6] when added in small quantities to cellulose acetate intended for film castings, impart a softness and smoothness to the film without a sticky feeling. In the E. Thorin method of acetaldehyde manufacture from acetylene[7], the latter is passed through a catalytic solution containing mercuric sulfate and sulfuric acid, the solution being continuously withdrawn from the reaction vessel and pumped through a tube in which mercury mud and other impurities settle out. The aldehyde is then transformed

1. Biochem. Zts. 1923, **141**, 274; abst. J. S. C. I. 1923, **42**, 1239-A.
2. Chemicals, **25**, #19, 9.
3. T. Tesse, U. S. P. 1426521; abst. C. A. 1922, **16**, 3766.
4. *Ibid.* U. S. P. 1521055; abst. C. A .1925, **19**, 739; J. S. C. I. 1925, **44**, 95-B. See E. P. 124763, 124844, 126989.
5. *Ibid.* U. S. P. 1521056; abst. C. A. 1925, **19**, 739; J. S. C. I. 1925, **44**, 95-B.
6. Tetralin Ges. m. b. H., D. R. P. 406013; abst. J. S. C. I. 1925, **44**, 202-B; Rev. Gen. Mat. Plast. 1927, #1, 49.
7. U. S. P. 1501502; abst. C. A. 1924, **18**, 2716; J. S. C. I. 1924, **43**, 770-B. E. P. 155775; abst. J. S. C. I. 1922, **41**, 391-A.

into acetic acid by oxygen in a reaction chamber filled with small pieces so spaced that oxygen trickles through the mass in small bubbles[1].

The manufacture of cinematograph film according to the J. Thornton process[2] combines a proportion of "fibrous" cellulose acetate incorporated with the gelatin as substratum, over which is superposed a cellulose acetate solution to increase resistance to wear. A small addition is made to cellulose acetate varnishes or dopes in order that they shall retain their viscosity[3]. If the dope is acid, a borate may be added. To diminish the inflammability[4], ammonium phosphate or ammonium magnesium phosphate is added to the lacquer. Metaldehyde has been patented as a solid fuel[5]. The industrial processes for cellulose acetate analysis were reviewed and amplified in 1922 by O. Torii[6].

An artificial silk has been described[7] in which cellulose acetate in filament form, and still in a swollen condition as a gel, is submitted under tension, to a cooling treatment, and then dried under tension. The addition of hydrogen halides, methyl halides or organic carboxylic acids to acetylene hydrocarbons takes place rapidly at 100-120° under 1-2 atms. pressure[8]. Details of manufacture of *b*-chlorpropylene, vinyl acetate and ethylidene diacetate are given. A material for the manufacture of lacquers and varnishes, a mixture of xylene 100, acetone 3.5, acetone-soluble acetyl- or formyl-cellulose is dispersed to a further indivisible mass

1. E. Thorin, Can. P. 243123.
2. J. Thornton, U. S. P. 1361783.
3. Titanine, Ltd., and P. Bowles, E. P. 136927; abst. J. S. C. I. 1920, **39**, 164-A; Ann. Rep. S. C. I. 1920, **4**, 324. See E. P. 129033.
4. Titanine, Ltd., T. Ward and J. Fletcher, E. P. 203847; abst. J. S. C. I. 1923, **42**, 1081-A. Can. P. 256395; abst. C. A. 1926, **20**, 2419.
5. N. Tommasi and H. Danneel, U. S. P. 1407101.
6. Jour. Chem. Ind. Japan, 1922, **25**, 118; abst. C. A. 1922, **16**, 2987; Ann. Rep. S. C. I. 1922, **7**, 138; J. S. C. I. 1922, **41**, 367-A; Caout. et Gutta. 1922, **19**, 11569.
7. E. Trachsler, Swiss P. 114677; abst. J. S. C. I. 1927, **46**, 185-B.
8. H. Traun's Forschungslaboratorium G. m. b. H., E. P. 156117; abst. J. S. C. I. 1922, **41**, 436-A. Dan. P. 27889, 28427.

in a colloid mill, when it dissolves almost instantly in the usual solvent mixtures without the appearance of any appreciable residue[1].

A solution of acetylcellulose alone or mixed with nitrocellulose, in a solvent as acetone and alcohol[2], is employed for filament manufacture, which is then treated with sulfuric acid, niter cake or calcium chloride in which the cellulose ester solvent is soluble, but not the ester. If cellulose nitrate is used, the product is denitrated. Sound records are formed of superposed paper sheets cemented together with a composition of cellulose acetate, with or without the use of rubber[3].

About 1.25% of cyclohexanone (based on the weight of the ester) is added to cellulose acetate solutions used for coating airplane surfaces, in order to prevent blushing of the dope[4]. A. de Vains[5] prepares wood pulp of suitable purity for esterification purposes by treatment with nascent chlorine to remove "all" hemicellulosic and similar products. An iridescent film or coating is produced on paper by floating on the surface of water an acetylcellulose solution in a fatty acid alkyl ester, the paper to be coated being drawn upwards through the solution on which the film floats, so that the film adheres to the paper[6]. Cyclohexanol, through the intermediate formation of cyclohexanone, is produced by the hydrogenation of phenol in the presence of platinum

1. H. Traun's Forschungs laboratorium G. m. b. H., E. P. 156142. Cites E. P. 155836.
2. Tubize Artificial Silk Co., E. Bindschedler and G. Juer, E. P. 211889; abst. C. A. 1924, **18**, 2255; J. S. C. I. 1925, **44**, 126-B. U. S. P. 1551791; abst. C. A. 1925, **19**, 3379; J. S. C. I. 1925, **44**, 844-B; Plastics, 1925, **1**, #2, 62; Caout. et Gutta. 1926, **23**, 13315.
3. F. Turner, J. Starck, J. Craig and P. Packman, E. P. 222177; abst. C. A. 1925, **19**, 1036.
4. T. Tyrer, U. S. P. 1339728; abst. C. A. 1920, **14**, 2095; J. S. C. I. 1920, **39**, 483-A; Chem. Ztg. 1920, **44**, 617; Paper, 1921, **27**, #21, 27; Kunst. 1920, **10**, 191. E. P. 130402; abst. J. S. C. I. 1919, **38**, 714-A.
5. E. P. 189561; abst. J. S. C. I. 1922, **41**, 1003-A. E. P. 198975; abst. Faser. 1924, **6**, 20. E. P. 201488; abst. Faser. 1924, **6**, 21. India P. 9932, 1924.
6. H. Valentine and E. Simpson, E. P. 202835; abst. C. A. 1924, **18**, 329; Paper, 1923, **33**, #8, 18.

black[1]. Advantageous properties are ascribed to an ester produced by slightly nitrating cellulose[2], then treating below 20° with acetic acid, acetic anhydride and sulfuryl chloride until a solid mass results. This is mixed with tetrachlorethane and hydrolyzed in the usual way, a cellulose mononitro-diacetate being formed. A better acetylation is said to result[3], if cellulose is treated with acetic acid and anhydride for several hours before the catalyst is added. The sulfuryl chloride may, with advantage, be replaced by phosphorous pentoxide[4]. For treatment prior to acetation[5], it is advocated to treat cellulose with a mixture of organic acids and 15-20% hydrochloric or sulfuric acids at a low temperature. The physical constants and uses of tetrahydronaphthalin and dekahydronaphthaline were published by H. Vollmann[6] in 1920.

An acetylcellulose solvent has been patented[7], consisting of "the residues of alcohol manufacture whereby phenols or oxyacids are added." Acetic anhydride may be prepared by reacting upon glacial acetic acid with chlorine under pressure[8], together with sulfur or sulfur chloride, the ratio of S to Cl in the mixture being 1:4. In the E. Wagner pro-

1. G. Vavon and J. Detrie, Compt. rend. 1921, **172**, 1231; abst. J. C. S. 1921, **120**, i, 505.

2. Verein f. Chemische Industrie, D. R. P. 335359. Aust. P. 88638; abst. Chem. Ztg. 1922, **46**, 730. Swiss P. 87761; abst. Chem. Zentr. 1921, II, 821.

3. *Ibid.* D. R. P. 339824; abst. Chem. Tech. Uebers, 1921, **45**, 310.

4. *Ibid.* Swiss P. 90874, Addn. to 87761; abst. Chem. Zentr. 1922, II, 345.

5. Verein Chem. Werke and K. Luedecke, D. R. P. 367677; abst. J. S. C. I. 1923, **42**, 546-A; Chem. Ztg. 1922, **46**, 1094.

6. Farben Ztg., **25**, 2386; Kunst. 1920, **10**, 66; abst. Chem. Zentr. 1920, IV, 682.

7. N. Voznesenskii and M. Chilikin, Russ. P. 4563; abst. C. A. 1928, **22**, 4844.

8. A. Wacker Ges. fur Elektrochem. Ind. and L. Hoermann, E. P. 211167; abst. C. A. 1924, **18**, 1836; J. S. C. I. 1924, **43**, 890-B. Ital. P. 200474. U. S. P. 1590097; abst. C. A. 1926, **20**, 3015; J. S. C. I. 1926, **45**, 692-B. F. P. 575853.

cess of esterification[1], partially acetylated cellulose obtained by the action of acetic acid on cellulose, is further acetylated by less than double its weight of acetic anhydride whereby insoluble acetyl compounds are converted into higher esters directly soluble in acetone. By this means, it is claimed a saving of acetic anhydride and catalyst results. The finished ester contains about 61% acetic acid.

The W. Webb cellulose acetylation process involves treatment of the cellulose with a mixture of acetic acid, acetic anhydride and hydrochloric acid[2], passing air over the mass to remove anhydride which is subsequently recovered, and adding prior to their separation, a substance which is inert towards acetyl compounds, but is capable of reacting with the acid hydrolyzing agents to form a non-volatile salt. A plastic combination has been described[3] prepared by dissolving cellulose acetate in warm, 98-99% cresylic acid, then adding formaldehyde (40% solution) in which a small amount of NaOH has been dissolved. The mixture is then heated 15-30 minutes at 90°, a liquid to solid mass being obtained depending upon the ratio of cellulose ester to condensate. For insulation, it is claimed to be practically water impervious. M. Whitaker[4] has described an electrically heated apparatus for catalytic reactions adapted for producing acetaldehyde from ethyl alcohol vapor. It comprises layers of catalytic material as pumice and copper, nickel or chromium placed across a cylindrical reaction chamber with corrugated electric resistance plates adjacent to the catalyzer. The reactions and

1. E. Wagner, D. R. P. 299181; abst. J. S. C. I. 1920, **39**, 400-A.
2. W. Webb, U. S. P. 1514274; abst. C. A. 1925, **19**, 177; J. S. C. I. 1925, **44**, 37-B. Cites U. S. P. 534968. U. S. P. 1516225; abst. C. A. 1925, **19**, 399; J. S. C. I. 1925, **44**, 67-B. Cites U. S. Reissue 12637. U. S. P. 666711, 1141879, 1183098, 1183393. Ward, Ital. P. 168298.
3. A. Weller and W. Robinson-Bindley, U. S. P. 1368867.
4. M. Whitaker, U. S. P. 1396389; abst. C. A. 1922, **16**, 514. Cites U. S. P. 1375345, 1376665.

applications of cyclohexanol have been described by Wilhelm[1].

Lonarit, a cellulose acetate plastic[2], has sp. gr. 1.45, can be heated to 180°, normal surface resistivity about 2300 megohms, break-down voltage for a thickness of 0.3 mm. is greater than 2000 volts, and may be as high as 13000 volts for a thickness of 1 mm. H. Williams[3] reviewed in 1921 our knowledge of the solvent action of sulfocyanates on cellulose. In the preparation of methyl formate[4], the H. Willkie method is to subject methyl alcohol to the action of a metallic catalyst, the action taking place between 175-230°. A film is producible by evaporation of a solution of acetylcellulose in a solvent having a dehydrating action and an alcohol adapted to form a mixture of constant boiling point with water and to carry off the latter during the evaporation of the solvent[5]. Ethyl acetate 98, ethyl alcohol 2 is such a mixture. A similarly acting solvent composition is claimed to be[6] diethyl phthalate 3.75, ethyl acetate 11.25, benzene 25. A composition containing cellulose acetate has been patented[7], comprising anhydrous ethyl acetate, alcohol and a very high boiling solvent (diethyl phthalate, ethyl acetoacetate, ethyl succinate, triacetin, dimethyl phthalate), sufficient to gelatinize only a portion of the cellulose ester when the volatile solvents have evaporated.

H. Willkie[8] has investigated and reported upon the advantages of the use of ethyl acetate alone or in conjunc-

1. Kunst. 1921, **11**, 68. P. Friesenhahn, D. R. P. 331050, 332909, 366146. F. Raschig, U. S. P. 900204. D. R. P. 174914. Badische Anilin & Soda-Fabrik, Swiss P. 59164, 64710. D. R. P. 272391. E. P. 21368, 1912. F. P. 459006. P. Breteau and H. Lervux, F. P. 409557. Dr. Schrauth, Zeits. der Deuts. Oel- & Fett-Industrie, 1921, 129.

2. Willers, Kunst. 1924, **14**, 36; abst. C. A. 1924, **18**, 2601.

3. H. Williams, J. S. C. I. 1921, **40**, 221-T; abst. Bull. Soc. Chim. 1922, **32**, 250. A. Dubosc, Bull. Soc. Ind. Rouen, 1905, 318. D. R. P. 275882.

4. H. Willkie, U. S. P. 1400195.

5. *Ibid.* U. S. P. 1400196; abst. J. S. C. I. 1922, **41**, 213-A.

6. *Ibid.* U. S. P. 1449156.

7. *Ibid.* U. S. P. 1449157.

8. Chem. Met. Eng. 1921, **25**, 1186; abst. Ann. Rep. S. C. I. 1922, **7**, 137. G. Ryland, Am. Chem. J. 1899, **22**, 384.

tion with anhydrous ethyl alcohol as a cellulose acetate solvent, the viscosities and physical characteristics of the solutions obtained being given in tables and graphs. L. Wilson[1] commented in 1921 upon the acetate silk of the British Cellulose Co. A composition for making tobacco pipes, gun stocks and other articles[2] consists of asbestos, powdered briar root and cellulose acetate as a binding medium. Powdered meerschaum or "manganese" may be added. After shaping, the solvent is dissipated, the product re-shaped and dried at 70-80°, after which the article is glazed and polished.

In the catalytic hydration of acetylene to acetaldehyde[3], mercury salts may be replaced by heavy metals which are not appreciably volatile (copper, cobalt, nickel, cadmium), the acetylene being mixed with a considerable excess of air and steam, heated to about 360°, when 70-80% of the theoretical yield of acetaldehyde is obtained, together with 5% of acetic acid. B. Walcott and C. Jennison[4] protect fabrics against rot by superficially butylating them, 100 parts cellulose in the form of yarn, canvas or duck being treated with *n*-butyric acid 400, butyric anhydride 300-400 and condensing agent 20-40. The cellulose butyrate formed does not increase the weight of the fabric more than 13%. when NaOH and CS_2 act upon cellulose acetate[5], a xanthated cellulose results, which, in contradistinction to xanthate derived from cellulose, appears to be derived from a parent substance containing five active hydroxyl groups. E. Worden published in 1919 a resume of patent and literature development on the hydration of cellulose acetate[6]

1. J. S. C. I. 1920, **39**, 307-A.
2. F. Wingender, E. P. 202964; abst. C. A. 1924, **18**, 312.
3. A. Wohl, E. P. 154579; abst. J. C. S. 1922, **122**, i, 430; J. S. C. I. 1922, **41**, 308-A. Belg. P. 291914. Norw. P. 38532. Swiss P. 92403; abst. Chem. Ztg. 1921, **45**, 1255.
4. U. S. P. 1474574.
5. R. Wolffenstein and E. Oeser, Ber. 1923, **56**, 785; abst. J. S. C. I. 1923, **42**, 492-A.
6. E. Worden, J. S. C. I. 1919, **38**, 370-T; abst. C. A. 1920, **14**, 1038; Ann. Rep. S. C. I. 1920, **5**, 323. Contains bibliographic and patent references exceeding two hundred.

which was taken exception to in an anonymous contribution which was published in Kunstoffe in 1921[1], and replied to[2] in the same publication.

Paint suitable for covering surfaces painted with black asphaltum paints and which will cover them with a light tinted coat in one application[3] results upon applying a cellulose acetate lacquer containing pigment therein, the degree of opacity desired being governed by the nature and amount of pigment incorporated. In protecting metal surfaces[4], it is advised to use as a paint a cellulose acetate solution with relatively high-boilers, in which has been admixed finely divided, relatively non-corrodible metal as aluminum. Vegetable parchment may be waterproofed by application thereto of an acetylcellulose lacquer, and this element is then attached to metal surfaces to protect them from oxidation[5].

In the manufacture of an ignitible polydyne filter for ultra-filtration and quantitative analysis[6], it is recommended to hold in place the filter plate of unglazed porcelain by a cylindrical insert impregnated with cellulose acetate. Polymerization products of coumarone and indene added to cellulose acetate[7], using a mixture of methyl alcohol and acetone as the solvent harmonious to both, has been patented as an advantageous lacquer and plastic for insulating purposes. Cellulose acetate may be formed by adding a halogen as chlorine or bromine, or a compound which yields a halogen to a mixture of cellulose, acetic anhydride and acetic

1. Kunst. 1921, **11**, 42.
2. E. Worden, Kunst. 1921, **11**, 1; abst. C. A. 1921, **15**, 2181; Chem. Ztg. 1921, **45**, 38.
3. J. Young, U. S. P. 1410790.
4. *Ibid.* U. S. P. 1418347.
5. *Ibid.* U. S. P. 1418349.
6. L. Zakarias, Z. angew. Chem. 1924, **37**, 425.
7. Zapon-Lack G. m. b. H., D. R. P. 281265; abst. C. A. 1915, **9**, 1850; Chim. et Ind. 1915, **38**, 87.

acid[1], especially low viscosity esters being produced, the ester having been marketed under the trade name of Acetose (*acet*ated cellu*lose*). A directly spinnable solution of cellulose acetylated as above is obtained by conducting the esterification in two stages[2], in the first without any condensing agent, and then continuing the reaction after condenser has been added, the condenser being preferably not greater than 1% on the weight of the cellulose. It is advised to carry the reaction out in such a manner that not to exceed nine times the weight of acetic acid to cotton is used[3]. This cellulose acetate, which shows a tendency to increase in viscosity on standing[4], may be stabilized by the addition of a small quantity of aqueous formaldehyde. Artificial filaments and films of increased strength may then be formed[5]. The advantages of the process were set out in 1922, in which was claimed great solvent economies on account of the low viscosity of the cellulose ester[6].

1. J. Zdanowich, E. P. 139232; abst. C. A. 1920, **14**, 2084; J. S. C. I. 1920, **39**, 483-A; Ann. Rep. S. C. I. 1920, **5**, 137; Chem. Met. Eng. 1920, **22**, 1175; Paper, 1921, **28**, 32; 1921, **27**, #25, 30; Chem. Ztg. 1920, **44**, 454; Chim. et Ind. 1921, **6**, 818. U. S. P. 1347801; abst. C. A. 1920, **14**, 2857; J. I. E. C. 1920, **12**, 1173; Chem. Met. Eng. 1920, **22**, 540; J. S. C. I. 1920, **39**, 624-A; Chem. Ztg. 1920, **44**, 850. F. P. 505608; abst. Caout. et Gutta. 1921, **18**, 10893; Paper, 1921, **29**, #6, 21. Australia P. 12966. Belg. P. 285696. Can. P. 220531; abst. C. A. 1922, **16**, 2989. Ital. P. 139232, 179376, 229815. See also E. P. 14255, 1906; 22237, 1911.

2. *Ibid.* E. P. 190732; abst. C. A. 1923, **17**, 2957; J. S. C. I. 1923, **42**, 179-A. U. S. P. 1445382; abst. C. A. 1923, **17**, 1549; J. S. C. I. 1923, **42**, 305-A. Australian P. 12965. Belg. P. 307374. Swiss P. 99047.

3. *Ibid.* E. P. 196641; abst. C. A. 1923, **17**, 3788; J. S. C. I. 1923, **42**, 650-A; Chem. Ztg. 1923, **47**, 474; J. Text. Inst. 1923, **14**, 196-A. U. S. P. 1457131; abst. C. A. 1923, **17**, 2505; J. S. C. I. 1923, **42**, 651-A. Belg. P. 319078. Australian P. 19169.

4. *Ibid.* E. P. 200186; abst. C. A. 1924, **18**, 329; J. S. C. I. 1923, **42**, 925-A; Caout. et Gutta. 1924, **21**, 12167; Faser. 1924, **6**, 20. U. S. P. 1528810; abst. C. A. 1925, **19**, 1497; J. S. C. I. 1925, **44**, 312-B. See F. P. 505608.

5. *Ibid.* E. P. 203599; abst. C. A. 1924, **18**, 752; J. S. C. I. 1923, **42**, 1017-A; Chem. Zentr. 1924, I, 383.

6. *Ibid.* Caout. et Gutta. 1922, **19**, 11381; J. Soc. Dyers Col. 1922, **38**, 204; C. A. 1923, **17**, 475; J. I. E. C. 1920, **12**, 1173; abst. C. A. 1921, **15**, 751. Mon. Sci. 1920, **10**, 158; abst. C. A. 1920, **14**, 3318.

Cellulose is not convertible into acetylbromocelluloses unless water is present[1], when degradation products of cellulose result. Starch is converted by technical acetylbromide (usually containing HBr and acetic acid as impurity) into acetylbromglucose. It is of interest to record that finely divided pine wood is completely soluble in acetyl bromide. Acetic and formic acids may be separated from a crude solution of carbohydrates obtained on hydrolyzing cellulosic materials with mineral acids[2], by passing steam through the solution. Methods for producing esters of polyfatty acids (ricinoleic, polyricinoleic, tetraricinoleic) have been described[3]. The R. Zsigmondy filter[4] is formed by preparing films of cellulose acetate containing water so as to obtain an opaque film, and utilizing this as a dialyzable membrane for filtering colloids.

Development of the Cellulose Ester Art, 1925-1928. In this quadrennial period activity has been more intensive, especially in connection with the textile art, of any preceding period of equal length, as indicated by the approximately fourteen hundred patents granted and contributions published, covering almost every conceivable phase of cellulose acetate and other organic cellulose ester usefulness.

Aceta, G. m. b. H.[5] claim peculiar and advantageous results by the admixture of cellulose acetate and nitrate filaments in various proportions before subjection to the weaving operation, especially in producing differential dye-

1. L. Zechmeister, Ber. 1923, **56**, 573; abst. J. S. C. I. 1923, **42**, 347-A; J. C. S. 1923, **124**, i, 306; Chem. Tech. Ueber, 1923, **47**, 157. Cf. M. Bergmann and F. Beck, Ber. 1921, **54**, (B), 1574; abst. J. C. S. 1921, **120**, i, 649. K. Hess, Ber. 1921, **54**, (B), 2867; abst. J. C. S. 1922, **122**, i, 12. P. Karrer and C. Naegeli, Helv. Chim. Acta, 1921, **4**, 185; abst. J. C. S. 1921, **120**, i, 311.

2. Zellstoffabrik Waldhof and V. Hottenroth, E. P. 147416.

3. E. Zollinger and A. Gruen, U. S. P. 1484826; abst. J. S. C. I. 1924, **43**, 343-B. E. P. 112624; abst. J. S. C. I. 1919, **38**, 427-A. D. R. P. 333155; abst. Chem. Zentr. 1921, II, 736. Cites E. P. 14767, 1913. Swiss P. 58669. D. R. P. 403644.

4. R. Zsigmondy and W. Bachmann, U. S. P. 1421341.

5. Belg. P. 363320.

ing effects. In printing surfaces[1], a cellulose acetate composition is used in forming matrices for typographic or stereotype plates, which are preferably made of material which softens at a lower temperature than the matrix. In the production of flexible gas containers for airships or balloons[2], as a substitute for rubber lining or goldbeaters skin, a textile fabric is coated with a solution of acetylcellulose plastified by xylenemonomethylsulfonamide and triphenyl phosphate in a volatile solvent, the coating augmenting the weight of the fabric from 76 gm. to 110 gm. per sq. meter.

In decolorizing waste material from coloring cellulose acetate films and filaments[3], treatment with substances which contain silicic acid and have active adsorbent surfaces as kieselguhr or Fuller's earth has been advocated. In the dyeing of acetated cellulose[4], the fibers are impregnated with a material capable of coupling with a diazo compound and a nitrite, and afterwards treated with an acidified solution of a diazotizable amine, or[5], the acetate silk is treated in the presence of ammonia and an oxidizing agent with arylamines or mixtures of amines and phenols suitable for production of indamines or indophenols. *pp'*-Dihydroxydiphenylamine gives brownish-red; 3.5-dichlor-4-amino-4'-hydroxydiphenylamine, bluish-red; 4-dimethylamino-4'-hydroxydiphenylamine, a blue; 4-amino-4'-hydroxydiphenylamine, a violet. Wall papers have been described[6], coated with cellulose acetate lacquer to waterproof them and form a smooth, shiny surface that may be

1. Actualite Illustree Soc. Anon., E. P. 234140; abst. C. A. 1926, **20**, 804.
2. Airship Guarantee Co., Ltd., and C. Burney, E. P. 239569; abst. C. A. 1926, **20**, 2254; J. S. C. I. 1925, **44**, 955-B.
3. M. Hagedorn and Akt. Ges. fur Anilin-Fabrikation, E. P. 245078; abst. C. A. 1927, **21**, 321; Kunst. 1926, **16**, 205. Can. P. 264485; abst. Chem. Zentr. 1927, I, 3163. Compare Ubbelohde, Handbuch der Oele und Fette, 1908, **1**, 797.
4. *Ibid.* E. P. 262537; abst. C. A. 1927, **21**, 3751.
5. *Ibid.* F. P. 605127; abst. J. S. C. I. 1927, **46**, 964-B; Caout. et Gutta. 1927, **24**, 13425.
6. Akt. Ges. fur Wasserdichte Stoffe "Filmos" Oftringen, D. R. P. 521520, Addn. to 456518; abst. C. A. 1931, **25**, 3484.

cleaned. C. Dreyfus in 1925 gave his impressions of the future of the cellulose acetate silk industry[1]. O. Alden[2] pointed out in 1928 the difficulties of identifying different types of rayon, especially in colored fabrics, and suggestions for satisfactory methods of differentiation.

In the fabrication of laminated glass[3], a sheet of cellulose acetate softened by tetralin is sandwiched between two glass sheets, and heat and pressure applied. Rubber dissolved in cyclohexanone or *ar*-tetrahydronaphthol may be mixed with cellulose acetate to make a homogeneous lacquer for coating purposes[4]. W. Alterhoff[5] has described the various methods of avivage, or the treatment which gives rayon the scroop feel and other qualities of simulating natural silk, the avivage bath usually comprises glue, gelatin, diastofor or malt preparations, with formic, acetic or lactic acids. It is claimed[6] that cellulose is rendered more easily esterifiable by treating it with such small quantities of acetic acid that the cellulose does not appear to be wet, the amount used being such that acetic acid of 70-85% strength is formed with the water retained hygroscopically by the cellulose. The usual acetylation treatment follows. In producing such esters as butyl, *iso*butyl and amyl acetates, butyl tartrate and amyl phthalate and formate[7], a reaction mixture of the acid and alcohol used is distilled to produce a constant boiling point mixture which is condensed to form separate liquid layers and then separated by gravity.

1. W. Albert, Rayon, 1925, **1**, #1, 27.
2. O. Alden, Kunstseide, 1928, **10**, 497; abst. C. A. 1929, **23**, 711.
3. H. Allen, U. S. P. 1655933.
4. P. Allman, H. Morris and L. Marlor, E. P. 274968; abst. C. A. 1928, **22**, 2292; Plastics, 1928, **4**, 508. See E. P. 275304.
5. Kunstseide, 1927, **9**, 368; abst. Rayon, 1927, **5**, #3, 24.
6. J. Altwegg and Soc. Chim. des Usines du Rhone, U. S. P. 1543310; abst. C. A. 1925, **19**, 2411; J. S. C. I. 1925, **44**, 667-B. E. P. 237567; abst. C. A. 1926, **20**, 1522; J. S. C. I. 1926, **45**, 49-B. F. P. 603791; abst. Caout. et Gutta. 1927, **24**, 13425. Can. P. 265930. Swiss P. 115706.
7. F. Arentz, E. P. 246526; abst. C. A. 1927, **21**, 415. Can. P. 278985.

In the recovery and utilization of plasticizing and softening agents from cellulose acetate waste, the material is treated with solvents (trichlorethylene or alcohol)[1] which are plasticizing agent solvents but non-solvents of the cellulose acetate. Alcohol, however, while not a solvent of cellulose acetate, is a solvent in conjunction with the plasticizer present in the waste. Formic acid is producible by reacting upon CO and water under pressure in the presence of cuprous chloride[2]. Cellulose acetonitrates of varying composition may be obtained by acetylating nitrocellulose with glacial acetic acid in the presence of sulfuric acid[3], the degree of acetylation being governed by regulating the proportion of acetic acid present[4]. K. Atsuki[5] detailed the status of the acetate silk industry in Japan in 1927.

Cellulose dibenzoate containing about 66% combined benzoic acid may be prepared by treating alkalicellulose with benzoyl chloride in benzene at 50-60°. Readily soluble in chloroform or acetone, yielding solutions of low viscosity forming brittle skins upon evaporation. The benzoate from natural cellulose is incompletely soluble in chloroform forming a turbid solution of high viscosity. The films give a tensile strength of 5 kgm. per sq. mm., and 5% elongation[6]. In continuation[7], it was established that in commercial cellulose benzoylation the degradation of the cellulose molecule should be kept as low as possible, and a powerful solvent used in forming solutions. As a stabilizer for acetyl-

1. P. Aron, F. P. 622074; abst. J. S. C. I. 1928, **47**, 121-B.
2. W. Arsem, U. S. P. 1606394; abst. C. A. 1927, **21**, 104; J. S. C. I. 1927, **46**, 125-B.
3. K. Atsuki, J. Fac. Eng. Tokyo, 1925, **15**, 309; abst. C. A. 1925, **19**, 1626; J. S. C. I. 1925, **44**, 396-B; Plastics, 1925, **1**, 73.
4. E. Berl and W. Smith, Ber. 1907, **40**, 903.
5. J. Soc. Chem. Ind. (Japan), 1927, **30**, 290; abst. C. A. 1927, **21**, 2383.
6. K. Atsuki and K. Shimoyama, Cellulose Industry, Tokyo, 1926, **2**, 35-A; abst. C. A. 1927, **21**, 4062; J. S. C. I. 1927, **46**, 70-B; Chem. Zentr. 1927, I, 70.
7. *Ibid.* Kunstseide, 1928, **10**, 250; abst. C. A. 1928, **22**, 4244.

cellulose[1], calcium naphthenate is advocated as its presence

1. K. Atsuki, R. Shinoda and Y. Tanaka, Rept. Aeronautical Res. Inst. Tokyo, 1928, **3**, 49, 71, 91, 103, 115; abst. C. A. 1928, **22**, 2473; J. S. C. I. 1928, **47**, 519-B. The examination of various mixed solvents for cellulose acetate by determinations of the solvent power, viscosity of the cellulose acetate solution, and the tensile strength and elongation of the film produced on drying, appears to prove that that solvent which has the highest solvent power yields a solution of minimum viscosity and a film of maximum strength and elongation. Using the most common solvents, the optimum composition is acetone 60%, ethyl alcohol 15-17%, benzene 19-21%, benzyl alcohol or triacetin 1-2%, triphenyl phosphate 1-2%; and the optimum concentration of cellulose acetate is 7-9%. With acetone-ethyl alcohol mixtures minimum viscosity is obtained when the content of alcohol is about 17%; with acetone-benzene mixtures the optimum point is at 20% of benzene; while with acetone-alcohol-benzene mixtures it is at 10% of alcohol and 30% of benzene. Addition of triacetin, benzyl alcohol, and triphenyl phosphate tends to increase the viscosity of solvent and solution, and the solvent power. Solutions containing more than 8% of cellulose acetate show appreciable plasticity.

II. Spontaneous decomposition of cellulose acetate is accelerated by sulfuric acid, which may be present in the incompletely purified product in the free state, as an adsorption compound, or as a cellulose ester, since it is used as a catalyst in the acetylating bath. The amount of sulfuric acid retained decreases as the ripening of the cellulose acetate proceeds, owing to hydrolysis of the sulfuric ester and the more ready diffusion of acid through the material. Details are given for four suggested stability tests for cellulose acetate, viz: 100° heat test, decomposition and carbonisation temperature determinations, and an acetic acid evolution test.

III. Owing to the presence in cellulose acetate of traces of cellulose sulfuric esters, it is desirable to add a stabiliser such as calcium naphthenate. This stabiliser reacts with the sulfuric esters present yielding naphthenic acid, which, like the calcium salt, is a gelatiniser and improves the mechanical properties of the cellulose acetate film. The amount of stabiliser required is usually 1-2%.

IV. On acetylation the cellulose fibre at first swells uniformly, and then locally. The swollen parts gradually disperse into the bath, and the residual short fibres slowly disappear. The triacetate is formed directly without intermediate formation of a mono- or di-acetylated product. If the acetylation is prolonged, the acetic acid content of the ester falls to a minimum and then increases. The most uniform material is obtained by continuing the acetylation until the solubility in acetone is a minimum. The velocity of acetylation is doubled by a rise of 10° between 30° and 50°, but above 50° a rise of over 20° is required to produce the same effect, since decomposition of the cellulose disturbs the relation between velocity increase and temperature.

V. The degree of ripening of cellulose acetate may be followed by determinations of viscosity, which varies with the time and temperature of ripening. The experimental results obtained may be expressed by the equation $T = ae^{kz}$, where T is the temperature, z the time of ripening required to obtain a given viscosity, and a and k are constants; but as the viscosity decreases the temperature range through which this formula holds also decreases.

exerts no injurious effect and it combines with sulfuric acid. The dyeing of cellulose acetate mixtures was discussed by Avram[1] in 1927.

The W. Bader process of acetic acid concentration[2] depends upon covering the surface of dilute acetic acid with a film of high boiling solvent as a petroleum distillate which has a selective action on the acid, and circulating over the film a rapid current of heated air. Acetic anhydride may be prepared by subjecting acetone to the action of CO_2 in excess under pressure of 750 lb. per sq. inch at about 350° and in the presence of a catalyst as manganous carbonate[3]. The receptivity of cellulose acetate for dyes may be augmented by treatment with potassium ethyl sulfate or sodium dicresyl phosphate during the dyeing process[4]. Or[5], where acetate plastics are to be dyed, the ester is milled with a softening agent and the coloring matter, and afterwards attenuated by adding liquid solvent to the degree desired. In dyeing cellulose acetate[6], unsulfonated azo dyes may be used containing at least one monoethanolamino group. Cellulose acetate is dyed orange or scarlet by diazotizing *p*-nitroaniline and coupling with monoethanol-*m*-toluidine, or by diazotizing 3-nitro-4-toluidine and coupling with monoethanolaniline.

1. M. Avram, Rayon, 1927, **4**, #8, 10.

2. U. S. P. 1609393; abst. C. A. 1927, **21**, 248. E. P. 204196; abst. Chem. Zentr. 1924, I, 2809. F. P. 568600; abst. Chem. Zentr. 1924, II, 524.

3. W. Bader, U. S. P. 1693331; abst. C. A. 1929, **23**, 608; J. S. C. I. 1929, **48**, 48-B. E. P. 237302; abst. J. S. C. I. 1925, **44**, 827-B.

4. Badische Anilin & Soda-Fabr. and R. Metzger, U. S. P. 1532427; abst. C. A. 1925, **19**, 1632; J. S. C. I. 1925, **44**, 497-B; Chem. Zentr. 1925, II, 351. E. P. 240514; abst. C. A. 1926, **20**, 2253; J. S. C. I. 1925, **44**, 916-B.

5. Badische Anilin & Soda-Fabr., E. P. 247288; abst. C. A. 1927, **21**, 649; J. S. C. I. 1926, **45**, 315-B. F. P. 588903, Addn. 33596, 35385; abst. C. A. 1929, **23**, 2569; 1930, **24**, 3901. Can. P. 250537. India P. 11022, 1925. Swiss P. 113741. C. Immerheiser, C. Neubauer and E. Scharf, U. S. P. 1589700; abst. C. A. 1926, **20**, 3084.

6. *Ibid.* E. P. 251155; abst. C. A. 1927, **21**, 1361; J. S. C. I. 1926, **45**, 741B; Rayon J., 1927, **4**, #2, 37. F. P. 600106; abst. J. S. C. I. 1926, **45**, 536-B. In this connection see E. P. 259634; abst. C. A. 1927, **21**, 3469.

Methyl or ethyl formates may be produced by action of CO on an alcohol at 60-100° in the presence of a metal alcoholate, as sodium alcoholate[1]. The F. Balch fluorescent X-ray screen contains an active layer of calcium tungstate with a low percentage of binder of cellulose acetate[2]. Phonograph record blanks may be made of cardboard discs impregnated with a resinous compound[3], afterwards coated with cellulose acetate varnish. K. Barleben[4] published in 1926 instructions for the handling and storage of acetate films. Excellent dyestuffs for acetated cellulose are obtained by combining *m*-nitroaniline and *a*-naphthylamine, or *m*-aminophenyloxamic acid and *b*-naphthol; or from an indigo-diacetic acid obtained by fusing *o*-carboxyphenyliminodiacetic acid with potassium hydroxide and oxidizing[5]. Or[6], by fusing citric acid with *p*-aminoazobenzeneazo-*b*-naphthol, yellow and orange shades being produced. However[7], citric acid may be fused with unsulfonated indigo or thioindigo dyes containing one or more free primary amino groups, *e.g.*, 7.7′-diaminothioindigo yields a product dyeing cellulose acetate violet-red.

In the manufacture of acetylcellulose[8], wherein acetylation is performed in the presence of a catalyzer, partial hydration or ripening is effected in the primary acetic solution by the addition of diluted acetic acid containing both hydrochloric and hydrofluoric acids. In the treatment of

1. Badische Anilin & Soda-Fabr. and R. Wietzel, E. P. 252848; abst. J. S. C. I. 1926, **45**, 646-B. U. S. P. 1572698; abst. J. S. C. I. 1926, **45**, 462-B.
2. U. S. P. 1532795, 1532796; abst. C. A. 1925, **19**, 1664.
3. C. Bancarel, E. P. 295228.
4. K. Barleben, Amer. Phot. 1926, **20**, 452.
5. C. Barnard and British Alizarine Co., Ltd., E. P. 252240; abst. C. A. 1927, **21**, 1553; J. S. C. I. 1926, **45**, 628-B.
6. *Ibid.* E. P. 281114; abst. C. A. 1928, **22**, 3534; J. S. C. I. 1928, **47**, 83-B.
7. *Ibid.* E. P. 281213; abst. C. A. 1928, **22**, 3536; J. S. C. I. 1928, **47**, 83-B.
8. H. Barthelemy and Ruth-Aldo Co., U. S. P. 1668482; abst. C. A. 1928, **22**, 2272; J. S. C. I. 1928, **47**, 477-B. E. P. 282789; abst. C. A. 1928, **22**, 3989; J. S. C. I. 1929, **48**, 595-B; Silk J. 1928, **4**, #47, 70. F. P. 638896; abst. C. A. 1929, **23**, 514. Belg. P. 352197. Ital. P. 256281, 258934. Cites U. S. P. 838850. E. P. 24067, 1906. F. P. 358079, 371447, 416752, 432046, 441864, 442512, 453835.

cellulose prior to acetylation[1], it is advocated to first use warm acetic anhydride vapors to soften the cellulose, followed by successive additions of the esterifying agent to complete the process. Or[2], the cellulose may be subjected to at least four successive partial acetylations, each of which is deferred until the prior one has terminated, the theory being that a more stable ester eventually results. Or[3], the cellulose may first be subjected to an alkaline solution containing peroxides and a soap to diminish the superficial contact tension and facilitate the diffusion of nascent oxygen, then subject the mass to the action of halogen and the vapor of acetic acid, finally proceding with acetylation in the normal manner. Especially valuable results are said to be obtained where the cellulose acetylated as above, is confined in a rotating vessel which presents discontinuous surfaces of contact such as a cube, or a cylinder turning on an axis inclined to the axis of symmetry[4].

Artificial filaments have been described[5], obtained by passing a solution of cellulose acetonitrate in acetone through spinneret orifices through a shallow bath of aqueous acetone and then delivered through a body of air. The acetonitrate is prepared[6] by dissolving nitrocellulose of high

1. H. Barthelemy, U. S. P. 1668483; abst. C. A. 1928, **22**, 2272; J. S. C. I. 1928, **47**, 477-B. Belg. P. 352200, 352201. F. P. 638897; abst. Plastics, 1929, **5**, 334; C. A. 1929, **23**, 513. Cites U. S. P. 1466401, 1546679. F. P. 473399, 507472, 573739, 596802.

2. H. Barthelemy and Ruth-Aldo Co., U. S. P. 1668484; abst. C. A. 1928, **22**, 2272; J. S. C. I. 1928, **47**, 477-B; Plastics, 1928, **4**, 626. E. P. 282788; abst. C. A. 1928, **22**, 3988; J. S. C. I. 1929, **48**, 714-B; Silk J. 1928, **4**, #47, 70. F. P. 638902, 638903; abst. C. A. 1929, **23**, 513; Plastics, 1929, **5**, 335. Belg. P. 352199. Ital. P. 256210, 256283. Cites U. S. P. 845374, 1236578, 1236579. E. P. 190732. F. P. 319948, 368738, 449253, 458079, 458263, 473399, 478436, 494832, 505608, 523738, 565654. D. R. P. 163316, 184201, 252706, 269193. Swiss P. 120810.

3. *Ibid.* U. S. P. 1668485; abst. C. A. 1928, **22**, 2272; J. S. C. I. 1928, **47**, 477-B. E. P. 282794; abst. J. S. C. I. 1929, **48**, 714-B; Silk J. 1928, **4**, #47, 70.

4. *Ibid.* F. P. 638900; abst. C. A. 1929, **23**, 513; Plastics, 1929, **5**, 335.

5. H. Bassett and T. Banigan, U. S. P. 1560965; abst. C. A. 1926, **20**, 115; J. S. C. I. 1926, **45**, 48-B.

6. *Ibid.* U. S. P. 1586437; abst. C. A. 1926, **20**, 2584.

N content in acetic acid and anhydride with sulfuric acid as catalyzer at a temperature below 15°. In the bleaching of cellulose acetate during its formation[1], decoloration with ozone added during the partial hydration stage subsequent to acetylation has been patented.

In the production of hydrolyzed cellulose acetate soluble in acetone[2], the chloroform-soluble modification produced by spray-drying, is treated with an acid as 10% nitric acid, until the powder dissolves in acetone. The solubility may be controlled, and is tested by means of a polariscope, using mercury green light. The desired ester when dissolved in acetone shows a specific rotation of —2 to —5 (i.e., is laevorotatory). P. Bean in 1926 gave a resume of the dyeing difficulties in coloring cellulose acetate silk[3]. A method of applying cellulose ester lacquers has been devised[4], comprising floating a layer of lacquer on an aqueous surface made denser than the lacquer by dissolving therein sodium chloride or sulfate, potassium iodide or sulfate, magnesium chloride or sulfate or calcium chloride, the lacquer solvent being substantially non-miscible with water. The object to be lacquered is dipped through the floating layer.

In dyeing acetate silk[5], a solution of logwood or hematine is applied, followed by treatment with a bichromate bath kept hot. A photographic medium has been described[6], comprising cellulose acetate sensitized with iodoform 1%, the image formed upon exposure to light being developed in a silver reducing solution containing silver nitrate and

1. R. Baybutt and E. Farrow, U. S. P. 1623519; abst. C. A. 1927, **21**, 1713; J. S. C. I. 1927, **46**, 362-B.

2. *Ibid.* U. S. P. 1635026; abst. C. A. 1927, **21**, 2985; J. S. C. I. 1927, **46**, 1774-B; Plastics, 1927, **3**, #11, 608. Cites E. P. 24067, 1906.

3. Chemicals, 1926, **26**, #3, 20; abst. C. A. 1926, **20**, 2908.

4. R. Beausejour, U. S. P. 1572461.

5. C. Bedford, E. P. 263222; abst. C. A. 1928, **22**, 171; Silk J. 1927, **3**, #35, 71.

6. M. Beebe, A. Murray and H. Herlinger, U. S. P. 1658510; abst. J. S. C. I. 1928, **47**, 317-B; Plastics, 1928, **4**, 202. Cites U. S. P. 1574357, 1587269, 1587270, 1587271, 1587272, 1587273, 1587274.

ammonia. W. Bennett[1] has given practical directions for printing solid, bi-color and multi-color effects on mixed viscose and cellulose acetate fabrics, and wool with cellulose acetate with the Kaline colors (Yellow T, Orange D, Scarlet L, Red G, Helio P, Bright Blue A, Blue M, Bright Violet R, and Sky Blue G), all of which are said to give excellent resists in strong shades, including compound mixings[2], and the formation of Celanese resist effects with azoic and vat colors on cotton-acetate silk unions[3]. The molecular weight of amylose triacetate, lichenin triacetate and inulin triacetate has been determined[4], and T. Bernsen[5] has detailed methods for printing cellulose acetate silk. The Acetate Products Corporation was launched in England in 1928 for the production of cellulose acetate plastics (safety celluloid)[6]. H. Blackshaw[7] discussed in 1926 processes for dyeing viscose and acetate silk in combination with cotton[72].

The sheen of delustered cellulose acetate yarns and fabrics may be restored by applying ethyl lactate or ethyleneglycol monomethylether and drying[8]. For the formation of pattern effects, acetate silk is completely delustered by padding with a solution of soap and steaming, then printed. R. Blochmann[9] has compared nitro and acetate films as to their stability and practical use. Electric conductors may be made by adding to a cellulose acetate solution, 5-10% silver nitrate and 1-3 nitric acid, reducing with

1. W. Bennett, Dyer, Calico Printer, 1928, **59**, 204; abst. C. A. 1928, **22**, 3533.
2. *Ibid.* Rayon, 1928, **7**, #2, 28, #3, 18; abst. C. A. 1929, **23**, 519. Compare Silk J. 1928, **4**, #44, 60, #45, 51; abst. C. A. 1929, **23**, 281.
3. *Ibid.* Silk J. 1927, **3**, #35, 52; abst. C. A. 1928, **22**, 872. Silk J. 1927, **4**, #41, 40, #42, 52, 58; abst. C. A. 1928, **22**, 872.
4. M. Bergmann, E. Knehe and E. von Lippmann, Anm. 1927, **452**, 141; **458**, 93; abst. J. S. C. I. 1927, **46**, 342-A, 1173-A.
5. T. Bernsen, Rayon J. 1926, **3**, #2, 22.
6. A. Blackall, Plastics, 1928, **4**, 644.
7. H. Blackshaw, Dyer & Calico Printer, 1926, **55**, 130; abst. C. A. 1926, **20**, 3817.
8. Bleachers' Assoc., Ltd., W. Kershaw, F. Barrett and R. Gaunt, E. P. 301567, 301568; abst. J. S. C. I. 1929, **48**, 127-B.
9. Kunst. 1925, **15**, 149; abst. C. A. 1926, **20**, 284; Chem. Zentr. 1925, II, 2329.

hydrogen sulfide and treating in an electrolytic bath[1]. An exhaustive study of the decomposition of acetic acid vapor and of acetone in both the gaseous and liquid phases has been made[2], using a uranyl sulfate- oxalic acid actionometer standardized against a Moll thermopile to measure the amount of radiant energy absorbed. The viscosity characteristics of cellulose acetate may be reduced to the degree desired[3], by dissolving in formic or acetic acids and subjecting the solution to the action of ultra-violet rays. It has been found[4] that cellulose acetate silk absorbs hydroquinone from its aqueous solution, but the partition coefficient decreases with increasing concentration of the phenol.

A method of acetic acid concentration has been devised[5], in which the acid in dilute solution flows downwardly, and ether upwardly in intimate contact through a column, the ether extract of acid being withdrawn from the top. Cellulose acetate may be dyed bright bluish-red by an anthraquinone dye prepared by boiling 2.4-dibrom-1-aminoanthraquinone with sodium sulfide, and condensing the product with chloracetic acid[6]. Anthrapyridone compounds prepared by cyclisation of an *α*-acetamidoanthraquinone are satisfactory dyes for cellulose acetate silk[7], being applied in aqueous suspension or colloidal solution. A bright red dye results by boiling 1.4-*bis*acetamidoanthraquinone for about 6 hrs.; reddish-yellow, bright orange and blue dyes by cyclisation of diacetylamino-, 1.5-*bis*acetamido-, and 1.5-

1. A. Borensztedt, F. P. 644430; abst. C. A. 1929, **23**, 1577.
2. E. Bowen and H. Watts, J. C. S. 1926, **129**, 1607; abst. C. A. 1926, **20**, 3390.
3. L. Branchen and C. Prachel, U. S. P. 1658368; abst. C. A. 1928, **22**, 1237; J. S. C. I. 1928, **47**, 295-B.
4. K. Brass and E. Steinhilber, Z. angew. Chem. 1927, **40**, 1218; abst. C. A. 1928, **22**, 1239. See also Z. angew. Chem. 1925, **38**, 853; abst. C. A. 1926, **20**, 113. Rev. gen. mat. color. 1926, **30**, 130; abst. C. A. 1926, **20**, 2752.
5. T. Brewster and H. Baker & Bro., Can. P. 247385; abst. C. A. 1925, **19**, 2345.
6. British Alizarine Co., Ltd., and C. Barnard, E. P. 252646; abst. C. A. 1927, **21**, 2388; J. S. C. I. 1926, **45**, 628-B.
7. 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.

diamino-4-8-*bis*acetamido-anthraquinone respectively. Yellow to orange shades are produced by nitroacridine compounds, as *a*- or *b*-nitroacridine, dinitroacridine or tetranitroacridine[1].

Cellulose phosphate and aceto-phosphate have been described[2], obtained by treating cellulose as linters, with 85-100% phosphoric acid at room temperature or lower, either alone or in conjunction with acetic acid, transparent films being produced therefrom. By a modification of quantities of acid[3], it is claimed cellulose acetates of technical value are producible without the use of any acetic anhydride. Viscosity of cellulose acetate may be lowered by treating the ester in suspension or solution with hydrogen peroxide and an iron salt (ferrous acetate)[4]. Acetylation may be effected in an iron vessel, or iron salts added, the hydrogen peroxide being added when acetylation is complete.

Fabrics containing cellulose acetate thermoplastics[5] may be pleated at a temperature and pressure sufficiently high to render the cellulose derivative plastic, thereby insuring permanent pleating, if prior to the operation the fabric is treated with a softener or solvent (acetone, diacetone alcohol, cyclohexanone, ethyl acetoacetate, acetic acid, ethyl acetate) or swelling agent (ammonium thiocyanate solution, stannic chloride). To avoid increasing luster during finishing[6], fabrics containing delustered cellulose acetate are ironed or calendered to remove moisture at

1. British Alizarine Co., Ltd., W. Dawson, C. Soutar and R. Wood, E. P. 275752; abst. C. A. 1928, **22**, 2471; J. S. C. I. 1927, **46**, 812-B.
2. British Celanese, Ltd., E. P. 263810; abst. Chem. Zentr. 1927, I, 2253.
3. *Ibid.* E. P. 269530; abst. Chem. Zentr. 1927, II, 655. Void.
4. British Celanese, Ltd., G. Schneider and C. Dreyfus, E. P. 273743; abst. C. A. 1928, **22**, 2056; J. S. C. I. 1928, **47**, 520-B; Chem. Zentr. 1927, II, 2582. Can. P. 282185; abst. C. A. 1928, **22**, 3528. Belg. P. 342814. For analogous process, see p. 441, n. 9.
5. British Celanese, Ltd., and C. Dreyfus, E. P. 293857; abst. C. A. 1929, **23**, 1760; Silk J. 1928, **5**, #53, 110.
6. British Celanese, Ltd., C. Dreyfus and C. Palmer, E. P. 295035; abst. C. A. 1929, **23**, 2046; J. S. C. I. 1930, **49**, 370-B.

about 100°. In damping warps and wefts in looms and knitting machines[1] where the cellulose acetate is to be woven or knitted, ethylene dichloride, with or without a diluent, is recommended.

Instead of applying vat and sulfur dyes to cellulose acetate fabric from a dye bath necessarily containing an alkaline hydroxide[2] so that the ester is deleteriously affected, the fabric is completely printed with a paste containing the dye and alkali and then steamed. The fabric is not adversely affected under these conditions, although partial hydrolysis of the ester occurs. An ink which may be applied with a stylograph pen and which is particularly adapted for marking cellulose acetate fabrics[3], being unaffected by dyeing or bleaching processes, comprises a cellulose ester solution with linseed or tung oil in which has been admixed vermilion, ultramarine or lead chromate. In sealing the edges of cellulose ester fabrics against fraying or raveling[4], the edges are subjected to a fusing, softening or dissolving treatment, and then permitted to solidify.

The British Celanese, Ltd.[5] have described the production of cellulose acetate in which the partial hydrolysis is carried on in two stages. First a mild hydrolysis is induced by allowing the ester to remain for a time with sufficient water, which may contain acetic acid or hydrogen dioxide, and, after addition of excess of water, the ripening of the precipitated ester is completed in the presence of dilute acid. Dilute or waste acetic or propionic acids may

1. British Celanese, Ltd., E. P. 295054.
2. British Celanese, Ltd., and C. Dreyfus, E. P. 295579; abst. C. A. 1929, **23**, 2305; J. S. C. I. 1930, **49**, 101-B; Silk J .1928, **5**, #55, 76.
3. British Celanese, Ltd., H. Platt and C. Dreyfus, E. P. 296759; abst. C. A. 1929, **23**, 2585.
4. British Celanese, Ltd., and C. Dreyfus, E. P. 298207, 299042; Addn. to 293858, 297712; abst. C. A. 1929, **23**, 2838; J. S. C. I. 1929, **48**, 204-B. See also E. P. 281271.
5. British Celanese, Ltd., and G. Schneider, E. P. 300140; abst. C. A. 1929, **23**, 3588; J. S. C. I. 1930, **49**, 655-B; British Plastics, 1930, **2**, 135. Cites E. P. 207562.

be concentrated and recovered by extraction with methylene chloride (which may be mixed with ether) and then distilling the extract[1].

Stiff fabrics are made of cellulose acetate yarns by giving them a high twist, especially filaments greater than 200 denier[2]. Fabrics may also be made of "spun" acetate yarn (so-called "short staple") by cutting the filaments into short lengths and spinning. Local or diversified effects are obtainable on acetate fabrics[3] by local application of a saponifying agent, and thereafter treating with a carbonizing solution whereby any regenerated cellulose fiber is removed. When the fabric is made wholly of cellulose acetate, holes are produced. Lower aliphatic acids as acetic are concentrated by heating, the ester (methyl acetate) with saponifying agents as sulfuric, meta- or pyro-phosphoric acids in the presence of only approximately the amount of water theoretically required, the materials being brought into contact counter-currentwise[4].

In the production of acetate silk[5], to avoid waste of spinning solution when a jet or nozzle is changed, there is associated with each spinning jet a valve adapted to close when the nozzle is removed, and to open when the nozzle is fitted or replaced. In re-lustering acetate silk, the fabric or fiber is treated with an aqueous solution of swelling agents (acetic acid, phenol, benzyl alcohol, triacetin, cyclohexanone, ammonium thiocyanate) and the goods afterwards treated for the removal of water by evaporation without reduction of ratio of solvent to water in the aqueous

1. British Celanese, Ltd., and H. Martin, E. P. 301734; abst. C. A. 1929, **23**, 4230.

2. British Celanese, Ltd., and C. Dreyfus, E. P. 302361; abst. C. A. 1929, **23**, 4353; J. S. C. I. 1930, **49**, 53-B; Silk J. 1929, **5**, #58, 80.

3. *Ibid.* E. P. 302363, Addn. to 274074; abst. C. A. 1929, **23**, 4352; Silk J. 1929, **5**, #58, 80.

4. British Celanese, Ltd., and W. Bader, E. P. 284582; abst. C. A. 1928, **22**, 4537.

5. British Celanese, Ltd., and J. Bower, E. P. 299405; abst. J. S. C. I. 1929, **48**, 14-B.

solution retained by the material[1]. Acetic acid or methyl acetate may be obtained by heating methyl alcohol with CO in the presence of an inorganic acid or a sulfonic acid. As catalysts may be used phosphoric, boric, arsenic and phosphomolybdic acids[2]. Aliphatic anhydrides as acetic anhydride may be produced by heating a dry mixture of sodium metaphosphate, sodium acetate and kieselguhr at 150-180°, glacial acetic acid being added during the course of the reaction[3]. Acetic and propionic acids may be extracted from aqueous solutions by means of ether, chloroform, acetone oils or petroleum hydrocarbons (benzene, toluene, gasoline)[4].

Unmercerized cotton or alkalicellulose is rendered more readily esterifiable by treatment with small quantities of liquid formic acid (70-90%), and by using 10-20% of the acid it is not necessary to remove residual acid before acetylation[5]. Acetic anhydride is formed by heating the vapor of acetic acid, the anhydride being condensed and separated from associated water by passing the vapors under the surface of a cooled "extraction liquid" as benzene, trichlorethylene, ether or chloroform in an apparatus which is described[6].

In dyeing, printing or stenciling cellulose acetate[7], vat

1. British Celanese, Ltd., J. Briggs, J. Kidd and C. Palmer, E. P. 259265; abst. C. A. 1927, **21**, 3461; J. S. C. I. 1926, **45**, 1008-B. Cites E. P. 165164.

2. British Celanese, Ltd., H. Dreyfus and W. Bader, E. P. 283989; abst. C. A. 1928, **22**, 4133. See also E. P. 264558, 284582.

3. *Ibid.* E. P. 299342; abst. C. A. 1929, **23**, 3234; J. S. C. I. 1928, **47**, 921-B. Cf. E. P. 280972.

4. British Celanese, Ltd., H. Dreyfus and C. Haney, E. P. 283702. U. S. P. 1696432; abst. C. A. 1929, **23**, 850. F. P. 635219; abst. C. A. 1928, **22**, 4537. Belg. P. 345492. Cites E. P. 20125, 1907.

5. *Ibid.* E. P. 288657; abst. C. A. 1929, **23**, 703; J. S. C. I. 1928, **47**, 444-B; Plastics, 1929, **5**, 637; Silk J. 1928, **5**, #50, 70. See also E. P. 6463, 1915; 14101, 1915; 100009, 101555, 249173, 207562, 263938.

6. *Ibid.* E. P. 298667; abst. C. A. 1929, **23**, 2989; J. S. C. I. 1928, **47**, 921-B.

7. British Celanese, Ltd., and G. Ellis, E. P. 227183, Addn. to 219349; abst. C. A. 1925, **19**, 2751; J. S. C. I. 1925, **44**, 204-B; Rayon J. 1926, **1**, #1, 18. U. S. P. 1641965; abst. C. A. 1927, **21**, 3752; J. S. C. I. 1927, **46**, 812-B.

dyestuffs of the anthraquinone series in the unreduced state (Indanthrene, Cibanone, Algol) are solubilized[1], and used for coloring. Example, Algol Pink R, incorporated with sodium sulforicinoleate is heated to 90° until the degree of solubilization desired is obtained. Coloring substances of the stilbine group which contain no sulfo groups have been brought forward as desirable cellulose acetate dyestuffs[2], the dyes being applied as such or formed within the fiber by coupling diazotized aminostilbine with developers as phenol, 1 -phenol-3-methyl-5-pyrazolone, diethylaniline, *m*-phenylenediamine, *a*-naphthylamine, *b*-naphthol or *b*-hydroxynaphthoic acid, which produce shades as gold, red, reddish-brown, plum and black. Or[3], the acetate silk may be impregnated with an amino body (as aniline, *p*-aminophenol, *p*-phenylenediamine, *p*-amidophenylamine, benzidine, tolidine) and subsequently oxidizing (as with sodium or potassium chlorates, bichromates, hypochlorites). Or the acetate silk materials may be dyed or printed with vat or sulfur dyes[4], hydrolysis of the ester being avoided by the use of sodium or potassium phenolate, cresolate, xylenolate, catecholate, resorcinolate, guaiacolate, quinolate, naphtholate, *p*-chlorphenate, or di-sodium (or potassium) leucoanthraquinonate.

Cellulose acetate may also be dyed with acidylaminoanthraquinones, suitable compounds including 1-acetamido-, 1-propionamido-, 1-acetamido-4-methoxy-, 1-acetamido-4-hydroxy-, 1.4-*bis*acetamido-, 1.4-*bis*propionmethylamido-, 1-acetmethylamido-4-methoxy-, and 1-acetamido-4-methylamino-anthraquinone, giving respectively, lemon-yellow, greenish-yellow, golden-yellow, orange, orange, bright red, orange, and reddish-violet shades[5]. The fastness to light

1. As described in E. P. 219349; abst. J. S. C. I. 1924, **43**, 906.
2. British Celanese, Ltd., and G. Ellis, E. P. 253978; abst. C. A. 1927, **21**, 2565. Can. P. 276512; abst. C. A. 1928, **22**, 2066.
3. *Ibid.* E. P. 255962; abst. Textile World, 1927, Feb. 12, p. 20. Can. P. 276513. U. S. P. 1793360.
4. *Ibid.* E. P. 262506; abst. C. A. 1927, **21**, 3752; J. S. C. I. 1927, **46**, 105-B.
5. *Ibid.* E. P. 263260; abst. C. A. 1928, **22**, 171; J. S. C. I. 1927, **46**, 216-B; Rayon, 1927, **5**, #11, 24.

of colors dyed or printed on cellulose acetate is improved by treating the material with a simple or substituted organic amino-compound as aniline, alkylanilines, or alkylphenylenediamines[1]. In dyeing cellulose acetate in combination with animal or other fibers deleteriously affected by alkalis, the caustic may be replaced when vat or sulfur dyes are used, by sodium phenoxide, potassium tolyloxide, sodium quinoxide, sodium *b*-naphthoxide or sodium *p*-chlorphenoxide[2].

Patterns are produced on cellulose acetate fabrics by local application of substances which modify the action of delustering bodies and then treating with such agents[3]. Suitable substances are waxes, resins, gums, pigments, phenols, chlorphenols or aryl halides. Cellulose formate or propionate yarn may be dyed by the use of an aqueous dispersion of a relatively insoluble coloring matter[4], by pretreating the latter with dispersing agents as ammonium sulforicinoleate, sodium sulfonaphthalenericinoleate or sodium sulforicinoleate or xylene. Dyeing as above is aided by the presence of secondary solvents[5], as chlorbenzenes and chlorphenols, dyestuffs as 3-(5.7 dibromoindole)-2′-thionaphthenindigo being readily solubilized.

In the production of new effects on acetate fabrics[6],

1. British Celanese, Ltd., and G. Ellis, E. P. 243841; abst. C. A. 1927, **21**, 179; J. S. C. I. 1926, **45**, 124-B; Jour. Soc. Dyers, 1926, **42**, #2, 69. Can. P. 271279; abst. C. A. 1927, **21**, 3469. Belg. P. 328736.

2. *Ibid.* E. P. 263473; abst. C. A. 1928, **22**, 171; J. S. C. I. 1927, **46**, 215-B.

3. *Ibid.* E. P. 266777; abst. C. A. 1928, **22**, 875; J. S. C. I. 1927, **46**, 406-B; Rayon, 1927, **5**, #2, 24.

4. *Ibid.* E. P. 284376; abst. C. A. 1928, **22**, 4834; J. S. C. I. 1928, **47**, 229-B. F. P. 642330; abst. C. A. 1929, **23**, 1287. Belg. P. 344889.

5. British Celanese, Ltd., G. Ellis and W. Goldthorpe, E. P. 242711; abst. Rayon, 1926, **2**, #4, 15. Belg. P. 328117. U. S. P. 1690481; abst. C. A. 1929, **23**, 528; J. S. C. I. 1928, **47**, 926-B. Can. P. 271278.

6. British Celanese, Ltd., G. Ellis and R. Mann, E. P. 277414; abst. J. S. C. I. 1927, **46**, 874-B; Silk J. 1927, **4**, #43, 66. U. S. P. 1773975; abst. C. A. 1930, **24**, 5168; J. S. C. I. 1930, **49**, 945-B; Cellulose, 1930, **1**, #8, 223. Belg. P. 342818. 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. Compare E. P. 224681, 224925, 227183, 237943. See C. A. 1925, **19**, 579, 1351, 1952, 2751; 1926, **20**, 1910.

they are printed locally with an aliphatic carboxylic acid (acetic, propionic, butyric, chloracetic, aminoacetic, glycollic, lactic, citric, succinic) and afterwards steamed. Useful dyestuffs for cellulose acetate are nitro derivatives of carbazoles[1], 1-nitrocarbazole solubilized with sodium sulforicinoleate dyeing bright yellowish green. Acetate silk may also be dyed with nitro-derivatives of compounds containing two or more aromatic residues, two of which are united by a single linking not consisting of nitrogen alone[2], as 3.3′-dinitrobenzidine, 2-nitro, 2.4-nitro-, and 4-chlor-2-nitro-*N*-benzylanilines, 3-nitro-4-aminodiphenyl ether, 3.3′-dinitro-4.4′-tetramethyldiaminobenzophenone, all giving various shades of yellow.

In obtaining ornamental effects on acetate fabrics[3], selected portions of the back of a fabric, the pile of which is composed of acetate filaments, are treated with a substance which will soften or weaken the ester pile filaments, which are then removed by brushing or suction. Lactic, formic or acetic acids or acetone are claimed as suitable. Acetate silk threads which have lost their luster by boiling aqueous liquids may be re-lustered to any desired degree by immersion in hot aqueous neutral salt solutions (ammonium, sodium, potassium, aluminum, chlorides or sulfates), and/or cane sugar[4]. The luster may also be modified and controlled by use, together with delustering media as hot water, steam or aqueous solutions[5], of protecting

1. British Celanese, Ltd., G. Ellis, H. Olpin and W. Miller, E. P. 283081; abst. C. A. 1928, **22**, 3996; J. S. C. I. 1928, **47**, 156-B.

2. *Ibid.* E. P. 283253; abst. C. A. 1928, **22**, 3996; J. S. C. I. 1928, **47**, 189-B. F. P. 639825; abst. C. A. 1929, **23**, 718. U. S. P. 1679935; abst. C. A. 1928, **22**, 3787; J. S. C. I. 1928, **47**, 745-B. See also E. P. 182830, 227183. F. P. 602603, 627427.

3. British Celanese, Ltd., G. Ellis, H. Olpin and E. Walker, E. P. 302208; abst. C. A. 1929, **23**, 4352; J. S. C. I. 1929, **48**, 202-B. U. S. P. 1783608; abst. C. A. 1931, **25**, 421.

4. British Celanese, Ltd., C. Palmer and S. Fulton, E. P. 259266; abst. C. A. 1927, **21**, 3461; J. S. C. I. 1926, **45**, 976-B. U. S. P. 1774184; abst. C. A. 1930, **24**, 5168. Can. P. 285049; abst. C. A. 1929, **23**, 996. See also E. P. 165164. U. S. P. 1554801.

5. *Ibid.* E. P. 260312; abst. C. A. 1927, **21**, 3471; J. S. C. I. 1927, **46**, 9-B; Rayon J. 1927, Feb. p. 49. Can. P. 275737. See also E. P. 246879.

soluble salts (ammonium, lithium, sodium, potassium, magnesium or aluminum sulfates, chromates, chlorides, nitrates, acetates, oxalates). Where the fabric contains threads of both normal and delustered cellulose acetate silk[1], due to the fact that the delustering operation decrease the affinity for basic dyes as Capri Blue, two color effects are possible by suitably dyeing. If the fabric comprises mixtures of cellulose acetate and animal fibers[2], as velvets, where the pile is the acetic ester, the pile may be destroyed by printing with inorganic acids or their salts (sulfuric acid, sodium hydrogen sulfate), and rèmoved by subsequent neutralization and brushing.

Acetic anhydride containing sulfur compounds[3] may be purified by mixing with at least one metallic acetate, preferably sodium acetate, introducing chlorine, and distilling the acetic anhydride. Cellulose acetate goods are dyed from a hyposulfite bath without hydrolysis by means of quinone arylides of the benzene or naphthalene series[4], or thiazines, azines or oxazines derived therefrom. To prevent hydrolysis of the cellulose, the operation is carried out preferably at 20°. After much experimentation[5], a satisfactory citron-yellow dyestuff for cellulose acetate has been produced, obtained by condensing 2.4-dioxychinolin with aniline or toluidine, which, in addition to excellent fastness to light, is non-phototropic. Brown shades fast to light and washing are obtained on cellulose acetate by the

1. British Celanese, Ltd., C. Palmer and S. Fulton, E. P. 278116; abst. J. S. C. I. 1927, **46**, 905-B. U. S. P. 1777445; abst. C. A. 1930, **24**, 6034; J. S. C. I. 1930, **49**, 1063-B. Cites E. P. 242393, 269960, 273819, 273820. U. S. P. 1618413, 1618414.

2. British Celanese, Ltd., and G. Rivat, E. P. 302592; abst. C. A. 1929, **23**, 4352; J. S. C. I. 1929, **48**, 976-B; Silk J. 1929, **5**, #59, 72.

3. British Celanese, Ltd., and W. Skertchly, E. P. 270809; abst. C. A. 1928, **22**, 1596; J. S. C. I. 1927, **46**, 541-B. U. S. P. 1696363; abst. C. A. 1929, **23**, 850; J. S. C. I. 1929, **48**, 123-B. Can. P. 283817; abst. C. A. 1928, **22**, 4539.

4. British Dyestuffs Corp., Ltd., J. Baddiley and H. Browning, E. P. 233813; abst. C. A. 1926, **20**, 823; J. S. C. I. 1925, **44**, 541-B.

5. British Dyestuffs Corp., Ltd., J. Baddiley and J. Hill, D. R. P. 450900; abst. Kunstseide, 1928, #1, 15.

use of insoluble disazo dyes of the type nitroarylamine, (*m*-, and *p*-nitroanilines, 2.4-dinitroaniline, picramic acid, 4.5-dinitro-*a*-naphthylamine), with an amine (aniline, *m*-toluidine, cresidine, *a*-naphthylamine, 1-amino-2-naphthylethyl ether) and amine of the benzene series *m*-phenylenediamine, *m*-toluidine, cresidine). Sulfonic groups must be absent[1].

Cellulose acetate may also be dyed by combining 5-nitro-2-anisidine with diethylaniline in the presence of lignonesulfonic acid[2], or by coupling tetrazotized 4.4′-diaminodiphenyl mono-, di-, or tri-sulfide with an aminonaphtholsulfonic acid, examples being, 4.4′-diaminodiphenyl sulfide coupled with salicylic acid and phenyl-Y-acid (brown), with phenyl-J-acid (bluish-red), or with phenylmethylpyrazolone and J-acid (scarlet)[3].

1. British Dyestuffs Corp., Ltd., J. Baddiley and H. Browning, 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.

2. British Dyestuffs Corp., Ltd., J. Baddiley, J. Hill and A. Shepherdson, Addn. 33009 to F. P. 623761; abst. C. A. 1929, **23**, 1281.

3. British Dyestuffs Corp., Ltd., R. Brightman and P. Chorley, E. P. 296011; abst. J. S. C. I. 1928, **47**, 782-B. India P. 13072, 1927. British Dyestuffs Corp., Ltd., and G. Frank, E. P. 226948; abst. J. S. C. I. 1925, **44**, 167-B. Although the majority of sulfonated dyestuffs have no affinity for cellulose acetate, monosulfonated dyestuffs containing no hydroxyl group, but having a sulfo group in *o*-position to the azo group, and monoazo dyestuffs prepared by combining an unsulfonated diazo compound containing no hydroxyl group with a naphthylaminemonosulfonic acid in which the sulfo group is in the peri position to the amino or substituted amino group and which also contains no hydroxyl group, have an affinity for cellulose acetate. A hydroxyl group is capable of increasing the activity of a sulfo group so that the affinity of a dyestuff for cellulose acetate is diminished. Dyestuffs suitable for application to cellulose acetate are obtained by coupling diazotised *p*-nitroaniline-*o*-sulfonic acid or diazotised 2:1-naphthylaminesulfonic acid with N-alkyl or N-aryl substituted amines, particularly substituted naphthylamines, or with *m*-toluylenediamine. For instance the products from diazotised *p*-nitroaniline-*o*-sulfonic acid combined with phenyl-*a*-naphthylamine, *p*-tolyl-*a*-naphthylamine, ethyl-*a*-naphthylamine, ethyl-*b*-naphthylamine, phenyl-*b*-naphthylamine, *aa*′-dinaphthylamine, and *bb*′-dinaphthylamine are brown, brown, orange-brown, violet, violet, brown, and blue-violet dyestuffs, respectively, having an excellent affinity for cellulose acetate, and by reduction of the nitro group, and coupling with a *m*-diamine, further useful dyes are obtained. *p*-Nitroaniline-azo-1:8-naphthylaminesulfonic acid (peri acid) and *p*-nitroaniline-azo-phenyl-peri acid are dyestuffs for cellulose acetate and contain a sulfo group in the peri position to the amino or substituted amino group.

Water-soluble dyes which may be used for dyeing cellulose acetate[1] are obtained from many acid dyes by converting their sulfonic acid groups into sulfonamides by successive treatment with phosphorous pentachloride and ammonia. Reddish-orange and orange dyes are obtained by coupling diazotized aniline with 1-naphthol-3.8-disulfonamide or 1.8-naphthasultam respectively. Or[2], dyeing may be affected after mordanting with aluminum, chromium or ferrous thiocyanides, aluminum, iron or chromium benzoates, salicylates or phthalates. If mixed fabrics containing acetate silk are to be dyed[3], sulfide colors may be used so that the vegetable fiber alone is dyed, by addition to the ordinary sulfide bath of ammonium sulfate to prevent saponification and consequent dyeing of the acetyl ester. Sulfate dyestuffs may also be used[4].

1. British Dyestuffs Corp., Ltd., R. Horsfall, L. Lawrie, J. Henderson and J. Hill, E. P. 257654; abst. C. A. 1927, **21**, 3134; J. S. C. I. 1926, **45**, 976-B. D. R. P. 479224; abst. C. A. 1929, **23**, 4831. U. S. P. 1759010; abst. C. A. 1930, **24**, 3656; J. S. C. I. 1930, **49**, 657-B. Cites U. S. P. 1483797, 1498315, 1534019. E. P. 207711.

2. British Dyestuffs Corp., Ltd., L. Lawrie, H. Blackshaw, E. P. 240293; abst. C. A. 1926, **20**, 2253; J. S. C. I. 1925, **44**, 955-B; Rayon, 1925, **1**, #10, 23.

3. British Dyestuffs Corp., Ltd., and H. Mudford, E. P. 238721; abst. C. A. 1926, **20**, 2079; J. S. C. I. 1925, **44**, 845-B. Cf. E. P. 19473, 1914.

4. British Dyestuffs Corp., Ltd., W. Perkin and G. Bate, E. P. 237739; abst. C. A. 1926, **20**, 1722; J. S. C. I. 1925, **44**, 754-B. See also E. P. 181750. A few of the sulfato dyestuffs described in E. P. 181750 (J.S.C.I. 1922, 625-A) are capable of dyeing cellulose acetate silk from a neutral, acid, or alkaline bath in shades fast to light and washing, the nitrated monoazo dyestuffs yielding the brightest shades. For example, cellulose acetate silk is dyed a bright scarlet by immersion for 1 hr. at 60°-80° in a liquor containing 3% of salt, 1% of sulfuric acid, and 1% of the dyestuff obtained by coupling diazotised *p*-nitroaniline with sodium sulfatoethylaniline. Sulfato dyestuffs containing amino groups, *e. g.*, *p*-aminobenzeneazo-*p*-sulfatoethylaniline, may be used, and the resulting shades subsequently diazotised and developed by the usual methods. Two-color effects on union materials containing cotton and cellulose acetate silk are obtained by dyeing in one bath with sulfato dyestuffs having an affinity for either but not both of the fibres. Suitable sulfato dyestuffs for cellulose acetate silk are obtained by coupling *m*-nitroaniline with sulfatoethylaniline (reddish-yellow) or ethylsulfatoethylaniline (yellowish-orange), *p*-nitroaniline with sulfatoethylaniline (reddish-orange), or sulfatoethyl-*o*-toluidine (bright red) or ethylsulfatoethylaniline (scarlet) or sulfatoethyl-*b*-naphthylamine (bright pink) or

Anthraquinone carbamides have affinity for cellulose acetate[1], and are obtained by condensing α-anthraquinonylethyl carbamate or α-anthraquinonylcarbamic chloride with equimolecular proportions of α-aminoanthraquinones, 1.4-, 1.5-, or 1.8-diaminoanthraquinone, diaminoanthrarufin, or diaminochrysazin. The latter, condensed with α-anthraquinonylethyl carbamate dyes a steel-grey shade, and diaminoanthrarufin with α-anthraquinonylethyl carbamate, a brown shade. If 1.5- or 1.8-diaminoanthraquinone is condensed in the presence of iodine with diaminoanthrarufin or diaminochrysazin[2], orange to brown and red shades result.

Ethylene glycol and ethylene oxide may be prepared by forcing ethylene chlorhydrin and steam through a tower against a counter-current of crude chlorhydrin[3]. Acetate silk is dyed directly by means of coeramidines (anthraquinone-acridines[4], those from 1-anilinoanthraquinone dyeing greenish-yellow, 1-anilino-2-methylanthraquinone (golden-yellow), 1.5-dianilinoanthraquinone (pink), 1.4-di-*p*-toluidino- (brownish-red), 1-amino-4-*p*-toluidino- (bluish-red), and 1-amino-5-*p*-toluidino-anthraquinone (violet). *Sym*-1.4-dialkylaminoanthraquinones are converted into products containing fewer alkyl groups by treatment with sulfuric acid at above 150°, the dye thus formed from 1.4-

sulfatoethyl-α-naphthylamine (magenta), 1-nitro-2-naphthylamine with methylsulfatoethylaniline (orange), 4-nitro-1-naphthylamine with ethylsulfatoethylaniline (brown), 3:5-dinitro-*o*-toluidine with ethylsulfatoethylaniline (cardinal red), *o*-chloro-*p*-nitroaniline with ethylsulfatoethylaniline (bluish-red) or sulfatoethyl-α-naphthylamine (bright violet), 2:4-dinitroaniline with benzylsulfatoethylaniline (bluish-red) or ethylsulfatoethylaniline (very blue red) or sulfatoethyl-α-naphthylamine (navy blue), and 2:4-dinitro-1-naphthylamine with sulfatoethyl-α-naphthylamine (greenish-blue).

1. British Dyestuffs Corp., Ltd., W. Perkin and G. Bate, E. P. 248858; abst. J. S. C. I. 1926, **45**, 398-B.
2. *Ibid.* E. P. 257353; abst. C. A. 1927, **21**, 3133.
3. British Dyestuffs Corp., Ltd., K. Saunders and H. Wignall, E. P. 286850; abst. J. S. C. I. 1928, **47**, 360-B.
4. British Dyestuffs Corp., Ltd., A. Shepherdson and A. Davidson, E. P. 268933; abst. C. A. 1928, **22**, 1482; J. S. C. I. 1927, **46**, 438-B; Rayon, 1927, **5**, #2, 24, #11, 24. Cites D. R. P. 126444, 262469.

dimethyldiaminoanthraquinone dyeing cellulose acetate bright violet-blue shades[1].

Clear white and colored discharge effects on cellulose acetate silk are obtained in the usual manner by means of reducing agents containing sodium formaldehyde-sulfoxylate[2], provided that thiocyanates (calcium, barium or ammonium) are present. Cellulose acetates of predetermined viscosity may be prepared by carrying out the acetation in the presence of definite amounts of water[3]. Highest viscosities are obtained when anhydrous esterifying mixtures and perfectly dry cellulose are used.

As a stiffener for toes and other parts of shoes[4], cellulose acetate gelatinized and impregnated in a fabric has been the subject of patent protection. H. Britton[5] has detailed the requirements for good airplane wing dopes, including the preferred acetyl values, viscosity, acidity and solvent combinations. In the manufacture of acetylcellulose lacquers[6], the addition of "polyvalent metallic salts of alkyl half esters of phthalic acid" has been recommended, such as copper, lead, cadmium, zinc, iron, manganese, nickel or cobalt monoethyl- (or propyl, butyl, amyl) phthalate. Properties of zinc (or lead, ferric, cupric, cadmium) butyl resins are detailed.

A wall-covering material has been described[7], comprising thin plywood veneer coated with cellulose acetate

1. British Dyestuffs Corp., Ltd., A. Shepherdson, W. Tatum and F. Lodge, E. P. 291814; abst. C. A. 1929, **23**, 1286.
2. British Dyestuffs Corp., Ltd., and L. Smith, E. P. 262254; abst. C. A. 1927, **21**, 3752; J. S. C. I. 1927, **46**, 71-B. U. S. P. 1651639; abst. C. A. 1928, **22**, 875; J. S. C. I. 1928, **47**, 50-B.
3. British Enka Artificial Silk Co., E. P. 263771; abst. C. A. 1928, **22**, 164; J. S. C. I. 1928, **47**, 444-B; Plastics, 1928, **4**, 386. India P. 11934, 11935, 11936, 11937, 11941, 11942.
4. British United Shoe Machinery Co., Ltd., W. Lund and L. Mellerio, E. P. 289496; abst. C. A. 1929, **23**, 720.
5. Aviation, 1927, **22**, 991; Industrial Chemist, 1927, **3**, 116; abst. C. A. 1927, **21**, 2070; Chem. Met. Eng. 1927, **34**, #5, 312. Industrial Chemist 1927, **3**, 59; abst. C. A. 1927, **21**, 1555.
6. B. Brown and C. Bogin, U. S. P. 1591652; abst. C. A. 1926, **20**, 3242; J. S. C. I. 1926, **45**, 783-B.
7. J. Bruning & Sohn A.-G., E. P. 283023; abst. C. A. 1928, **22**, 3972.

and consolidated under the action of heat and high pressure. The veneer is so thin that when coated[1], it may be rolled up and glued to the wall like paper, the surface being embossed and patterned. It has been found that cellulose acetate is peptized by neither alcohol or ether[2], but readily so by acetone or methyl alcohol at room temperature. Likewise with tetrachlorethane alone or with absolute alcohol.

When formic acid is added to a mixture of calcium formate and sodium chloride[3], and sulfuric added, formic acid is liberated in high concentration and may be collected by distillation. H. Buchholz[4] has described the formation of a molding material of cellulose acetate 200, powdered glass 18, animal glue 12, and magnesite 3. J. Bulmer[5] acetylates by mixing cellulose with 98% acetic acid, lowers the temperature well below 0°, which crystallizes the acid, after which acetic anhydride and catalyst are added until an ester of desired solubility is obtained. The theory is that crystallization causes disruption of the cellulose, which thus becomes chemically more receptive. After hydrolysis of the acetated cellulose is carried on in two stages[6], first only sufficient water is added to induce mild hydrolysis, the ester then being precipitated and treated with dilute acid for further hydrolysis. Dentures and cleft palate obturators have been described made of cellulose ethers (p. 107, n. 4), and of cellulose acetate in association with colloiding agents as benzyl alcohol, benzoin, benzil and triacetin[7].

1. J. Bruning & Sohn A.-G., E. P. 283024; abst. C. A. 1928, **22**, 3972.

2. M. Bryon, J. Phys. Chem. 1926, **30**, 1116.

3. G. Buchanan and J. Osborne, U. S. P. 1666437; abst. C. A. 1928, **22**, 1981; J. S. C. I. 1928, **47**, 397-B. Cites U. S. P. 1359257.

4. U. S. P. 1568955; abst. C. A. 1926, **20**, 822; Plastics, 1926, **2**, #6, 206.

5. U. S. P. 1692622; abst. C. A. 1929, **23**, 704; J. S. C. I. 1929, **48**, 429-B; Plastics, 1929, **5**, 452. E. P. 298819; abst. C. A. 1929, **23**, 3098; J. S. C. I. 1929, **48**, 126-B; Silk J. 1929, **5**, #56, 80.

6. *Ibid.* E. P. 300824; abst. C. A. 1929, **23**, 4071; J. S. C. I. 1929, **48**, 513-B; Silk J. 1929, **5**, #57, 74; British Plastics, 1929, **1**, #2, 71.

7. A. Burlin, S. Leicester and L. Holman, U. S. P. 1615212; abst. C. A. 1927, **21**, 822. E. P. 251373; abst. C. A. 1927, **21**, 1355; Rayon J. 1926, Sept. 39.

A plastic material suitable for the manufacture of fancy goods is made by uniting one or several thicknesses of cloth between two sheets of cellulose acetate[1], coapted by combined heat and pressure. In order to increase the absorptiveness of cellulose acetate for weighing materials as tin chloride[2], it is recommended to first treat the acetate with 15-20% formic or acetic acid to gel it. A. Caille[3] has studied the stability of acetylcellulose and cellulose acetosulfate. He finds[4] that for a given sample of cellulose acetate, the viscosity of its acetone solution decreases with the proportion of combined sulfuric acid in the sample. The

1. C. Cachon, F. P. 633626; abst. C. A. 1928, **22**, 3499.

2. E. Cadgene and G. Rivat, E. P. 259899; abst. C. A. 1927, **21**, 3470. D. R. P. 492148; abst. C. A. 1930, **24**, 2600. G. Rivat, U. S. P. 1631062; abst. C. A. 1927, **21**, 2388. Can. P. 271232. G. Rivat, E. Cadgene and C. Dreyfus have patented the use of ferric chloride with logwood black for dyeing acetate silk, Can. P. 284751; abst. C. A. 1929, **23**, 994.

3. A. Caille, Chim. et Ind. 1925, **13**, 11; abst. C. A. 1925, **19**, 1495; J. S. C. I. 1925, **44**, 280-B; Chim. et Ind. 1926, **15**, 189; abst. C. A. 1926, **20**, 1719; J. S. C. I. 1926, **45**, 355-B. In this connection see E. Knecht and F. Thompson, J. Soc. Dyers Col. 1921, **37**, 270; abst. C. A. 1922, **16**, 1872. The sulfo-celluloses were prepared, using a mixture of 50 parts glacial acetic acid and 50 of 100% sulfuric acid, and maintained at 45° for 30 mins. The resulting product was divided and washed in 3 ways: With alsolute alcohol, distilled water and ordinary water with a rapid rinse in distilled water. It was found that alcohol and ordinary water gave a product in 2 or 3 hours' washing, neutral to litmus, whereas, with distilled water the material was acid to litmus after washing for 6 hours. Upon treatment with lime water, the sulfo-cellulose was saponified. Its behavior was entierly analogous to the action of calcium hydroxide on aceto-cellulose containing sulfate radicals. The stability of sulfo-cellulose to heat was roughly determined, and was found in the sample washed with alcohol when treated so that the temperature increased at 1° per min. that a yellow coloration appeared at 110°, at 155° the material became gray, and at 180° the mass was black. The final product was found to contain free sulfuric acid and the blackening was due to carbonization of the cellulose by the acid. Sulfo-cellulose washed with lime water for 41 hrs. was observed to maintain a clear yellow color when heated at 180°, the stability of the material being increased by this treatment. In working with the sulfo-acetates of cellulose, the use of lime water for washing is shown to be advantageous since it removes the sulfuric acid present, hydrolyzes the sulfate groups, leaving an aceto-cellulose of high quality.

4. A. Caille, Chim. et Ind. 1928, **19**, 402; abst. J. S. C. I. 1928, **47**, 600-B; Plastics, 1928, 447.

analysis of acetic anhydride by the 2.4-dichloraniline[1] method was reported upon in 1925.

In the mercerization at the usual temperature of cotton fabric containing cellulose acetate silk[2], protective substances are required for addition to the mercerizing liquid to prevent deterioration of the ester by hydrolysis. There has been patented for this purpose sodium chloride, chlorate, sulfate, glycollate, and zinc oxide, chloride, sulfate. Also sucrose, glycerol, phenol and resorcinol. In another method[3], there is added to the mercerizing bath a liquid which neither mixes with nor reacts with alkali solution of mercerizing strength, as benzene, toluene, hydrogenated naphthalenes, solvent naphtha and essential oils.

In obtaining pattern effects on acetate silk[4], the material is printed with a salt of a delustering agent as sodium phenolate or aniline chloride, and subsequently treated with hot dilute inorganic acid to decompose the salt and free the delustering agent. Damask effects are produced on cellulose acetate by printing with caustic alkali to saponify the ester, washing, and finally treating with a delustering agent (boiling water, formic, acetic or lactic acids, acetone, furfuraldehyde, pyridine, aniline) by which the unsaponified portion is delustered without inducing change in luster of the saponified part[5].

Copper, aluminum, tin, lead, zinc or alloys are used in the form of rough and unflaked particles with pitted or jagged surfaces to form paints with cellulose acetate as

1. W. Calcott, F. English and O. Wilbur, J. I. E. C. 1925, **17**, 942.
2. Calico Printers' Assoc., Ltd., and L. Lantz, E. P. 259394; abst. J. S. C. I. 1926, **45**, 976-B. See W. Marshall, E. P. 210484; abst. J. S. C. I. 1924, **43**, 290-B.
3. Calico Printers' Assoc., Ltd., L. Lantz and C. Keyworth, E. P. 273830; abst. C. A. 1928, **22**, 2068; J. S. C. I. 1927, **46**, 746-B; Rayon, 1927, Oct. 30, 24; Nov. 15, 24.
4. Calico Printers' Assoc., Ltd., and J. Whinfield, E. P. 275357; abst. C. A. 1928, **22**, 2279; J. S. C. I. 1927, **46**, 776-B.
5. 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; Rayon, 1928, May 15, 30.

binder[1], which coatings may afterwards be burnished. Pleasing effects are said to be produced on cellulose acetate by treatment with 40-55% solution of ferric chloride[2]. If it is desired to produce colored patterns[3], a swelling agent for acetylcellulose is first applied, then a water-insoluble dye which has previously been solubilized.

By passing acetylene gas into an aqueous solution containing a catalyst at a speed four times the rate of absorption, acetaldehyde is formed in nearly theoretical amount[4]. C. Candlish in 1927 gave directions and recent developments in the dyeing of celanese mixtures[5]. Bibenzyl (m. pt. 51.8°) has been advocated as a cellulose ester plastic and camphor substitute[6]. It is odorless. Likewise, as cellulose acetate solvents and plasticizers have been introduced mono- and di-alkyl ethers of ethylene glycol, comprising the monomethyl, dimethyl, monoethyl, diethyl, monopropyl, dipropyl, monoallyl and *iso*butyl ethers, boiling at 125°, 183°, 135°, 124°, 150°, 160°, 159°, 181° respectively[7]. Acetate lacquers may also be produced by adding to dissolved acetylcellulose a polymerized olefine derivative[8], as polymerized vinyl acetate, vinyl chloride, styrol, divinyl ether and polymerized allylene compounds. *o*-Cresyl *p*-toluenesulfonate[9] with acetone-soluble cellulose acetate has been recommended

1. Canada British Syndicate, Ltd., E. P. 244819; abst. Chem. Zentr. 1926, II, 112.
2. Canadian Celanese, Ltd., E. P. 284751.
3. G. Ellis, E. Greenhalgh, H. Dreyfus and Canadian Celanese, Ltd., Can. P. 281180; abst. C. A. 1928, **22**, 3051. In this connection see British Dyestuffs Corp., Ltd., E. P. 262254; abst. C. A. 1927, **21**, 3051.
4. H. Reid, W. Hovey and Canadian Electro Products Co., Can. P. 270333; abst. C. A. 1927, **21**, 3368.
5. J. Soc. Dyers Col. 1927, **43**, 37; abst. C. A. 1927, **21**, 1358; J. S. C. I. 1927, **46**, 215-B.
6. J. Davidson, U. S. P. 1617237; abst. Plastics, 1927, **3**, 218. Carbide and Carbon Chemicals Corp., Can. P. 268571.
7. Carbide and Carbon Chemical Corp., U. S. P. 1644417, 1644418, 1644419, 1644420. E. P. 238485; abst. C. A. 1926, **20**, 2073; Chem. Zentr. 1926, I, 1076. F. P. 605085; abst. Caout. et Gutta. 1927, **24**, 13242. Can. P. 260464; abst. C. A. 1926, **20**, 3561.
8. *Ibid.* E. P. 285049.
9. S. Carroll, U. S. P. 1560542; abst. C. A. 1926, **20**, 111; J. S. C. I. 1926, **45**, 48-B.

especially for film formation, and tributyrin[1] (usually about 10-35%) to induce the proper flexibility (see p. 569, n. 1).

In order to produce cellulose acetate plastics of relatively low inflammability, brominated mono- and poly-hydric phenols (tribromphenol, *p*-bromphenol, bromhydrochinone)[2], monobrom-naphthalene and -anthracene[3], monobrom-benzene, -toluene, -xylene, -mesitylene, -ethylbenzene, -cumene and -cymene[4], or 2.4.6-tribromaniline and bromtoluidines[5] have received patent protection. A. Cassal and J. Rolland[6] have published a study with numerous references on acetylcellulose by X-rays, and L. Cassella & Co.[7] has given dyeing formula with dyed samples of the Azonine direct colors on acetate silk, and of indophenols[8], producing blue and bluish-green shades.

Acetate silk may also be dyed with ordinary dyes working in an alkaline bath which hydrolyzes the exterior of the filament and thereby admits of the use of substantive dyestuffs[9], including the ionamine and duranol colors. A solidifiable paste for use in the manufacture of tubes and as electrical insulating material has been brought forward by C. Castro[10], comprising methyl acetate 200, triphenyl phosphate 16-40, and sufficient cellulose acetate to impart the desired solidity upon evaporation. Ethyl-*p*-toluenesulfona-

1. S. Carroll, U. S. P. 1572232; abst. C. A. 1926, **20**, 1324; J. S. C. I. 1926, **45**, 315-B.
2. *Ibid.* U. S. P. 1631468; abst. C. A. 1927, **21**, 2558; J. S. C. I. 1927, **46**, 675-B; Plastics, 1927, 540.
3. *Ibid.* U. S. P. 1641411; abst. C. A. 1927, **21**, 3460; J. S. C. I. 1927, **46**, 873-B.
4. *Ibid.* U. S. P. 1641412; abst. C. A. 1927, **21**, 3460; J. S. C. I. 1927, **46**, 873-B.
5. *Ibid.* U. S. P. 1641413; abst. C. A. 1927, **21**, 3460; J. S. C. I. 1927, **46**, 873-B.
6. Rev. gen. Mat. Color. 1928, **32**, 333; abst. C. A. 1930, **24**, 2287.
7. Textile Colorist, 1925, **47**, 231; abst. C. A. 1925, **19**, 1950.
8. L. Cassella & Co., Die Kunstseide, 1928, 16.
9. P. Castan, Mon. Sci. 1925, **15**, 145; abst. C. A. 1925, **19**, 3377.
10. E. P. 252999; abst. C. A. 1927, **21**, 2558. F. P. 605770; abst. Kunst. 1926, **16**, 206.

mide[1] is alleged to be equally applicable for the above purposes in conjunction with acetylcellulose, especially[2] when dissolved in a solvent mixture consisting of a high- and low-boiling solvent.

W. Chase has contributed an illuminating paper on the application and properties of the Duranol, Dispersol, Ionamine, Azonine direct, Setyl direct, Cellit, Celatene, and S. R. A. dyes on acetylcellulose fibers[3]. Water paints and colored varnishes are prepared by shaking together cellulose ester varnishes and aqueous pastes of mineral pigments or lakes[4]. Azo dyes may be formed on cellulose acetate goods by coupling diazotized aminoarylglycol ethers or aminoarylglycerol ethers with the usual components[5].

The preparation of effect threads resistant to direct dyestuffs, may be obtained by acetylating cellulose in any form in a bath, the activity of which has been so moderated by adjustment of nature or quantity of catalyst that the cellulose is directly converted into mono- and di-acetates while retaining the original morphological structure of the cellulose (which is not new), and the reaction continued until the ester is completely resistant to substantive dyes[6]. To facilitate drying of gelatin papers without supplementary hardening[7], a thin non-adhesive coating of acetylcellulose is applied to the sensitive layer, with or without the addition of hardening agents.

1. Cello Products Inc., Can. P. 264990.
2. M. Mueller and Cello Products, Inc., Can. P. 264991; abst. C. A. 1927, **21**, 996.
3. Textile World, 1927, **71**, 1424; abst. C. A. 1927, **21**, 1551.
4. Chemische Fabrik Griesheim-Elektron, E. P. 233891; abst. C. A. 1926, **20**, 832.
5. Chemische Fabrik vorm. Sandoz, E. P. 245758; abst. C. A. 1927, **21**, 328; J. S. C. I. 1927, **46**, 469-B. Swiss P. 120985, 120986, 120987, 120988, 120989, 120990, 120991, 120992, 120995; abst. Die Kunstseide, 1927, 18, 64, 611. E. P. 197809, 200873, 204280, 212029.
6. *Ibid.* E. P. 280493; abst. J. S. C. I. 1928, **47**, 812-B. F. P. 635304; abst. C. A. 1928, **22**, 4816. D. R. P. 525084; abst. C. A. 1931, **25**, 4136.
7. Chemische Fabrik auf Aktien vorm. E. Schering, E. P. 271107; abst. C .A. 1928, **22**, 1552. D. R. P. 461175; abst. Chem. Zentr. 1928, II, 840.

Acetic acid may be prepared by adding calcium acetate to a paste of gypsum (calcium sulfate) in acetic acid as obtained by the reaction of sulfuric acid on calcium acetate while avoiding excess of sulfuric acid[1], and formic acid[2] of high concentration by treating the aqueous acid with an anhydrous salt (copper or magnesium sulfate) which can tenaciously retain a portion of its water of crystallization, then distilling. In the production of acetic acid from calcium acetate and sulfuric acid by the E. Schering process[3], the acetate is used in solution in acetic acid in a mud or paste of plaster of Paris.

Lacquers have been described prepared from cellulose esters and glycolmonoalkyl ethers (methyl, ethyl, *iso*propyl, butyl, cyclohexyl) esters of ethylene (or propylene or butylene) glycol, as cyclohexylpropyleneglycol ether[4], said to possess superior adhesive properties. J. Chittick has suggested new effects that may be produced by fiber blends and ply yarns of acetylcellulose in combination with wool and silk[5], and A. Claessen[6], new uses for the cellulose esters.

J. Clancy has described the use of liquid anhydrous ammonia for dissolving cellulose acetate[7], liquid sulfur dioxide for the same purpose[8] or for dissolving cellulose nitrate[9], or cellulose nitrate with liquid ammonia[10]. H. Spencer peptizes nitrocellulose to reduce the viscosity by

1. Chemische Fabrik auf Aktien vorm. E. Schering, E. P. 284143; abst. C. A. 1928, **23**, 4133; J. S. C. I. 1928, **47**, 255-B. See E. P. 7301, 1900; 4976, 1910.
2. *Ibid.* E. P. 250199; abst. Chem. Zentr. 1927, I, 179. F. P. 613983. D. R. P. 501833; abst. C. A. 1929, **24**, 4792; Chem. Zentr. 1930, II, 2572. Compare E. P. 308731; abst. C. A., 1930, **24**, 380.
3. *Ibid.* F. P. 637129; abst. C. A. 1929, **23**, 608.
4. Chemische Fabriken vorm. Weiler ter Meer, F. P. 606763; abst. Chem. Zentr. 1926, II, 1795.
5. Textile World, 1927, 1716.
6. India P. 11301, 1925. Ital. P. 254515.
7. U. S. P. 1544809; abst. C. A. 1925, **19**, 2745.
8. U. S. P. 1544810; abst. C. A. 1925, **19**, 2745.
9. U. S. P. 1544811; abst. C. A. 1925, **19**, 2745.
10. U. S. P. 1544812; abst. C. A. 1925, **19**, 2745.

means of anhydrous ammonia[1]. H. Clarke[2] has described the application of pentaerythritol tetracetate as a cellulose acetate solvent (see p. 52, n. 14), and a method for its preparation by the action of glacial acetic acid 1000, and sulfuric acid 1, on pentaerythritol 250 parts[3]. Formulae have been given for combining the tetracetate with acetylcellulose[4]. Cellulose esters (acetate, propionate, butyrate, valerate, caproate, heptylate) containing one molecular proportion of fatty acid component for approximately 24 atoms of cellulose, the fatty acid containing less than 8 C atoms[5], are prepared by heating cellulose with the fatty acid until the acyl percentage becomes substantially constant. Hydrated cellulose may be used as the initial cellulosic material[6]. These esters may be re-esterified by heating the partially hydrolyzed ester from which acid radicals have been split off[7], and by the employment of mercerized instead of normal cellulose[8], use of acid anhydride being avoided.

H. Clarke and C. Malm[9], in an endeavor to reduce the inflammability to the minimum, while still conserving maximum of stability, have described cellulose esters of chlor- (and brom) substituted propionic, *n*-butyric, *n*-valeric, *iso*-valeric, *n*-caproic, *n*-heptylic, caprylic, pelargonic, capric, lauric, myristic, palmitic, stearic, crotonic, cyclohexanecarboxylic, benzoic, *o*-methoxybenzoic, *o*-chlorbenzoic, ace-

1. U. S. P. 1797843.
2. U. S. P. 1548932; abst. C. A. 1925, **19**, 3018; Plastics, 1926, **2**, 26; Caout. et Gutta. 1926, **23**, 13315; J. S. C. I. 1925, **44**, 843-B.
3. H. Clarke, U. S. P. 1583658; abst. J. S. C. I. 1926, **45**, 645-B.
4. *Ibid.* U. S. P. 1552795; abst. J. S. C. I. 1925, **44**, 915-B; Caout. et Gutta. 1926, **23**, 13316. For pentaerythritol formate and nitrate, see E .Worden, "Technology Cellulose Esters," I, 1857-1860.
5. H. Clarke and C. Malm, U. S. P. 1668944; abst. C. A. 1928, **22**, 2272; Plastics, 1928, 627.
6. *Ibid.* U. S. P. 1668945; abst. J. S. C. I. 1928, **47**, 478-B; Plastics, 1928, 688.
7. *Ibid.* U. S. P. 1668946; abst. C. A. 1928, **22**, 2272; J. S. C. I. 1928, **47**, 478-B; Plastics, 1928, 688.
8. *Ibid.* U. S. P. 1687059; abst. Plastics, 1929, 142.
9. *Ibid.* U. S. P. 1687060; abst. Plastics, 1929, 142. See E. Geinsperger, Monats. Chem. 1905, **26**, 1459. O. Hauser and H. Muschner, Zts. ang. Chem. 1913, **26**, 137, for preparation of cellulose benzoate, dibenzoate and chlorbenzoate.

tylsalicylic, phenylacetic, hydrocinnamic and cinnamic acid, such as cellulose *ab*-dibromphenylpropionate, acetocrotonate, aceto-*ab*-dibrombutyrate, crotonostearate, acetoundecylenate and acetostearate. These mixed (?) esters may be prepared by the esterification of cellulose with the appropriate acid and anhydride in the presence of magnesium perchlorate as catalyst. In a later disclosure[1], further details of the above haloid-substituted cellulose esters have been detailed. Cellulose esters containing nitro substituted esters of halogen-substituted aliphatic or acrylic series have also been described[2], including cellulose nitro-acetate, -propionate, -butyrate, -acrylate, -crotonate, and -undecylenate, and their chlor- and brom-substituted bodies, as cellulose nitrobromacetate. Magnesium perchlorate trihydrate is the preferred catalyst.

In the dyeing of acetylcellulose with vat dyes as brom-indigo or pyrogene indigo[3], the dyeing is best effected in a hyposulfite bath kept weakly alkaline by ammonia. Black shades are produced by treating with diphenyl black base in the presence of acetic acid[4]. Acetate silk may also be satisfactorily dyed with the so-called "ice colors" which are developed on the fiber[5]. The operation is facilitated by the addition of inorganic salts (magnesium chloride) to the dyebath and protective colloids (gelatin, soap) to the developing bath. Or[6], for the production of development

1. H. Clarke and C. Malm, U. S. P. 1690620; abst. C. A. 1929, **23**, 512; J. S. C. I. 1929, **48**, 203-B; Plastics, 1929, 264. E. P. 289853; abst. C. A. 1929, **23**, 980; J. S. C. I. 1930, **49**, 279-B.

2. *Ibid.* U. S. P. 1690621; abst. J. S. C. I. 1929, **48**, 554-B; Brit. Plastics, 1929, **1**, 113. E. P. 290570; abst. C. A. 1929, **23**, 980; J. S. C. I. 1929, **48**, 976-B; Plastics, 1929, **5**, 699; Brit. Plastics, 1930, **1**, #8, 329. E. P. 287880, 290571.

3. R. Clavel, U. S. P. 1546969; abst. C. A. 1925, **19**, 2880; J. S. C. I. 1925, **44**, 709-B. E. P. 191553; abst. J. S. C. I. 1923, **44**, 221-A. U. S. P. 1448432.

4. *Ibid.* U. S. P. 1547789; abst. C. A. 1925, **19**, 3024.

5. *Ibid.* U. S. P. 1549906; abst. C. A. 1925, **19**, 3599; J. S. C. I. 1925, **44**, 801-B; Caout. et Gutta. 1926, **23**, 13315; Plastics, 1925, 62. E. P. 187964; abst. J. S. C. I. 1923, **42**, 844-A. U. S. P. 979966, 1378443.

6. *Ibid.* U. S. P. 1571320; abst. C. A. 1926, **20**, 992; Plastics, 1926, **2**, 206.

dyes, the acetylcellulose is treated with two of the three (base, diazotizing material, developer) in one bath, and the third factor in another bath.

Material particularly suitable as a leather substitute is made by impregnating acetate threads with solutions of benzenoid phenolic compounds as tannins and then reacting upon by a bath of bismuth nitrate or ferric chloride[1]. Acetate yarns that have been delustered either to produce a wool-like effect or by accident[2], may be relustered by treating them with swelling agents (formic or acetic acids, ethyl acetate, calcium thiocyanate) and then exposing in a dry condition to dry steam. Such yarns may be loaded by forming in them an insoluble metal salt, preferably such as act as loading agents for natural silk[3]. Tin, zinc, tungsten or aluminum phosphates or silicates are suitable for the purpose[4]. Albumin and ammonium carbonate followed by a solution of tin chloride containing phosphoric acid[5], have also been brought forward as a desirable cellulose acetate loading material. Preliminary treatment with phosphoric or trichloracetic acids with addition of glue[6], followed by precipitated inorganic salts, or placing the acetate yarn in a centrifuge and successively treating with salt and precipitant without intermediate washing[7], has also been proposed[8].

If acetate silk is treated with acacia, ethyl alcohol and rhoduline orange in paste condition[9], pressed by a desired

1. R. Clavel, E. P. 252661; abst. C. A. 1927, **21**, 2397; J. S. C. I. 1927, **46**, 599-B. F. P. 611401; abst, J. S. C. I. 1927, **46**, 362-B. Can. P. 275369. D. R. P. 509400; C. A. 1931, **25**, 840.
2. *Ibid.* E. P. 269605; abst. C. A. 1928, **22**, 1474; J. S. C. I. 1927, **46**, 473-B; Rayon, 1927, Aug. 15, 32; Die Kunstseide, 1927, 471. See E. P. 206818; abst. J. S. C. I. 1924, **43**, 743-B.
3. *Ibid.* E. P. 269615; abst. Rayon, 1927, Oct. 30, 24.
4. *Ibid.* E. P. 270987; abst. C. A. 1928, **22**, 1693; J. S. C. I. 1927, **46**, 553-B.
5. *Ibid.* E. P. 277602; abst. J. S. C. I. 1928, **47**, 154-B.
6. *Ibid.* E. P. 280094; Addn. to E. P. 277602; abst. J. S. C. I. 1928, **47**, 296-B; Rayon, 1928, June 15, 46.
7. *Ibid.* E. P. 296017.
8. *Ibid.* D. R. P. Anm. C-37609.
9. *Ibid.* D. R. P. 446486; abst. Kunstseide, 1927, 375; Chem. Zentr. 1927, I, 1219.

design and well dried, on washing in cold water, the pressed places will become lustrous and the deadened appearance disappear. Instead of the use of a swelling medium, acetate yarn may be lustered by treatment with steam under pressure as high as 5 atmospheres[1]. Acetate silk may be economically weighted by treatment with phosphoric acid 2%, ethyl alcohol 1%, squeezed and then immersed in zinc chloride solution[2]. If tin phosphate is used as loading material[3], the yarn may be weighted before dyeing or printing. In 1925 R. Clavel gave directions for producing mixed color effects in the dyeing of woven or knitted fabrics containing threads of acetate silk, with a list of dyes suitable for the purpose[4].

A mixed solvent for acetylcellulose has been patented[5] comprising a non-solvent (amyl alcohol, amyl acetate) with acetone. In general, where the non-solvent is of substantially higher boiling point and hence of lower evaporative tendency than is the solvent portion, our experience is that the film obtained is deficient in tensile strength, due primarily to the increment of precipitant during the evaporation. In the production of acetate threads or films[6], the solution is projected through a slit or orifices into a saponifiable oil (castor or linseed), the acetylcellulose solvent mixture being miscible with the oil used for precipitating. To prepare long films or thin strips[7], a metal spiral is coated with gelatin on both sides, then immersed in a cel-

1. R. Clavel, D. R. P. 451110; abst. Kunstseide, 1927, 567. Can. P. 275559; abst. C. A. 1928, **22**, 1243.

2. *Ibid.* D. R. P. 471370; Addn. to D. R. P. 468017, 468018; abst. C. A. 1929, **23**, 3356. E. P. 266640, 283019. F. P. 634641.

3. *Ibid.* D. R. P. 521613; abst. C. A. 1931, **25**, 3496. F. P. 621380. U. S. P. 1806043. Can. P. 249726. Ital. P. 210072.

4. *Ibid.* Color Trade J. 1926, **16**, 129; abst. C. A. 1925, **19**, 1950.

5. L. Clement, Can. P. 261371; abst. C. A. 1926, **20**, 3568. F. P. 601546, 601547.

6. L. Clement and C. Riviere, U. S. P. 1634980; abst. C. A. 1927, **21**, 2985; Plastics, 1927, **3**, 608. Can. P. 261823; abst. C. A. 1926, **20**, 2588. E. P. 224404. Holl. P. 16297.

7. E. Closmann and L. Flatow, E. P. 242165.

lulose acetate solution, which upon evaporation of solvent, leaves a thin film readily detachable.

The transmission of ultra-violet and of visible radiation through cellulose acetate silks has been measured[1]. A glass substitute for window glass, the roofs of hothouses, hotbeds, and cold frames[2], is prepared by immersing a reticular metallic base in a cellulose acetate solution, and evaporating the volatile solvent therefrom (see p. 194, n. 1). Acetic anhydride is formed when acetic acid vapor is passed over heated sodium, potassium or lithium metaphosphate[3], which may be mounted on a carrier of silica or silicon carbide, the activity of the catalyst being obtained by heating it to above 700°. In producing acetals by the reaction of acetylene upon a mono- or poly-hydric alcohol in the presence of a mercury salt[4], the product should be continuously removed as soon as formed to prevent its conversion into resinous compounds. If the alcohols contain water[5], the former is converted into acetaldehyde. The manufacture of acetaldehyde by the action of acetylene on water in presence of a mercury compound is improved by the presence in the reaction mixture of an organic solvent for acetylene (ethyl alcohol, phenol)[6].

In the production of acetic anhydride[7], acetic acid vapor is heated in the presence of a catalyst at 400-800° by

1. W. Coblentz, R. Stair and C. Schoffstall, U. S. Bur. Stand. J. Res., 1928, **1**, 105; abst. J. S. C. I. 1929, **48**, 48-B.
2. J. and A. Colle, U. S. P. 1580287; abst. Plastics, 1927, **3**, 280.
3. Consortium Fur Elektrochemische Ind., E. P. 230063; abst. C. A. 1925, **19**, 3271; J. S. C. I. 1925, **44**, 568-B. U. S. P. 1636701; abst. C. A. 1927, **21**, 3057; J S. C. I. 1927, **46**, 764-B. Can. P. 278935, 278936; abst. C. A. 1928, **22**, 2755.
4. *Ibid.* E. P. 257622; abst. C. A. 1927, **21**, 3057. D. R. P. 502431; abst. C. A. 1930, **24**, 4792.
5. *Ibid.* E. P. 264791; Addn. to E. P. 257622; abst. J. S. C. I. 1927, **46**, 541-B. H. Deutsch and W. Herrmann, D. R. P. 513796; Addn. to D. R. P. 502431; abst. C. A. 1931, **25**, 1537.
6. *Ibid.* E. P. 260305; abst. C. A. 1927, **21**, 3368; J. S. C. I. 1927, **46**, 541-B.
7. *Ibid.* E. P. 272923; abst. C. A. 1928, **22**, 1783; J. S. C. I. 1928, **47**, 474-B. (R. Meingast and M. Mugdan) D. R. P. 488573; abst. C. A. 1930, **24**, 2144. F. P. 634466; abst. C. A. 1928, **22**, 3669. Swiss P. 127521; abst. C. A. 1929, **23**, 1419. Norw. P. 45975, 1929. Can. 253734.

passage through a vessel the heat-transfer surfaces of which are of silicon, silicon carbon, or copper, and especially acid-resistant alloys containing nickel (chromium-iron, chromium-iron-nickel). It is better to preheat the acetic acid before treatment with catalyst[1], or to heat with a gaseous catalyst (phosphoric, hydrochloric or boric acids)[2]. Vinyl acetate boiled under fractionating reflux with acetic acid and a little sulfuric acid[3], gives acetaldehyde and acetic anhydride in about 70% yield. Or[4], vinyl acetate may be boiled with aqueous acetic acid and phosphoric acid, and the acetaldehyde removed by column distillation. Acetic acid may be concentrated[5] by treating it below —20° with solvents of acetic acid as the chlorinated hydrocarbons, butyric acid being formed in an analogous manner[6]. Formic acid of (probably) 99.99% pure gave freezing point 8.26°, and density 1.2456 at 0° and 1.2206 at 20°[7]. Methyl butyrate has been used in the dehydration of volatile fatty acids[8].

Cotton, mercerized, and hence not susceptible to satisfactory acetylation[9], is rendered suitable by pretreat-

1. Consortium für Elektrochemische Ind., E. P. 272951; abst. C. A. 1928, **22**, 1783; J. S. C. I. 1928, **47**, 515-B. F. P. 643114; abst. C. A. 1929, **23**, 1419. Norw. P. 45797. Ital. P. 237298. Belg. P. 345491. (R. Meingast and M. Mugdan), D. R. P. 442256; abst. J. S. C. I. 1928, **47**, 596-B. D. R. P. 488157; abst. C. A. 1930, **24**, 2473; Chem. Zentr. 1930, I, 1368.

2. *Ibid.* E. P. 279070; abst. C. A. 1928, **22**, 2755; J. S. C. I. 1929, **48**, 235-B; Chem. Age. 1927, **17**, 557. (R. Meingast and M. Mugdan) D. R. P. 475885; abst. C. A. 1929, **23**, 3716. See E. P. 194719, 230063.

3. *Ibid.* E. P. 288549; abst. C. A. 1929, **23**, 608; J. S. C. I. 1929, **48**, 122-B. (H. Deutsch and W. Herrmann), D. R. P. 503131; abst. C. A. 1930, **24**, 5045. See D. R. P. 515307; abst. C. A. 1931, **25**, 1537.

4. *Ibid.* E. P. 288213; abst. C. A. 1929, **23**, 609; J. S. C. I. 1930, **49**, 275-B.

5. H. Mugdan and J. Wimmer (Consortium Für Elektrochemische Industrie), D. R. P. 519973; abst. C. A. 1931, **25**, 3360. F. P. 671283; abst. C. A. 1930, **24**, 2142.

6. *Ibid.* U. S. P. 1730587. E. P. 271103.

7. A. Coolidge, J. A. C. S. 1928, **50**, 2166; abst. C. A. 1928, **22**, 3324.

8. E. Coppée, E. P. 228832; abst. J. S. C. I. 1925, **44**, 377-B.

9. Courtaulds, Ltd., U. S. P. 1681103. E. P. 269012; abst. C. A. 1928, **22**, 1473. F. P. 632636; abst. C. A. 1928, **22**, 3528. Can. P. 276825. D. R. P. 512225; C. A. 1931, **25**, 1082. See F. P. 355016.

ment with phenol, *m*-cresol or a mixture of cresols. Excess phenol is removed before acetylation. H. Gardner[1] spins a 10% cellulose acetate solution in acetic acid through orifices into water as a precipitating bath, so that the threads travel through the bath at a speed of 3-5 feet per minute, or the aqueous bath may be replaced by an oil (castor, linseed, cod-liver), which is afterwards dissolved out by a liquid non-solvent of the cellulose ester (benzene or toluene)[2]. A. Craver[3] prepares acetaldehyde by passing ethyl alcohol vapor with air or other O-containing gas into contact with vanadium oxide at a temperature of about 300°.

A. Cubitt[4] produces relief effects in projected images by periodically introducing a disturbing refracting member into the projection beam, or by moving elements of the lens, the disturbing member being a cellulose acetate film. As a penetrating ink for shellac coated or painted surfaces, diethyl phthalate, ethyl lactate or ethyl oxalate are recommended as solvents for the coloring matter[5]. Glycols result from heating chlorhydrins with caustic alkali and water in a closed tube[6], ethylene chlorhydrin yielding ethylene glycol. A modified cellulose for the manufacture of acetylcellulose[7], is obtained by treating cellulose with a mixture of 80% formic acid, 100 parts, 66° Be. sulfuric

1. Courtaulds, Ltd., and H. Gardner, E. P. 239622. Can. P. 261766.

2. Courtaulds, Ltd., and H. Hegan, E. P. 229075; abst. C. A. 1925, **29**, 3018; Rayon J. 1926, **1**, #3, 36. U. S. P. 1599233; abst. C. A. 1926, **20**, 3579.

3. A. Craver, U. S. P. 1636952; abst. C. A. 1927, **21**, 3057; J. S. C. I. 1927, **46**, 796-B.

4. E. P. 252085. See E. P. 236639.

5. C. Cunningham, U. S. P. 1562544; abst. Plastics, 1926, **2**, 62. Can. P. 265988.

6. G. Curme, E. P. 264124; abst. C. A. 1928, **22**, 92. Can. P. 268570; abst. C. A. 1927, **21**, 2274.

7. M. Cusin and P. Chevalet, U. S. P. 1671513; abst. C. A. 1928, **22**, 2663; J. S. C. I. 1928, **47**, 521-B; Plastics, 1928, 626. E. P. 264181; abst. J. S. C. I. 1928, **47**, 258-B. Can. P. 273732; abst. C. A. 1927, **21**, 4069.

acid, 15 parts, duration of immersion 2 hours. The E. Czapek process is similar[1].

H. Dabisch[2] has given methods of analysis of cellulose ester varnishes and their components, including separation of nitro- from acetyl-cellulose by precipitating the latter with methyl alcohol, and J. Davidson[3] a resume of the glycol ethers and their use in the lacquer industry. H. Davies[4] has described the dyeing of cellulose acetate silk. Stencil sheets for mimeograph work are prepared by dissolving cellulose acetate with benzoylbutyl tartrate (prepared by reacting upon di-*n*-butyl tartrate with benzoyl chloride)[5] and tetra-, penta- or hexa-chlornaphthalene, zinc oxide being added to induce opacity. Sheets of Yoshino paper are then coated with the above. Details of the use of "Milanese cloth" (cellulose acetate silk)[6] in the arts has been published, and combinations of nitro- and acetyl-cellulose silks[7].

In the direct production of acetic acid from pyroligneous acid[8], the crude acid vapors from which the tar has been removed, are distilled at a temperature at which acetic acid is just volatile. M. Deschiens[9] has comprehensively described the role of cellulose acetate for aviation dopes with many representative formula. In France, benzyl alcohol, triacetin and eugenol, with dimethylphenyltolylurea as antacid appears to be the preferred high-boiler compon-

1. Ital. P. 254540. For the manufacture of solutions of cellulose derivatives see Swiss P. 129593. D. R. P. 237152, 249256, 257227, 218010, 421383. U. S. P. 798061, 1187929, 634751. E. P. 28538, 1908.
2. Farben-Ztg., 1927, **32**, 1609; abst. C. A. 1928, **22**, 324; J. S. C. I. 1927, **46**, 418-B.
3. J. Davidson, J. Ind. Eng. Chem. 1926, **28**, 669.
4. Proc. Am. Assoc. Textile Chem. Colorists, 1924, 179; 1925, 251; 1926, 101. Am. Dyestuff Rep. **13**, 753; **14**, 887; **15**, 197; abst. C. A. 1925, **19**, 401; 1926, **20**, 669, 1718.
5. A. Davis, U. S. P. 1639080; abst. Pulp & Paper Mag. 1929, 323; Plastics, 1927, **3**, 540.
6. W. Davis, Silk J. 1927, **4**, #37, 56.
7. J. Delpech, E. P. 229026; abst. C. A. 1925, **19**, 3024.
8. E. Deperrois, F. P. 601156; abst. J. S. C. I. 1927, **46**, 701-B.
9. M. Deschiens, J. S. C. I. 1925, **44**, 902; C-I; abst. C. A. 1925, **19**, 3604; J. S. C. I. 1926, **45**, 248-B; C. A. 1925, **19**, 3604. Chim. et. Ind. 1926, **15**, 18; abst. C. A. 1926, **20**, 1330.

ents for proper tautening effect on the canvas. A review of the manufacture, properties and applications of cellulose acetate has been published by him[1], especially in the plastic and film industry[2], as coatings for metals[3], and the use of the viscosimeter for standardizing cellulose acetate solutions[4].

In the production of concentrated acetic acid by extracting the superheated vapor of the dilute acid with a solvent (cresol) of higher boiling point than acetic acid[5], the dissolved solvent is recovered from the aqueous condensate by extraction with fatty oils, oleic acid or anthracene oils[6]. Or[7], by carbon tetrachloride, dichlorethylene or trichlorethylene, or[8] quinoline or dimethylaniline. The manufacture of acetylated castor oil has been patented[9]. In preparing stencils for duplicating machines (see p. 57, n. 2; 96, n. 6; 109, n. 2; 164, n. 1) sheets are coated with a cellulose acetate composition containing a tempering agent (amyl or butyl tartrate or phthalate, mon-, di- or tri-acetin), and a substance lessening the resistance of the composition to being parted in making type-out stencils (chlornaphthalene, zinc stearate) with oils (castor, rape, olive, almond, peanut) to induce pliability[10]. Starch acetate is also included.

1. M. Deschiens, Rev. prod. Chim. 1926, **29**, 5; abst. C. A. 1926, **20**, 3565. Rev. gen. mat. Plastiques, 1926, **2**, 99; abst. C. A. 1927, **21**, 320. Plastics, 1926, **2**, 438. Rev. gen. mat. Plastiques, 1926, **2**, 291; abst. C. A. 1926, **20**, 3565; Chem. Zentr. 1926, II, 843. Rev. prod. chim. 1927, **30**, 41; abst. Chem. Zentr. 1927, II, 195.
2. *Ibid.* Rev. prod. chim. 1926, **29**, 767; abst. C. A. 1927, **21**, 1008.
3. *Ibid.* Chim. et Ind. (special No.) 1927, May, 479; abst. C. A. 1927, **21**, 3472; Chem. Zentr. 1928, I, 121.
4. *Ibid.* Chim. et Ind. 1928, **20**, 1023; abst. C. A. 1929, **23**, 2032; J. S. C. I. 1929, **48**, 167-B.
5. Destilacija Drva D. D., D. R. P. 494416; Addn. to D. R. P. 451179; abst. C. A. 1930, **24**, 2756.
6. *Ibid.* D. R. P. 507416; abst. C. A. 1931, **25**, 524.
7. *Ibid.* D. R. P. 508092; abst. C. A. 1931, **25**, 714. See also H. Suida, Aust. P. 116377; abst. C. A 1930, **24**, 2473.
8. *Ibid.* D. R. P. 517497; abst. C. A. 1931, **25**, 2155.
9. A. De Waele, E. P. 284415; abst. C. A. 1928, **22**, 4878.
10. A. B. Dick Co. and E. Hill, E. P. 261806; abst. Pulp & Paper Mag., 1929, Feb. 28, p. 323. Can. P. 270537. U. S. P. 1608743.

The U. Diem-Bernet light sensitive film[1] comprises cellulose acetate or citrate, which are resistant to mechanical influences and can be used without a support, and therefore may be exposed from either side. This sensitivity may be brought about by impregnation with silver halides or ferric salts[2]. As initial cellulose for esterifying purposes, cellulose prepared from corn cobs has been patented[3], stated to be of especial value for cellulose formate and acetate production. R. Dort has detailed the properties and application of the S. R. A. dyes for cellulose acetate[4], and recent developments in Celanese fabrics[5], including Marquisette fabric, Ninon, Celanese Faille Moire, Jacquard Faille, Crepe Marocain, Shantunese, warp prints and spun yarns.

The H. Dover toe stiffener[6] comprises outer layers of swansdown, a central layer of felt and powdered cellulose acetate containing plasticizers. Before use, the ester stiffening agent is softened by volatile solvent, heat and pressure being afterwards applied. Ethylhexylacetic acid and its methyl, ethyl, propyl, butyl ester have been described[7], of possible value as plasticizing agents. In the C. Dreyfus method of esterification[8], cellulose materials are treated at not substantially above room temperature with a mixture of concentrated acetic and sulfuric acids containing not more than 15% water. He prevents textiles from becoming fluffy and losing appearance[9], by treating the yarns with an acetylcellulose solution to impart a permanent finish,

1. F. P. 617929; abst. J. S. C. I. 1928, **47**, 69-B.
2. E. P. 271507; abst. C. A. 1928, **22**, 1552.
3. N. Ditman, U. S. P. 1522618; abst. C. A. 1925, **19**, 894; Chem. Zentr. 1925, I, 2270.
4. Chemicals, 1925, **24**, #19, 19; #23, 19. 1926, **25**, #1, 22; #5, 21; abst. C. A. 1926, **20**, 1325; Chem. Zentr. 1926, I, 3102.
5. Rayon, 1928, **7**, #9, 28. 6. E. P. 298371.
7. A. Dox, J. A. C. S. 1925, **47**, 3008; abst. C. A. 1926, **20**, 363.
8. E. P. 262157; abst. J. S. C. I. 1927, **46**, 71-B. U. S. P. 1546211; abst. J. S. C. I. 1925, **44**, 707-B.
9. Can. P. 280645; abst. C. A. 1928, **22**, 3051. F. P. 635028; abst. C. A. 1928, **22**, 3997. Belg. P. 351906, 352411. Ital. P. 253674.

preserving the luster, if desired[1], by treatment with a small amount of aqueous calcium thiocyanate.

Differential effects are obtainable on mixed fabrics containing cellulose acetate[2], by applying thereto a mixture of infusorial earth 12, dextrin 5, lactic acid and water, each 3. This mixture is allowed to remain in contact with the fabric until at least a part of the cellulose ester is removable by washing with water. Phosphoric acid may be used in the place of sulfuric acid in cellulose acetylation[3], the operation being carried out in suspension by the addition of benzene so that the cellulose ester is in the original fibrous form. Fabric containing cellulose may be so esterified, after which it does not rot on exposure to sea air. Mixed fabrics containing cellulose acetate when treated with 6-13° Be. solution of aluminum chloride at 32° removes the vegetable fibers therefrom[4]. The viscosity of cellulose acetate may be lowered (see p. 53, n. 2; 162, n. 7) by treatment with hydrogen dioxide in the presence of iron or iron salts[5].

In producing color effects, cops or bobbins of acetate silk threads may be plunged into a bath containing several colors having different speeds of penetration[6], withdrawing them before they have become uniformly colored. Differential effects on acetate fabric may also be induced[7] by treatment with two or more different mordants of variable speeds of action.

In the production of acetic anhydride by the H. Dreyfus methods, acetic acid vapor may be heated in the presence of

1. C. Dreyfus, Can. P. 285048; abst. C. A. 1929, **23**, 995. See Belg. P. 354978, 352643, 351775, 346991.
2. *Ibid.* Can. P. 276367; abst. C. A. 1928, **22**, 2067. F. P. 613647; abst. Chem. Zentr. 1927, I, 1218.
3. *Ibid.* F. P. 632614, 632615; abst. C. A. 1928, **22**, 3528. E. P. 269529, 269530. Can. P. 276517.
4. C. Dreyfus, R. Dort and H. Platt, Can. P. 285047; abst. C. A. 1929, **23**, 995.
5. C. Dreyfus, F. P. 636272; abst. C. A. 1929, **23**, 277; Plastics, 1929, **5**, 335. Ital. P. 259734, 256606.
6. *Ibid.* F. P. 632339; abst. C. A. 1928, **22**, 3537. E. P. 269195; abst. Chem. Zentr. 1927, II, 642. Ital. P. 254337. Belg. P. 346990, 345564, 342815, 346989.
7. C. Dreyfus, G. Rivat and E. Cadgene, Belg. P. 342817, 345565.

o-, *m*- or pyro-phosphoric acids[1], sodium sulfate or calcium sulfate[2] or by heat alone[3]. The presence of a product having a high affinity for water as zinc chloride, sodium bisulfate or pyrosulfate[4], or calcium chloride[5], or by the use of the oxide or carbonate of a metal whose acetates yield acetone on pyrogenetic decomposition[6] (barium or calcium carbonate, zinc dust, cadmium, lead or iron in finely divided form)[7].

In the dyeing of cellulose acetate the following diphenylamine derivatives have been patented, yielding greenish-yellow, golden-yellow, orange and brown shades: 2-nitro-4-chlor-4′ (or 3′) methyl-, 2-nitro-4-chlor-4′-ethoxy- (or acetamido-), 2-nitro-4-brom- (or methyl-), 2-nitro-4-brom-4′-methoxy-, 2-nitro-, 2-nitro-4′-chlor- (or brom-), 2-nitro-4′-acetylamido-, besides 2-nitro-4-methyl-4′-ethoxy-diphenylamine[8]. To preserve the luster on acetate silk (prevent delustering)[9], treatment with certain aqueous salt solutions (ammonium bromide or chloride, sodium or magnesium chloride or sulfate, barium, strontium or aluminum chloride) has been recommended.

Acetate silk may be weighted with combinations of tin chloride and thiocyanate[10]. In the production of acetic

1. H. Dreyfus, E. P. 280972; abst. C. A. 1928, **22**, 3417; J. S. C. I. 1928, **47**, 82-B. Can. P. 283662. Belg. P. 341999.
2. *Ibid.* E. P. 256663; abst. C. A. 1927, **21**, 2906. Belg. P. 323101. Can. P. 278840.
3. *Ibid.* Swiss P. 126820; abst. C. A. 2929, **23**, 847. E. P. 279916; abst. C. A. 1928, **22**, 2951. F. P. 633856; abst. C. A. 1928, **22**, 3669.
4. *Ibid.* E. P. 257968; abst. C. A. 1927, **21**, 3057. Can. P. 278841. F. P. 613841.
5. *Ibid.* E. P. 289972; abst. C. A. 1929, **23**, 850; J. S. C. I. 1928, **47**, 515-B. U. S. P. 1817614; abst. C. A. 1931, **25**, 5435.
6. *Ibid.* Can. P. 283817. Belg. P. 339107.
7. *Ibid.* E. P. 256664; abst. C. A. 1927, **21**, 2906. Can. P. 278842. Belg. P. 341998.
8. *Ibid.* F. P. Addn. 36013 to 595759; abst. C. A. 1930, **24**, 4171. E. P. 237943; abst. J. S. C. I. 1925, **44**, 801-B. U. S. P. 1618415; abst. J. S. C. I. 1927, **46**, 249-B. Can. P. 265238; abst. C. A. 1927, **21**, 1018.
9. *Ibid.* F. P. 601297; abst. Chem. Zentr. 1927, I, 1219.
10. *Ibid.* F. P. 642331; abst. C. A. 1929, **23**, 1267. See also Can. P. 285802.

acid, H. Dreyfus heats methyl alcohol and CO together under pressure in the presence of substances which are capable of forming acetates and which split off acetic acid below 450° (copper, tin, lead or zinc oxide; copper or zinc acetates; zinc, aluminum or tin methylate)[1], or finely divided zinc, aluminum or copper[2]. Potassium or sodium acetate or methoxide[3] are also stated as suitable. Instead of alcohol and CO, methyl formate may be used as initial acetic acid forming material[4], and heating conducted in the presence of a sulfonic acid or sodium benzenesulfonate[5]. The acetic acid formed may be removed with extraction, as with ethyl ether or petroleum ether[6].

Methyl alcohol, formaldehyde, keten and acetic acid are formed from mixtures of CO and H at high pressures[7], keten requiring 5-50 atm. pressure, if a catalyst is not used[8]. If a catalyst as zinc or copper oxide, copper or zinc chromate, zinc aluminate or potassium zincate is used, temperatures of 200-300° are preferred[9]. Waste acetic acid from the production of cellulose acetate[10], is recoverable by reduction to acetaldehyde by gases as H, concentrated and then transformed into acetic acid or anhydride.

Cellulose prior to esterification is treated with formic or acetic acid[11], a portion of the acid removed by passage

1. H. Dreyfus, E. P. 264558; abst. C. A. 1928, **22**, 91; J. S. C. I. 1927, **46**, 268-B. Compare E. P. 254819.
2. *Ibid.* E. P. 268845; abst. C. A. 1928, **22**, 1365; J. S. C. I. 1927, **46**, 521-B. U. S. P. 1784583; abst. J. S. C. I. 1931, **50**, 150-B.
3. *Ibid.* E. P. 262832; abst. C. A. 1927, **21**, 3906; J. S. C. I. 1927, **46**, 125-B. Belg. P. 343439. U. S. P. 1743659; abst. C. A. 1930, **24**, 1392; J. S. C. I. 1930, **49**, 234-B.
4. *Ibid.* E. P. 259641; abst. C. A. 1927, **21**, 3368.
5. *Ibid.* F. P. 637763; abst. C. A. 1929, **23**, 397.
6. *Ibid.* Can. P. 285052; abst. C. A. 1929, **23**, 850.
7. *Ibid.* E. P. 263503; abst J. S. C. I. 1927, **46**, 237-B. Cites E. P. 20488, 1913, 227147, 229714, 229715, 262364, 262494, 262832.
8. *Ibid.* E. P. 273622; abst. C. A. 1928, **22**, 1981.
9. *Ibid.* E. P. 262364; abst. C. A. 1927, **21**, 3626; J. S. C. I. 1927, **46**, 125-B.
10. *Ibid.* E. P. 273810; abst. C. A. 1928, **22**, 1981.
11. *Ibid.* Can. P. 283660; abst. C. A. 1928, **22**, 4815. E. P. 264937; abst. C. A. 1928, **22**, 317; J. S. C. I. 1927, **46**, 248-B; Plastics, 1928, **4**, 386. Ital. P. 255928. Cites Ital. P. 220640, 242635. See also E. P. 207562, 263938.

of air therethrough, and then subjected to the action of acetic acid until the desired solubility in acetone results[1]. of benzene, in order to produce a fibrous acetated cellulose. Hydration is carried on in the usual manner with diluted acetic acid until the desired solubility in acetone results[408]. If acetic acid is used as solvent in the acetylation mixture[2], the proportion should not exceed 6 times the weight of cellulose esterified, and the condensing agent reduced to 0.5-3% based on weight of cellulose. Or[3], the cellulose may first be converted into alkalicellulose and afterwards esterified in the usual manner. While this treatment facilitates the esterization process, the ester produced as the result is usually of diminished stability and tensile strength in film and filament form. However[4], if the cellulose is pretreated by heating with acetic acid vapor, its reactivity is considerably augmented without the tensile strength being seriously impaired. Formic acid vapor is the analogue of acetic acid for pretreatment purposes[5], or 70-90% strength being preferable[6]. A mixture of formic and acetic acids has been patented for this purpose[7], advantage not obvious.

As plasticizing bodies for cellulose acetate in the production of celluloid-like bodies (see p. 60, n. 1, 2, 3, 4; 102, n. 2) isomeric xylene diethyl- (or methylethyl) sulfonamide in conjunction with mono-, di- or tri-methyl (or ethyl) urea

1. H. Dreyfus, Swiss P. 127790. Ital. P. 261118. E. P. 275286. See Swiss P. 67113, 68001, 105945. Ital. P. 255929, Addn. to Ital. P. 220640. India P. 12612.

2. *Ibid.* E. P. 263939; abst. C. A. 1928, **22**, 164; J. S. C. I. 1927, **46**, 247-B; Plastics, 1928, **4**, 386. Ital. P. 241135. Belg. P. 354320.

3. *Ibid.* Can. P. 267551; abst. C. A. 1927, **21**, 1713. E. P. 249173. Ital. P. 232704.

4. *Ibid.* Can. P. 283661; abst. C. A. 1928, **22**, 4815. Ital. P. 242291, 258992. Belg. P. 328669.

5. *Ibid.* Can. P. 284877; abst. C. A. 1929, **23**, 980; Plastics, 1929, **5**, 638. Ital. P. 242635.

6. *Ibid.* F. P. 642329; abst. C. A. 1929, **23**, 1504. Ital. P. 256738.

7. *Ibid.* Can. P. 285051; abst. C. A. 1929 ,**23**, 979; Plastics, 1929, **5**, 632. Ital. P. 253704, 258384.

has been patented and developed primarily by H. Dreyfus[1]. They are liquids at ordinary temperatures. He spins acetate filaments by the dry method dissolved in a liquid boiling below 40° (i.e. under acetone), using formaldehyde, acetaldehyde or mixtures of both[2]. Or[3], threads may be spun from solutions having viscosities of not less than 30 Engler reckoned as 6% solution in acetone, at a temperature of 25°. If the filaments are to be weighted with insoluble metallic substances[4], they are first treated with boiling water or damp steam, protecting agents as sodium chloride or sulfate being added to the water to prevent delustering.

Differential effects on acetate silk are possible by combining in the same cloth lustrous and delustered filaments[5], then dyeing with the usual solubilized dyes for acetate silk which color the lustrous threads differently from the delustered. Variegated effects are also obtainable by printing the acetate silk with a paste containing aluminum acetate, drying, and applying aqueous preparations of insoluble colors in undispersed form[6].

Local differences of luster are produced on acetate cloth by the local application to the cloth of mono- and poly-basic carboxylic acids of the aliphatic series[7], with subsequent treatment with steam. H. Dreyfus has described a method of cellulose acetylation whereby the product is subsequently submitted to a partial hydration treatment prolonged beyond the usual stage of solubility in alcohol-benzene mix-

1. H. Dreyfus, U. S. P. 1530987; abst. C. A. 1925, **19**, 1629; J.S.C.I. 1925, **44**, 351-B. E. P. 154334; abst. J.S.C.I. 1921, **40**, 42-A. F. P. 634165. Cites U. S. P. 1353384, 1353385, 1501206. See Belg. P. 326762, 326763, 331345, 340540.
2. *Ibid.* U. S. P. 1616787; abst. J. S. C. I. 1927, **46**, 295-B. F. P. 593102. Belg. P. 354874. Can. P. 279892. Cites E P. 209125.
3. *Ibid.* U. S. P. 1620636; abst. C. A. 1927, **21**, 1548. E. P. 275286; abst. C. A. 1928, **22**, 2273; J. S. C. I. 1927, **46**, 774-B. Belg. P. 342075. Cites E. P. 20977, 1911; 6463, 14101, 1915; 100009, 101555, 210108. U. S. P. 1217722. Belg. P. 342077, 355931, 342076. India P. 13468.
4. *Ibid.* F. P. 638248; abst. C. A. 1929, **23**, 290.
5. *Ibid.* F. P. 637468; E. P. 278116; abst. C. A. 1929, **23**, 705.
6. *Ibid.* Belg. P. 353463. Can. P. 281191. Ital. P. 252600.
7. *Ibid.* F. P. 635396; abst. C. A. 1928, **22**, 4836.

tures whereby a gradual diminution in viscosity takes place without a corresponding reduction in tensile strength of film or filament formed therefrom[1]. For example, cellulose 100, glacial acetic acid 900-1000, acetic anhydride 200-250, sulfuric acid 3-10, is treated at an initial temperature of 0-5°, which may be allowed to rise to 10-15° toward the close of acetylation. When the esterification is completed, excess of acetylating agent is destroyed by the addition of water, and the mixture allowed to stand at about 10° until soluble in acetone containing 3-10% water, when the ester is then precipitated[2].

In the loading of acetate yarn and fabric[3], in order to increase the receptivity of the ester for loading agents, it is submitted to a preliminary treatment with swelling agents as cyanate, isocyanate or thiocyanate of sodium, potassium or ammonium, or urea, urethane, thiourea, thiourethane, guanidine, or their alkyl or aryl substituents. If thiocyanates are used, it is advisable that concentration of cyanate radical present be in excess of that chemically equivalent to the mordant metal radical afterwards used for mordanting and weighting purposes[4]. For relustering[5], treatment with thiocyanates as above, or with acetic acid, phenol, benzyl alcohol, triacetin or cyclohexanone is advised. By the introduction of aqueous solutions of salts as sodium chloride, sulfate and acetate[6], as protectives, boiling the acetate silk may be resorted to without serious diminution of original luster.

Acetate fabrics may be simultaneously loaded and pre-

1. H. Dreyfus, Can. P. 284876; abst. C. A. 1929, **23**, 980; Plastics, 1929, **5**, 632.

2. *Ibid.* Can. P. 283818; abst. C. A. 1928, **22**, 4835. Belg. P. 340538, 340539, 343506.

3. *Ibid.* Can. P. 285802.

4. *Ibid.* Can. P. 285978; abst. C. A. 1929, **23**, 1286. Belg. P. 345566.

5. *Ibid.* Can. P. 276514; abst. C. A. 1928, **22**, 2068. E. P. 165164, 259265.

6. *Ibid.* Can. P. 260319; abst. C. A. 1926, **20**, 3578. Belg. P. 343504.

pared for dyeing with basic colors[1], by first soaking in an aqueous solution of tin, zinc, tungsten or aluminum chloride, then treating with a soluble phosphate or silicate to precipitate the insoluble salt in the interstices of the filament. Destuffs as *p*-nitrodiphenylamine[2] may then be applied. If Indanthrenes, Cibanones, Algols, Helindones, or other anthraquinone vat dyestuffs are employed, they are preferably used in the unreduced state[3]. Or[4], the acetate silk may be dyed with a coloring compound in which an aryl dye nucleus is linked through N to at least one glyceryl residue. If sulfur dyestuffs liable to be deleteriously affected by alkaline sulfide are used[5], the dyestuffs are applied in conjunction with both alkali sulfide and alkali hydrosulfite. If monosulfonated dyes containing 2 or more anthracene or anthraquinone rings are employed[6], the dyeing is carried out in the presence of a high percentage of such inorganic salts as sodium or ammonium sulfates, in which 1.2′-dianthraquinonylaminesulfonic acid, 2.6-di-*α*-anthraquinonylanthraquinonesulfonic acid and its 4.4′-dimethoxy derivative are especially recommended.

In dyeing, printing or stencilling fabrics of formyl-, acetyl-, methyl-, ethyl-, or benzyl-cellulose[7], an aqueous solution of ammonium thiocyanate is first applied, then dyed with an aqueous dispersion of a relatively water-insoluble color, the dispersion being prepared by preheating the compound with sodium sulforicinoleate as a solubilizing agent.

1. H. Dreyfus, Can. P. 285800; abst. C. A. 1929, **23**, 1267. Belg. P. 355930.
2. *Ibid.* Belg. P. 350137. Ital. P. 255838, Addn. to 222812, 241615. See Ital. P. 222812, 233801, 233902, 238137, 280069.
3. *Ibid.* Can. P. 249159. Ital. P. 254320, 258319. Belg. P. 346286, 348212.
4. *Ibid.* Can. P. 276556; abst. C. A. 1928, **22**, 2067. Belg. P. 343505. F. Addn. 32949 to 627071. Can. P. 281193; abst. C. A. 1928, **22**, 3051. Belg. P. 328802.
5. H. Dreyfus, G. Ellis, H. Olpin and E. Walker, Can. P. 281192, 281195; abst. C. A. 1928, **22**, 3051.
6. H. Dreyfus, F. P. 640013; abst. C. A. 1929, **23**, 994.
7. *Ibid.* Can. P. 281194; abst. C. A. 1928, **22**, 3051. Can. P. 285798; abst. C. A. 1929, **23**, 1287. Belg. P. 324538, 328668, 338391, 340537, 346285, 346287, 352815.

A. Dubosc[1] proposes to prepare cellulose acetate by double decomposition by treatment of cellulose with monohydrated sulfuric acid to form a cellulose sulfate or sulfonate, which with acetic esters produces a cellulose acetate, theoretically possible, but commercially impracticable. An ultra-filter membrane useful for dialysis has been described[2], in which cellulose acetate in porous form is obtained by precipitation from solutions by the addition of a non-solvent (water or alcohol), being especially suitable for dialysis from benzene solutions. From a study of the mechanism of ultra-filtration[3], it would appear that the structure of a cellulose acetate membrane is fibrous and firm, and independent of the penetrative liquid. E. Duhem in 1925 reviewed the various processes which had been brought forward up to that time for the dyeing of acetate silk[4].

Material suitable for the strings of musical instruments, tennis rackets or as a substitute for gut filaments[5] is formed of silk, ramie, cotton, wool, hemp or jute impregnated with a viscous solution of cellulose acetate, and twisted together, after which the cellulose ester is coagulated and dried.

Cellulose acetate may be dyed or printed by applying the ester salt of a leuco-vat dye, steaming, and developing at a high temperature with sulfuric acid, a nitrite or bichromate[6], solid shades being thus obtainable on a mixed cotton and acetate fabric. The fabric is padded with a solution containing the ester salt of leucotetrabrominidigo, leuco-4.4′-dimethyl-6.6′-dichlordithioindigo or leuco-dimethoxydibenzanthranone, tragacanth and sodium nitrite,

1. Bull. Soc. Ind. Rouen, 1926, **54**, 227; abst. C. A. 1927, **21**, 493.
2. J. Duclaux, U. S. P. 1693890. E. P. 262131; abst. C. A. 1927, **21**, 3718.
3. J. Duclaux and J. Ererra, Koll.-Zeits., 1926, **38**, 54.
4. E. Duhem, Tiba, 1925, **3**, 1067; abst. C. A. 1926, **20**, 113.
5. Dunlop Rubber Co., Ltd., and R. Truesdale, E. P. 264640; abst. C. A. 1928, **22**, 165.
6. Durand et Huguenin, Soc. Anon. E. P. 274094; abst. C. A. 1928, **22**, 2066; J. S. C. I. 1928, **47**, 891-B. See E. P. 220964.

steamed, then developed in a sulfuric acid bath at 80°. In a series of five articles[1], W. Dyes in 1928 gave a general review of the economic and commercial sides of the development of cellulose acetate and filaments made therefrom with especial references to the technical processes for the production of Celanese, Rhodiaseta and Aceta types[2], and the difficulties of mass production of homogeneous hydrocellulose acetate (hydroacetylcellulose)[3].

The desirability of methylene chloride as a solvent for the cellulose acetate was published in 1925, together with harmonious and incompatible liquids to be admixed therewith in acetate compositions[4]. Difficultly inflammable solutions are obtained by dissolving acetone-soluble acetylcellulose in a mixture of methylene chloride with alcohol or acetone, films of high luster resulting[5], and acceptable filaments being possible[6]. A. Eichengruen[7] contributed in 1927 a polemical article on the development of the cellulose acetate art (see p. 589, n. 1).

In 1927 E. Ellis reviewed comprehensively the 20 SRA colors comprising the range of acetylcellulose dyestuffs of this class[8], with suggestions for their application to best advantage. For solubilizing azo dyes or other coloring matters intended for acetate dyeing, a Twitchell reagent is used. Cellulose acetate may be dyed with unsulfonated stilbene compounds as azo stilbene dyes[9], or by azo or polyazo compounds containing *α*-naphthylamine as an end com-

1. Chem. Ztg., 1928, **52**, 554; abst. C. A. 1928, **22**, 4244.
2. Kunstseide, 1928, **10**, 441; abst. C. A. 1929, **23**, 701.
3. Kunst., 1928, **18**, 272; abst. C. A. 1929, **23**, 3342; Cellulose, 1930, **1**, #2, 66.
4. A. Eichengruen, E. P. 243030; abst. Chem. Zentr. 1926, I, 2628.
5. *Ibid.* E. P. 243031; abst. C. A. 1926, **20**, 2826; J. S. C. I. 1927, **46**, 305-B; Rayon, 1926, **2**, #5, 8.
6. *Ibid.* E. P. 243350; abst. C. A. 1926, **20**, 3823; J. S. C. I. 1927, **46**, 579-B.
7. Chem. Ztg., 1927, **51**, 25; abst. C. A. 1927, **21**, 1707; Chem. Zentr. 1927, I, 1910.
8. E. Ellis, Rayon J. 1927, **2**, #2, 15.
9. G. Ellis, U. S. P. 1694413; abst. C. A. 1929, **23**, 718. Can. P. 269849; abst. C. A. 1927, **21**, 2384. E. P. 242393. See U. S. P. 1600277, 1618413, 1618414, 1618415.

ponent, such as benzeneazo-, naphthaleneazo-, or benzeneazonaphthaleneazo-*α*-naphthylamine[1].

Patterns are producible on fabrics containing cellulose acetate by the local application of substances which accentuate or diminish the delustering action of hot aqueous media or moist steam, and then steaming[2]. It has been found that all members of the indigo group in the leuco form can be used to dye acetate fibers[3], but their fastness leaves much to be desired[4]. The SRA colors may be used in conjunction with the indanthrenes[5] with augmentation of fastness to light.

In the formation of cellulose formate or formylnitrate[6], cellulose is treated with 98-100% formic acid at 5-20° in the presence of gaseous HCl or phosphoric anhydride and at least 40% (on the weight of cellulose) of a swelling agent as zinc chloride or calcium bromide. At the close of esterification (1-4 hrs. depending on temperature), the reaction is stopped by addition of water, the ester washed and dried. Instead of cellulose, a slightly nitrated cellulose is used as the initial cellulosic material. The ester formed is soluble in sodium, potassium, ammonium, calcium or strontium thiocyanates, nitromethane, formamides, glycerol formates, or chlorhydrin.

For the manufacture of hollow acetate filaments[7], solid or liquid particles are distributed in the solution prior to being spun, as an emulsion or dispersion. Bone oil, paraffin

1. G. Ellis, Can. P. 271280; abst. C. A. 1927, **21**, 3469. F. P. 603921.
2. *Ibid.* Can. P. 281352; abst. C. A. 1928, **22**, 3052.
3. *Ibid.* J. Soc. Dyers Col. 1925, **41**, 95; abst. C. A. 1925, **19**, 1780.
4. *Ibid.* Color Trade J. 1925, **16**, 82; abst. C. A. 1925, **19**, 2415.
5. *Ibid.* J. Soc. Dyers Col. 1926, **42**, 184; abst. C. A. 1926, **20**, 2752.
6. E. Eloed, E. P. 275641; abst. C. A. 1928, **22**, 2273; J. S. C. I. 1929, **48**, 202-B; Plastics, 1928, **4**, 508. F. P. 638431; abst. C. A. 1929, **23**, 278. Holl. P. 22542. D. R. P. 528148; abst. C. A. 1931, **25**, 4706.
7. Erste Bohmische Kunstseidefabrik A.-G., E. P. 258582; abst. C. A. 1927, **21**, 3129.

oil or sodium oleate dissolved in viscose solution have been found suitable, being afterwards removed by means of benzene, carbon bisulfide, amyl alcohol or benzine. In differential printing, mixed fabrics of cellulose acetate and cotton are printed with a color having affinity for acetate silk[1], steamed and rinsed, and the whites finally cleared with 0.1% solution of sodium hydrosulfite. Duranol and Setacyl colors are diluted with water and thickened with gum. Instead of hydrosulfite, 0.1% sulfuric acid or 0.2-0.3% sodium hyposulfite may be used[2], or 2-2.5% potassium permanganate[3].

The physical properties of filaments dry-spun from 18% solutions of nitrocellulose (11.33% N) and cellulose acetate have been compared[4]. The dry tensile strength of the filaments decreases with increasing proportion of acetate, the wet tensile strengths being about 5% less. Extensibility of the dry filament is inappreciably affected by change in composition, but in the wet state gave an extensibility of about 12%. The inflammability of cellulose acetate filament containing but 5% nitrocellulose was equal (?) to that consisting entirely of the nitric ester.

By treating cellulose with concentrated formic acid at 5° or lower, and a catalyst (phosphorous tri-, penta- or oxy-chloride, sulfuryl chloride, HCl or sulfuric acid) until cellulose formate is formed, then rendering the catalyst inactive, it may be immediately spun into filaments without further treatment. Mixed esters may be made by adding (say) cellulose acetate in solution in a cellulose formate solvent, and spinning this physically mixed ester[5].

1. Etabl. Petitdidier (Anc. Maison Jolly-Belin), 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, Addn. to 256238; abst. J. S. C. I. 1928, **47**, 50-B.

3. *Ibid.* F. Addn. 32658 to 615301; abst. C. A. 1928, **22**, 4835.

4. H. Evers, Textilber. 1927, **8**, 873; abst. C. A. 1928, **22**, 502; J. S. C. I. 1928, **47**, 47-B.

5. Fabriek van Chemische Production, A. Ter Horst and J. Jurling, E. P. 260650; abst. C. A. 1927, **21**, 3459; J. S. C. I. 1927, **46**, 103-B; Rayon, 1927, **5**, #1, 24. U. S. P. 1656119; abst. C. A. 1928, **22**, 1040; J. S. C. I. 1928, **47**, 121-B.

In the preparation of cellulose formate, acetate, propionate or aceto-formate[1], the cellulose is first subjected to partial formylation by means of strong formic acid and zinc chloride, succeeded by the usual esterification procedure, using as catalyst HCl alone or with sulfonyl chloride or phosphorous oxychloride. 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 and a special range of Imacol dyes evolved capable of dyeing immune yarn to shades fast to night and washing[2].

Acetylcellulose compositions for coating and impregnating are produced by dissolving in a mixture of 50% acetic acid and a chlorhydrin or dichlorhydrin and water[3], methyleneacetoacetic ester being added as a softener. In spinning acetylcellulose solutions into an aqueous saline precipitating bath[4], a substance other than a thiocyanate or zinc chloride having a swelling action on the acetic ester is added to the bath, chlorbenzene and calcium chloride being satisfactory. In the wet spinning of cellulose acetate filaments, the ester is dissolved in acetone and pyridine or chlorbenzene, and spun into a 23% solution of calcium chloride. Unsaturated fatty acids of high molecular weight (linoleic, linolenic, oleic) are esterified with polysaccharides (glucose, starch, cellulose, saccharose) in the pres-

1. Fabriek van Chemische Production, E. P. 287540; abst. C. A. 1929, **23**, 514; J. S. C. I. 1929, **48**, 126-B; Silk J. 1928, #49, 80. F. P. 642706; abst. C. A. 1929, **23**, 1504.

2. M. Fahrlaender, Textilber, 1926, **7**, 463; abst. J. S. C. I. 1926, **45**, 703-B. Cf. E. P. 246609.

3. Farbenfabriken, vorm. Friedr. Bayer & Co., E. P. 228518; abst. C. A. 1925, **19**, 2878; Chem. Zentr. 1925, I, 908, 2732. D. R. P. 406426; Addn. to 383699; abst. J. S. C. I. 1925, **44**, 217-B.

4. Farbenfabriken, vorm. Friedr. Bayer & Co., E. Hubert, O. Leuchs and L. Lock, E. P. 233342; abst. C. A. 1926, **20**, 670; J. S. C. I. 1925, **44**, 985-B. U. S. P. 1583717; abst. C. A. 1926, **20**, 2080; J. S. C. I. 1926, **45**, 483-B. E. P. 219333; abst. J. S. C. I. 1925, **44**, 843. F. P. 426436. Compare D. R. P. 274260. E. P. 179234.

ence of dimethylaniline, by means of the corresponding chloride[1], cellulose linoleate being an example.

The stability of cellulose acetate solutions in glycerol and other monochlorhydrins is improved by the addition of small quantities of such organic bases as aniline[2], pyridine, glycocoll, guanidine, a typical mixture being cellulose acetate 10, acetone 65, ethylene chlorhydrin 20, monochlorhydrin 5, glycine 0.5. In the dyeing of acetylcellulose filaments[3] mono-azo dyes are recommended, made by coupling the diazo-compound from 2.4-dinitroaniline-6-sulfonic acid with an *a*-aminoalkyl-2-aminonaphthalene or derivative. The acetate filaments may first be treated in a bath of barium hydroxide and barium chloride[4], then washed with dilute acetic acid, when the goods may then be dyed with substantive dyestuffs. Acetate silk is dyed blue to violet shades by monosulfonated 1.4-diaminoanthraquinone or 1.4-aminohydroxyanthraquinone[5], or an alkyl, aralkyl or aryl derivative having the sulfo group in the 2- or 3-position.

It has been found[6] that glycines, obtained by the action of halogen-acetic acids on non-sulfonated aromatic bases, including particularly water-soluble salts of basic dyestuffs, are suitable for dyeing acetylcellulose. Yellow, deep blue and reddish-violet shades are obtained by using glycines formed from aminoazobenzene, 1.4.5.8-tetraaminoanthraquinone, and 1-aminoanthraquinone respectively. A violet-black shade of excellent fastness is obtained with the glycine of *a*-naphthylamine, diazotized and coupled with *b*-hydroxynaphthoic acid. As solvents for the cellulose

1. Farbenfabriken, vorm. Friedr. Bayer & Co., E. P., 239726; abst. C. A. 1926, **20**, 2167. D. R. P. 411900. Cites E. P. 208685.
2. *Ibid.* E. P. 243722; abst. J. S. C. I. 1926, **45**, 796-B; Rayon, 1926, **2**, #4, 15; Caout. et Guttap. 1926, **23**, 13314.
3. *Ibid.* E. P. 253457; abst. C. A. 1927, **21**, 2563.
4. Farberci de la Rize, F. P. 590733; abst. Rayon, 1927, **5**, #7, 24.
5. Farbwerke vorm. Meister, Lucius & Brüning, E. P. 228557; abst. C. A. 1925, **19**, 2880; J. S. C. I. 1925, **44**, 845-B; Chem. Age. (London) 1925, **12**, 363; Chem. Zentr. 1925, I, 2664. F. P. 591708.
6. *Ibid.* E. P. 232599; abst. C. A. 1926, **20**, 296; J. S. C. I. 1925, **44**, 956-B; Rayon, 1925, **2**, #10, 23.

esters, cyclic acetals have been patented[1], especially valuable being ethylene ethylidene ether, ethylenebutylidene ether and the acetal of 1.3-butyleneglycol.

E. Farrow modifies the solubility of cellulose acetate[2] by dissolving chloroform-soluble acetylcellulose in 45-80% nitric acid until the acetone solubility desired has been attained, then precipitating. He recovers acetic values for a cellulose acetate mixture[3] by treating with a liquid capable of forming an acetic ester, but chemically inert toward, and a non-solvent of, cellulose acetate, as ethyl alcohol, or[4], the solubility may be modified by treatment with phosphoric acid solution until the chloroform solubility disappears and an acetone solubility appears. A device has been patented and illustrated[5] for precipitating cellulose acetate from viscous reaction mixtures in a highly divided form by gradually associating water with the mass by means of rapidly revolving blades. Instead of using phosphoric acid for ripening the solubility of cellulose acetate from chloroform-soluble to acetone-soluble, a mixture of phosphoric and acetic acids may be employed—a delicate distinction from a patentability viewpoint, inasmuch as acetic acid is always present in an acetating mixture[6].

In facilitating the acetation process for cellulose[7], the latter may be first treated with HCl of strength greater than 25% at room temperature free from oxidizing agents, the action being stopped before the physical appearance of

1. Farbwerke vorm. Meister Lucius & Brüning, R. Leopold and A. Michael, D. R. P. 419223; abst. Chem. Zentr. 1926, I, 1058.
2. U. S. P. 1521876; abst. C .A. 1925, **19**, 729; J. S. C. I. 1925, **44**, 202-B.
3. U. S. P. 1536334; abst. C. A. 1926, **20**, 503; J. S. C. I. 1925, **44**, 540-B.
4. E. Farrow, U. S. P. 1557147; abst. C. A. 1926, **20**, 111; J. S. 1926, **45**, 48-B.
5. *Ibid.* U. S. P. 1560554; abst. C. A. 1926, **20**, 111; J. S. C. I. 1926, **45**, 48-B.
6. *Ibid.* U. S. P. 1634986; abst. C. A. 1927, **21**, 2985; J. S. C. I. 1927, **46**, 746-B; Plastics, 1927, **3**, 540.
7. *Ibid.* U. S. P. 1679966; abst. C. A. 1928, **22**, 3777; J. S. C. I. 1928, **47**, 810-B; Plastics, 1929, **5**, 88.

the cellulose is appreciably altered, thereafter acetylating in the usual manner. This pretreatment greatly augments the activity of the cellulose for ester formation. Resilient films are said to result by combining acetylcellulose with phenol-formaldehyde condensates in the presence of triphenyl or tricresyl phosphates[1].

In the waterproofing of textiles and paper[2], the article to be treated is first soaked in a mixture of dextrin, casein and sodium carbonate or silicate, dried, and treated with cellulose acetate dissolved in acetone and benzyl alcohol. Activin has been brought forward on account of its stability[3] as especially suited to the bleaching of rayon and acetate silk. A magnet core has been described[4], made from long strips of iron-nickel alloy containing 5-15% Ni and covered by a layer of acetylcellulose.

C. Ferguson[5] has devised a lacquer of cellulose acetate with various organic compounds as *p*-dichlorbenzene, benzoic acid and triphenyl phosphate, which when evaporated to dryness, especially if lightly tinted, produces beautiful effects from the crystallization and irradiation of the salts towards the close of the evaporative process. Frosted glass and translucent and semi-opaque effects are possible in an almost unlimited number of crystallographic forms. These crystalline aggregates are usually in radiating lines, and have a very attractive appearance. The A. Pearl coated paper is similar[6], and employs as the crystallizable body monobromcamphor, salicylic or benzoic acids, resorcinol, borneol, terpene hydrate, menthol and thymol.

A non-hygroscopic cellulose ester lacquer is made by dissolving nitro- or acetyl-cellulose in a medium giving a

1. O. Faust, Belg. P. 327430.
2. M. Favresse and J. Peres, F. P. 629291; abst. J. S. C. I. 1929, **48**, 241-B.
3. R. Feibelmann, Textilber. 1926, **7**, 47; abst. C. A. 1926, **20**, 1720; Chem. Zentr. 1926, I, 2055.
4. Felten & Guilleaume Carlswerk A.-G., D. R. P. 472623; abst. C. A. 1929, **23**, 2926; Chem. Zentr. 1929, I, 2217.
5. C. Ferguson, U. S. P. 1589875; abst. C. A. 1926, **20**, 3084.
6. U. P. S. 1775691; abst. C. A. 1930, **24**, 5516.

clear solution, such as methyl glycollate[1]. R. Flint[2] has contributed an instructive exposition of the economic phases of the acetate silk industry, with inclusion of the interrelations existing among the firms engaged in the manufacture of acetate silk.

In a method of cellulose acetate manufacture patented in 1928, cellulose is dissolved in boiling glycerol, sulfuric added, and the solution treated with acetic anhydride vapors. Nothing is said as to the formation of acetin[3]. R. Foulds[4] in 1927 detailed modern methods of dyeing acetate silk and mixtures of cotton and animal fibers therewith, the information being carried on the next year[5] by J. Franek. Cellulose oxalates are prepared by treating cellulose, hydrocellulose, or regenerated cellulose with the chloride of an oxalic acid monoester (oxalyl chloride) in the presence of a tertiary amine (nitrobenzene, pyridine)[6]. The products are soluble in organic solvents and may be used for films and filament manufacture.

Acetyl silk 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 group, or *(b)* monoazo dyes from unsulfonated diazo compounds containing no OH group and 1-naphthylamine-8-sulfonic acid or its phenyl derivative[7].

1. G. Fey & Co., Swiss P. 135221; abst. C. A. 1930, **24**, 2622. Swiss P. 132923; abst. C. A. 1930, **24**, 515.
2. Kunst. 1928, **18**, 275; abst. C. A. 1929, **23**, 3342; Cellulose, 1930, **1**, #2, 66.
3. J. Folchi and L. Didiere, Belg. P. 352522; abst. C. A. 1929, **23**, 2569.
4. Industrial Chemist, 1927, **3**, 273; abst. C. A. 1927, **21**, 3272; Chem. Met. Eng. 1927, **34**, 632.
5. Chem. obzor, 1928, **3**, 12; abst. C. A. 1928, **22**, 3533.
6. G. Frank, D. R. P. 499053; abst. C. A. 1930, **24**, 4156.
7. G. Frank and British Dyestuffs Corp., Ltd., E. P. 226948; abst. C. A. 1925, **19**, 2136. Although the majority of sulfonated dyestuffs have no affinity for cellulose acetate, monosulfonated dyestuffs containing no hydroxyl group, but having a sulfo-group in *o*- position to the azo group, and monoazo dyestuffs prepared by combining an unsulfonated diazo compound containing no hydroxyl group with a naphthylaminemonosulfonic acid in which the sulfo group is in the peri position to the amino or substituted amino group which also contains no hydroxyl group, have an affinity for cellulose acetate. An hydroxyl group is capable of increasing the activity of a sulfo group

In separating sheets of gold foil[1], the sheets of gold or other metal to be beaten out are separated by films of cellulose acetate or cellulose hydrate (Cellophane), the foils being coated in the manner commonly applied to gut-skins.

Acetolysis of cellulose from various sources, under mild conditions[2], furnishes uniformly 48-51% of the theoretical yield of cellobiose, cellulose acetate giving 46%. It is claimed that the addition of foreign substances as *b*-pentacetylglucose to cellulose acetate solutions in acetic acid prevents the re-association of the mono-molecular cellulose acetates formed spontaneously during the first hours of dissolving. In the preparation of acetic anhydride[3], chlorine is passed into a mixture of sodium acetate, sulfur and acetic anhydride, and the mixture kept at 90° for 1 hr., then distilled.

W. Fuchs has found that by the acetylation of pine wood with sulfuric acid as catalyst, a product was obtained of 41% acetyl in a yield of 150%, based on the weight of wood taken[4]. The methoxyl content of the wood remained substantially the same. The cellulose acetate was isolated by extraction with chloroform and shown to be a triacetate.

so that the affinity of a dyestuff for cellulose acetate is diminished. Dyestuffs suitable for application to cellulose acetate are obtained by coupling diazotised *p*-nitroaniline-*o*-sulfonic acid or diazotised 2:1-naphthylaminesulfonic acid with *N*- alkyl or *N*- aryl substituted amines, particularly substituted naphthylamines, or with *m*- toluylenediamine. For instance the products from diazotised *p*- nitroaniline-*o*-sulfonic acid combined with phenyl-*a*- naphthylamine, *p*-tolyl-*a*-naphthylamine, ethyl-*a*-naphthylamine, ethyl-*b*-naphthylamine, phenyl-*b*-naphthylamine, *aa'*-di-naphthylamine, and *bb'*-dinaphthylamine are brown, brown, orange-brown, violet, violet, brown, and blue-violet dyestuffs, respectively, having an excellent affinity for cellulose acetate, and by reduction of the nitro group, and coupling with a *m*-diamine, further useful dyes are obtained. *p*-Nitroaniline-azo-1:8-naphthylamine-sulfonic acid (peri acid) and *p*-nitroaniline-azo -phenylperi acid are dyestuffs for cellulose acetate and contain a sulfo group in the peri position to the amino or substituted amino group.

1. S. Freund and B. Stauffer, E. P. 261266; abst. C. A. 1927, **21**, 3462; Chem. Zentr. 1927, I, 1093.

2. H. Friese and K. Hess, Ann. Chem., 1927, **456**, 38; abst. J. S. C. I. 1927, **46**, 861-A.

3. E. Fritzman, Zuhr. Prikladnoi Khim, 1928, **1**, 27; abst. C. A. 1929, **23**, 4191; J. S. C. I. 1929, **48**, 510-B, 1007-B.

4. W. Fuchs, Ber. 1928, **61**, 948; abst. Chem. Met. Eng. 1928, **35**, 432.

In the production of photomechanical printing plates[1], a base as aluminum, zinc, glass or cellulose acetate is coated with an elastic, non-sensitive layer of gelatin with an overlying sensitive layer, and the object to be printed photographically transferred onto the sensitive layer.

The film-forming composition of H. Gardner[2] comprises a resin obtained from *p*-toluenesulfonamide and an aldehyde, dissolved with cellulose acetate in a lacquer solvent as butyl acetate. He has given particulars of the application of this class of synthetic resins in conjunction with cellulose derivatives[3], and data on the durability of airplane dopes and varnishes, with tautening and proofing schemes for fabric surfaces[4]. In the metallizing of various surfaces[5], non-conducting materials as cellulose acetate with urea and phenol condensation products, are treated with a suspension or paste of a metal salt and metal and exposed to light or reducing agents as formaldehyde or furfural.

Cellulose stearate, palmitate or laurate are prepared by acting upon hydrocellulose with the corresponding acid chlorides of the particular acid with which the cellulose is to be esterified[6], mono-, di- and tri-esters being produced. The plastic properties of these esters depend to a large degree upon the amount of degradation of the cellulose molecule. When normal cellulose is esterified, the products are insoluble, but all are soluble in aromatic hydrocarbons. Further details of procedure have been given[7]. In a study

1. A. Galetzka, U. S. P. 1557354; abst. C. A. 1926, **20**, 155.
2. U. S. P. 1564664; abst. J. S. C. I. 1926, **45**, 202-B.
3. U. S. Paint and Varnish Mfrs. Assoc. ,Cir. 261, Feb. 1926.
4. H. Gardner, Paint Mfr. Assoc. of U. S. Circ. 1926, #274, 61; abst. C. A. 1926, **20**, 2756.
5. A. & E. Gates-Warren and Precious Metal Industries, Ltd., E. P. 299903; abst. C. A. 1929, **23**, 3548.
6. E. Gault and P. Ehrmann, Bull. Soc. Chim. 1926, (4), **39**, 873; abst. Rev. Gen. Mat. Plast., 1927, #1, 42; Plastics, 1927, **3**, #3, 126; J. S. C. I. 1926, **45**, 942-A; C. A. 1926, **20**, 3806; Chem. Zentr. 1926, II, 1408.
7. *Ibid.* Caout. et Guttap. 1926, **23**, 13030, 13064, 13099, 13138, 13175, 13240, 13275, 13312, 13388; abst. C. A. 1926, **20**, 3805; 1927, **21**, 1350. Contains bibliography of 123 references.

of the carbohydrate sulfuric esters[1], cotton, treated with chlorosulfonic acid in the cold for 24 hrs. gives chlorglucose tetrasulfate, hygroscopic crystals[2]. If the reaction mixture is slowly added to acetic anhydride, *a*-pentacetyl-*d*-glucose is formed; acetyl chloride or bromide yielding *b*-acetochlorglucose.

Solid preparations which by merely mixing with water yield dispersions suitable for dyeing cellulose acetate[3], are prepared by grinding insoluble dyes with dispersing agents, i.e. aminoazobenzene ground with soap; indophenol with Turkey red oil; 1.4-diaminoanthraquinone with naphthalenesulfonic acid, and dianisidine with saponin or sodium ligninsulfonate. J. Gendre in 1928 reviewed the methods used for the recovery of acetic acid in acetate silk manufacture[4]. Glykom is an odorless, non-sticky preparation used for treating artificial filaments before weaving, to retain the original luster[5].

In the coating of fibers[6], they are steeped in a solution containing cellulose acetate 10-15, methyl acetate or acetone 20-30, benzene 15-20, and plasticizer 15-30, then drained and dried. In the formation of coating compositions[7], cellulose acetate in the undissolved condition is ground with oil, varnishes and lacquers, and applied to a surface in the undissolved condition. The surface is then sprayed with cellulose acetate solvent as with an airbrush to dissolve the ester and produce a homogeneous coating, which is said to have extreme adhesiveness.

In printing on acetate silk[8], basic dyes may be applied

1. E. Gebauer-Fuelnegg, W. Stevens and E. Krug, Monatsh. 1928, **50**, 324; abst. C. A. 1929, **23**, 1622.
2. P. Claesson, J. prakt. Chem. 1879, **20**, 18.
3. J. Geigy Akt-Ges., E. P. 272896; abst. C. A. 1928, **22**, 1859.
4. J. Gendre, Rev. chim. ind., 1928, **37**, 378; abst. C. A. 1929, **23**, 1265; Chem. Zentr. 1923, II, 1098.
5. Made by General Dyestuff Corp., New York City.
6. A. Girard and M. Roumazeilles, F. P. 611899; abst. Caout. et Gutta-Percha, 1927, **24**, 13534; J. S. C. I. 1927, **46**, 579-B.
7. Glasurit-Werke M. Winkelmann A.-G., E. P. 288221; abst. C. A. 1929, **23**, 721.
8. B. Gmelin, Melliands' Textilber. 1928, **9**, 225; abst. C. A. 1928, **22**, 1690.

by using tannin antimony mordant or Celloxan, acid dyes made up with Glyezin A or Fibrit D resisting cold washing. Most mordant dyes are suited only to acetate-cotton mixtures, but certain chrome mordant dyes as Alizarin Yellow GG, may be fixed on acetate silk alone as in cotton printing. The Indigosols may be applied as to cotton, but a longer development at higher temperature is desirable. The Celliton and Celliton Fast Colors are prepared with Glyezin A, acetoacetic ester and butyl alcohol. To remove stains from acetate filaments[1], any solvent cleanser having no dissolving power for cellulose acetate is applicable.

Acetaldehyde and acetic acid result by the action of air or oxygen upon ethyl alcohol with silver as catalyst[2] at temperatures of 400-420°. Intensity variations of diffused daylight do not influence the rate of hydrolysis of ethyl acetate in aqueous NaOH at 25°[3]. To produce cellulose acetate free from haze and graininess[4], it is recommended to treat the cellulose with an aqueous non-esterifying bath containing 35-75% sulfuric acid, stopping the reaction before the cellulose is degraded (if such a thing is possible with this strength acid), removing acid from cellulose until neutral, then acetylating in the presence of a catalyst weaker than sulfuric acid.

A process for making cellulose acetate has been described[5], comprising pretreating cellulose with glacial acetic acid containing a mixed catalyst of sulfuric and phosphoric acids in which the latter is from 1-5 times the weight of the former, pretreatment being carried on below 40° until 1-3.5% acetyl has combined with cellulose, then

1. M. Goldman and C. Hubbard, Am. Dyestuff Rept., 1927, **16**, 237; abst. C. A. 1927, **21**, 2191.
2. S. Goldschmidt, E. P. 290523; abst. C. A. 1929, **23**, 850. U. S. P. 1666447; abst. C. A. 1928, **22**, 1981.
3. W. Gooch, J. A. C. S. 1927, **49**, 2257; abst. J. S. C. I. 1927, **46**, 1036-A; Chem. Zentr. 1927, II, 2274.
4. H. Gray and C. Staud, U. S. P. 1668959; abst. C. A. 1928, **22**, 2272; J. S. C. I. 1928, **47**, 565-B; Plastics, 1928, **4**, 688.
5. *Ibid.* U. S. P. 1683347; abst. C. A. 1928, **22**, 3989; Plastics, 1929, **5**, 142.

completing the esterification with acetic anhydride. Or[1], the esterification reaction may be conducted below the solution point of cellulose acetate in the mixture, the reaction being continued until the material is fully converted into the chloroform-soluble ester still in the undissolved state. C. Green[2] has given details of the burning, solvent and acetate tests to identify cellulose acetate silk, while F. Greenhalgh[3] has pointed out defects in acetate silk manufacture, including the theory and practice of artificial silk dyeing[4] with especial applicability to Celanese. He has postulated a theory of artificial silk dyeing from a colloidal standpoint[5]. A rubber tubing of diminished porosity and suitable for carrying coal gas[6] is provided with an external reinforcing of fabric doped with a plurality of cellulose acetate coats. A. Grimshaw[7] in 1925 contributed practical details on the skein sizing of acetate filaments, and pre-

1. H. Gray and C. Staud, U. S. P. 1690632; abst. C. A. 1929, **23**, 513; J. S. C. I. 1929, **48**, 554-B; British Plastics, 1929, **1**, #3, 113; Plastics, 1929, **5**, 264. Cites E. P. 11164, 1902. H. Ost, Zeits. Angew. Chem. 1906, **19**, 993.

2. Textile Colorist, 1925, **47**, 107; abst. C. A. 1925, **19**, 1201.

3. Dyer, Calico Printer, 1927, **57**, 122; abst. C. A. 1927, **21**, 2562.

4. Dyer, Calico Printer, 1927, **58**, 160; abst. C. A. 1928, **22**, 872.

5. Silk J. 1927, **4**, #42, 53.

6. A. Gregg, E. P. 300357; abst. C. A. 1929, **23**, 4103.

7. Textile World, 1925, **67**, 320; abst. C. A. 1925, **19**, 898. It was found that skein sized celanese yarns show that 1% gelatin, 8% gum tragasol, 5% white dextrin, 5% Amidex or 5% Irish moss give the best appearance; 3.5 parts of 40 fluidity corn starch with 1.5 parts pearl corn starch, 2 parts softener and 125 parts water (III) give the softest sizing, while 2.5% K gum, or 5% Amidex also gives almost as good results. For binding power, 3.5 parts of 40 fluidity corn starch with 1.5 parts pearl corn starch and 125 parts water (I), as well as 1% gelatin, 33% celanese size, or 9.5 parts corn starch with 0.5 part Arcy and 250 parts water give best results. Best results on pulling over the thumb nail were obtained with I, 1.5 parts 40 fluidity corn starch with 3.5 parts pearl corn starch and 125 parts water, 4% of 50 fluidity corn starch, 4% of 75 fluidity corn starch or 1 part gelatin with 1 part glucose, 1 part softener, 5 parts 50 fluidity corn starch and 125 parts water (II). The sized skeins retained 10.21% of 33% celanese size, 4.29% of 1% gelatin, 4.84% of 5% potato starch, 5.37% of 4% 75 fluidity corn starch, 5.37% of II, 5.91 % of I and 3.17% of III. It appears that special slashers may give a better result than hank sizing.

ferred methods of scouring and bleaching acetate silk and cotton mixtures[1].

The hollow yarn "Celta" is claimed to be lighter in weight and has greater covering power than ordinary rayon[2], resembling wool in softness. A label or tag for use with goods which have to be dyed has been patented[3], which consists in attaching to the goods an identifying tab composed of a fabric tape of cellulose acetate and cotton yarn, so that the surface is mainly composed of acetylcellulose. In molding rubber[4], molds are lined with thin sheets of organic material as cellulose acetate, the articles being formed by pressing together two halves of a mold each lined with foil and acetate coated.

In the production of aliphatic organic acids[5], an alcohol of b. pt. below 350° is passed in vapor form in countercurrent with a catalyst consisting of a metal oxide reducible by the corresponding aldehyde. The alcohol meets reduced metal at about 280° and is dehydrogenated to the aldehyde, which is later oxidized by the metal oxide to acid[6]. Cuprous oxide containing 1% of silver is the preferred catalyst. In an illuminating article published in 1926, A. Hall[7] discusses the development of dyestuffs for acetate silk and the theory of their application, including the preparation and properties of acetylcellulose[8], and the action of swelling agents thereon with respect to removing or restoring luster[9].

1. A. Grimshaw, Textile World, 1925, **67**, 579; abst. C. A. 1925, **19**, 1200.
2. F. Grove-Palmer, Textile Colorist, 1928, **50**, 666; abst. C. A. 1929, **23**, 283; Textile Mfr. **53**, 428; Rayon, 1928, p. 36.
3. O. Gunnell, U. S. P. 1677475.
4. A. Gustafson, E. P. 247514; abst. C. A. 1927, **21**, 674.
5. W. Hale and W. Haldeman, E. P. 287064; abst. J. S. C. I. 1929, **48**, 671-B.
6. N. Grunstein and P. Berge, Can. P. 262271; abst. C. A. 1926, **20**, 3397.
7. Dyer & Calico Printer, 1926, **56**, 26; abst. C. A. 1926, **20**, 3087.
8. Dyer & Calico Printer, 1926, **56**, 46; abst. C. A. 1926, **20**, 3565.
9. J. Textile Inst. 1927, **18**, 222; abst. Chem. Met. Eng. 1928, **35**, 111.

In the hope of discovering dyes soluble in water, but applicable to cellulose acetate without the agency of soap or other solubilizing agent[1], some azo-compounds containing arsinic and stibinic groups have been prepared. The dyes, the properties of which are summarized in a table in the original article, were prepared by diazotizing and coupling from sulfanilic, *p*-aminobenzoic, *p*-arsanilic and *p*-stibanilic acids. None of the compounds were suitable as a dye for acetate silk, but the results indicate it should be possible to prepare azo-dyes containing arsinic and stibinic acid groups capable of satisfactory application for this purpose. The affinity for cellulose acetate increases in the order: sulfonic, arsinic, stibinic, carboxylic.

Some blue and violet S. R. A. dyes undergo change in shade when exposed to bright light subsequent to treatment with sodium nitrite and sulfuric acid. By applying these dyes to a cellulose acetate (Celastoid) film, treating with nitrite-vitriol and exposing behind a negative, photographic prints have been obtained which show serious fading only on exposure to direct sunlight[2]. Dyes found effective were S. R. A. blues, III, IV, V and VII; Violet II, Heliotrope I. C. Halle[3] in 1925 reviewed with citations, the history and development of cellulose acetate lacquers, airplane dopes and plastic combinations. A lubricating (?) compound has been described[4], comprising cellulose ester 6, graphite (or talc) 1.

Under the auspices of the Associated Knit Underwear Mfrs. of America[5], the U. S. Bur. of Standards issued a comprehensive report on the physical constants of artificial filaments. In order to separate acetic acid from a mixture

1. A. Hall and M. Aische, J. Textile Inst. 1926, **17**, T-104; abst. C. A. 1926, **20**, 1525; J. S. C. I. 1926, **45**, 270-B.
2. A. Hall and R. Hill, J. Soc. Dyers Colorists, 1927, **43**, 291; B. J. Phot. 1927, **74**, 597; J. S. C. I. 1927, **46**, 861-B.
3. Farbe u. Lacke, 1925, 397, 424; abst. C. A. 1926, **20**, 116.
4. T. Hamilton, U. S. P. 1599963.
5. C. Hamlin, Bur. of Standards, Preliminary report No. 1, 1926.

also containing acetylene, C. Hand[1] passes the mixture through an aromatic compound as aniline (the reaction between aniline and acetaldehyde is exothermic), at 70-90°. In order to render relatively permanent, sheets of cellulose origin from viscose, copper-ammonia cellulose or denitrated nitrocellulose[2], the films or pellicles are coated on one or both sides with a plastic solution of acetylcellulose.

The properties, tests and reactions of diethyl phthalate, an acetylcellulose solvent, have been detailed[3]. Acetic anhydride results when a mixture of sulfur 1 and chlorine 4, is caused to react on acetic acid, preferably at an elevated temperature[4].

Products have been described as suitable for film and filament manufacture, indefinitely chemically characterized[5], and obtained by acting upon cellulose, starch, or other carbohydrate xanthate with nitrogen trioxide or tetroxide, or nitrous acid or a nitrite, in the presence of a weak acid as acetic. The cellulose esters resulting contain a small proportion of fixed nitrogen. The J. Haste composite cellulose acetate and nitrate film[6], comprises a layer of acetate composition containing moisture to induce flexibility, covered on both sides with a nitrate coating which restrains exit of water from the middle layer. His photographic film[7] comprises a light-sensitive gelatino-silver halide layer at-

1. C. Hand and Rubber Service Laboratories Co., U. S. P. 1696479; abst. C. A. 1929, **23**, 850; J. S. C. I. 1929, **48**, 123-B. E. P. 269556; abst. J. S. C. I. 1928, **47**, 82-B. Can. P. 277760.
2. H. Hands, E. P. 243032. See L. Bethisy, E. P. 11927, 1898. Soc. des Etablissements Gaumont, E. P. 3198, 1915.
3. A. Handy and L. Hoyt, J. Am. Pharm. Assoc. 1925, **14**, 219; abst. C. A. 1925, **19**, 3001. See also J. Am. Pharm. Assoc. 1924, **13**, 600; abst. C. A. 1925, **19**, 152. J. Am. Pharm. Assoc. 1922, **11**, 928; abst. C. A. 1923, **17**, 853. J. Am. Pharm. Assoc. 1926, **15**, 454; abst. C. A. 1926, **20**, 3779; J. S. C. I. 1927, **46**, 315-B. J. Am. Pharm. Assoc. 1927, **16**, 7; abst. C. A. 1927, **21**, 2359; J. S. C. I. 1927, **46**, 398-B.
4. L. Harmann and F. Kaufler, Can. P. 245985; abst. C. A. 1925, **19**, 1284.
5. A. Harrison, E. P. 264261.
6. U. S. P. 1532818; abst. C. A. 1925, **19**, 1776; J. S. C. I. 1925, **44**, 479-B.
7. U. S. P. 1532819; abst. C. A. 1925, **19**, 1668; J. S. C. I. 1925, **44**, 479-B.

tached by a gelatinous substratum to an acetylcellulose coating. Details of acetic anhydride manufacture by the Beatty and McLang process have been published[1], and the J. Nelson method of concentrating aqueous formic and acetic acids[2]. P. Hayemal[3] has reviewed the uses of cellulose acetate in the plastic and artificial leather industries, and R. Hazard[4] in the field of artificial filaments.

In the manufacture of composite sheets of cellulose acetate and glass[5], diacetone alcohol is used alone or with acetone, methylcyclohexanone or cyclohexanone to cause satisfactory adhesion. The glass is preferably preliminarily cleaned with diacetone alcohol, and a sugar solution containing a small addition of nitric acid also may be used to assist cleaning and adhesion. In the treatment of mixed fabrics containing acetate silk[6], a woven figured effect is producible by dissolving the acetate silk from portions of the fabric by the application thereto of a paste containing acetone or other acetylcellulose solvent.

If cellulose is treated with an acid or neutral swelling agent (sulfuric or nitric acid, zinc chloride), and after removal of the latter by washing, acetylation may then be conducted in the usual manner, producing an ester of unusual stability and adaptability for film and filament formation[7]. Or[8], esters may be obtained by heating the potassium salt of the acid with an alkyl or aralkyl halide in the presence of pyridine or quinoline; example, benzyl chlo-

1. H. Haunschild, Chemicals, 1926, **26**, #1, 7.
2. W. Haworth and J. Nelson, Ltd., E. P. 281827; abst. C. A. 1928, **22**, 3669; J. S. C. I. 1928, **47**, 117-B. Can. P. 284886. D. R. P. 513574; abst. C. A. 1931, **25**, 1843.
3. Ing. Chim. 1927, **15**, 94; abst. C. A. 1928, **22**, 3986.
4. Russa, 1928, **3**, 469, 597, 599, 725, 727, 859, 861; abst. C. A. 1930, **24**, 4150. Contains bibliography of 91 references, mostly patents.
5. P. Head, E. P. 299900; abst. C. A. 1929, **23**, 3553.
6. G. Heberlein, U. S. P. 1667892; abst. C. A. 1928, **22**, 2280. E. P. 237909; abst. Rayon J. 1926, **1**, #7, 36.
7. *Ibid.* E. P. 298087; abst. C. A. 1929, **23**, 2822; J. S. C. I. 1930, **49**, 184-B.
8. F. Hefti and W. Schilt, E. P. 229958; abst. J. S. C. I. 1925, **44**, 338-B.

ride, potassium acetate and pyridine give benzyl acetate, 80% theory; benzyl cinnamate, 88% theory is similarly obtained, using sodium cinnamate. Details for printing of cellulose acetate mixed fabrics were published[1] in 1928.

Cellulose intended for esterification purposes is pretreated with 80% lactic acid at 80°, washed and dried[2], or with concentrated formic acid[3]. A filtration method has been described[4] comprising an edge filtration or separation apparatus having a separating element, consisting of acetylcellulose sheets. Plastic masses have been described[5] consisting of starch condensed with formaldehyde in the presence of lactic acid or phthalic anhydride, the products having the deportment of esters, as starch lactate or phthalate.

Aldols are formed when acetaldehyde or higher homologue[6] is neutralized by NaOH solution in a non-oxidizing atmosphere, then dilute sulfuric acid added, the unconverted aldehyde being distilled *in vacuo* below 50°. Yield, 83% of theory. Acetaldehyde is produced by causing acetylene to react upon water in the presence of acid mercury compounds[7], adding solvents to dissolve the acetylene. K. Herstein[8] contributed a paper in 1927 on various methods of delustering rayon and acetate filaments, and the bleaching and dyeing of acetate silk[9], and A. Herzog[10] on the

1. E. Heim, Z. Farben-Ind. 1928, **20**, 65; abst. C. A. 1928, **22**, 2843.
2. H. Heinman and A. Bayerl, Can. P. 273515; abst. C. A. 1927, **21**, 3742. E. P. 268289; Addn. to E. P. 263128.
3. I. G. Farbenindustrie, E. P. 263128; abst. Chem. Zentr. 1927, II, 2376.
4. H. Hele-Shaw and J. Pickard, Can. P. 281702.
5. Herold, A.-G., D. R. P. 507997; abst. C. A. 1931, **25**, 784.
6. C. Herrly, U. S. P. 1598522; abst. J. S. C. I. 1926, **45**, 995-B.
7. W. Herrmann and H. Deutsch, Can. P. 274219; abst. C. A. 1927, **21**, 3907.
8. Rayon J. 1927, **2**, #4, 13.
9. Rayon J. 1927, **2**, #10, 13; abst. C. A. 1928, **22**, 872.
10. A. Herzog, Kunstseide, 1927, **9**, 7; abst. C. A. 1927, **21**, 2558. Expt. Sta. Record, **58**, 394; abst. C. A. 1928, **22**, 3302. Jentgen's Artificial Silk Review, 1928, Oct. p. 6. The average diameter of the dry-spun fiber ranged between 26.4 and 40.3 microns, and of the wet-spun, 17.1-23.9. The dry-spun varieties were 3-5 deniers in fineness, the specific weight averaging 1.33 gm. Electric conductivity very slight. Melts at 200-300° into an amorphous mass, becoming brown on further heating. Average light refraction, 1.473. Birefringent.

physical properties of Celanese, Milanese and Aceta[1]. He has also investigated the crystalline structure of acetyl- and nitro-cellulose by Roentgen-ray analysis with tables and diagrams[2], some of the results obtained being afterwards corrected[3]. The measurement of transmission of ultra-violet radiation through cotton, wool, linen, silk, rayon and cellulose acetate was published in 1928 by the U. S. Bur. of Standards[4]. R. Herzog[5] has also published X-ray diagrams for cellulose acetate and viscose, and given details of the chemistry and physical constants of acetate silk[6], while K. Hess[7] has investigated the cryoscopic behavior of cellulose acetate, and has given rotatory power constants, including results upon the acetolysis of cellulose[8], it having been found that cellulose dextrin when treated with less sulfuric acid ordinarily used in acetylation forms first acetylcellulose, then a hexacetylbiosan, finally splitting into cellobiose, glucose and a hexosan. The crystalline structure of the acetylated celluloses has been reported upon[9].

1. See also W. Massot, Lehne'sche Farber-Zeit. 1907, 10. A. Herzog, Chem. Zeit. 1910, **34**, 40; Kunst. 1913, **3**, 9.

2. R. Herzog, Helv. Chim. Acta, 1926, **9**, 631; abst. C. A. 1926, **20**, 3348; J. S. C. I. 1926, **45**, 782-A.

3. *Ibid.* Helv. Chim. Acta, 1926, **9**, 798; abst. C. A. 1927, **21**, 174.

4. The results obtained for the five varieties of goods, i.e. Voile, Dress goods, Satin, Twill and Satin (sample #2) are as follows: Observed transmission in percent, 250-400 microns, 60., 25., 12.5., 15.3, 16.; 250-310 microns, 59., 20.5, 12.1, 11., 10.3; 310-400 microns, 61., 29., 13.2, 19.1, 21.3; through interstices, 43., 1.5, 0.3, 1.3, 0.3; transmission through thread in percent, 250-310 microns, 28.1, 19.3, 11.8, 9.8, 10.; 310-400 microns, 31.6, 27.9, 12.9, 18., 21.1; thread count of warp, 63, 105, 120, 125, 105; thread count of filler, 66, 54, 72, 100, 115; weight, Oz. per sq. yd., 1.4, 3.0, 2.5, 2.3, 2.7.

5. Paper Trade J. 1926, **83**, #7, 51.

6. R. Herzog, Papier-Fabr. 1927, **25**, 17; abst. C. A. 1928, **22**, 4797; J. S. C. I. 1927, **46**, 163-B; Caout. et Gutta. 1927, **24**, 13640.

7. K. Hess, Annalen, 1927, **457**, 307; abst. C. A. 1927, **21**, 4062; J. S. C. I. 1928, **47**, 48-A; Chem. Zentr. 1927, II, 2179.

8. *Ibid.* Chem. Ztg. 1928, **52**, 786.

9. *Ibid.* Koll. Chem. Beih., 1926, **23**, 93; abst. J. S. C. I. 1926, **45**, 1127-A. Cellulose acetate crystallises in well-defined needles from dilute solutions of cellulose triacetate in tetrachlorethane concentrated gradually at the ordinary temperature; the needles are unstable, and change slowly into compact rhombs. If the crystallisation is very slow, only the rhombic form separates. Cellulose diacetate is obtained in fine needles by the repeated cooling of a warm 10% solu-

Whereas previous methods of acetylating have involved the use of hydrolytic agents as catalysts, danger thus involved is (at least partially) avoided when cellulose[1], after the customary purification, is immersed in NaOH solution, and subsequently washed with water until free from alkali. The water is dispersed with pyridine, and the material thus obtained shaken with pyridine and acetic anhydride during 24 hrs., after which it is heated to 40-45° for some time. The cellulose triacetate thus obtained resembles closely in appearance the original cellulose, but differs from all other acetated celluloses previously described by its almost complete insolubility in organic solvents and thereby becomes only a museum specimen in interest. The action of acetic anhydride in the presence of cellulose has been critically studied[2], and the characteristics of the crystallized

tion of cellulose diacetate in a 50% mixture of benzene and alcohol. The triacetate needles show positive double refraction in the direction of their long axis, whilst the diacetate needles show optically active cellulose-copper compound formed from the hydrolytic product of cellulose acetate, it is shown that the carbohydrate in cellulose acetate is actually unchanged cellulose. The cryoscopic glacial acetic acid leads to the conclusion that the structure of cellulose may be represented by that of a glucose anhydride, which, contrary to the behaviour of other known glucosans, is capable of swelling and is sparingly soluble in water.

1. K. Hess and N. Ljubitsch, Ber. 1928, **61**-B, 1460; abst. C. A. 1928, **22**, 4793; J. S. C. I. 1928, **47**, 705-B.

2. K. Hess, W. Weltzien and R. Singer, Ann. 1925, **443**, 71; abst. C. A. 1925, **19**, 3161; J. S. C. I. 1925, **44**, 440-B. The action of acetic anhydride, in the presence of sulfuric acid, on cellulose gives as a first product "true" cellulose acetate followed by cellulose acetate *A*; cellodextrin acetates, which are divisible into a number of groups in accordance with their solubility or insolubility in alcohol and ether; cellobiose octa-acetate and dextrose penta-acetate. Slow separation of the cellodextrin acetates, from very dilute alcoholic solution, permits the isolation of a crystalline substance which has been identified as cello*iso*biose acetate. The, approximately straight, graph showing the relationship between molecular weight and specific rotation of the various fractions of the cellodextrin acetates indicates that the latter are mixtures of a few substances, and the approximation to the straight line between cellulose acetate *A* and cello*iso*biose acetate points to the conclusion that these are the only two substances present. Cellulose acetate is a primary product of the acetolytic degradation of cellulose, since it gives rise to cellobiose octa-acetate. The yields are considerably lower than those obtained from acetyl-free cellulose. This diminution of yield is further observed with the cellodextrin acetates, which have already suffered partial hydrolysis and subsequent

acetylcelluloses[1], including the cryoscopic behavior[2]. In

acetylation to such an extent that with increasing acetyl content cellobiose octa-acetate is no longer obtained. The acetyl-free dextrins give a good yield of cellobiose octa-acetate. Cellobiose can be derived only from products in which the hydroxy group produced during hydrolysis is not acetylated, whereas after acetylation these products yield monose derivatives soluble in water. Hence cellobiose cannot be considered to exist preformed in cellulose, but is formed from the first products of its degradation. The recognition of cello*iso*biose acetate in the cellodextrin acetates and the convertibility of cello*iso*biose into cellobiose octa-acetate indicate the probability that cello*iso*biose plays an important part in the conversion of cellulose into dextrose, the reaction proceeding to its final stage either by direct hydrolysis or through the intermediate production of cellobiose.

1. K. Hess, G. Schultze and E. Messmer, Ann. 1925, **444**, 266; abst. C. A. 1926, **20**, 664; J. S. C. I. 1925, **44**, 841-B; Caout. et Gutta. 1926, **23**, 13211. The acetone soluble, chloroform insoluble cellulose acetate known as cellite is prepared on a large scale by partial hydrolysis of cellulose triacetate with sulfuric-acetic acid according to the Bayer D. R. P. 252706. This is found to be a mixture of triacetate and isomeric diacetates in the ratio 1:4, together with acetates of dextrose and cellobiose. The rate of acetylation varies considerably with different cellulose preparations, the time required ranging from 1¼ hours for Kahlbaum's "defatted" cotton to above 48 hours for mercerised "linters." Mercerisation cannot therefore be regarded as a depolymerisation, but is rather a surface polymerisation effect. A further result of mercerisation is the much slower hydrolysis of triacetate in solution to diacetate. After about six precipitations from benzene-alcohol, the mixture of tri- and di-acetates shows signs of crystallisation, and well defined crystals are eventually obtained. These are stable only in contact with the solvent and become amorphous when dry. Like the triacetate crystals, they show no X-ray line spectrum. That the crystalline acetate is derived from chemically intact cellulose is proved by the identity of the rotatory power curves in ammoniacal copper solution for the hydrolysed product and for pure cotton cellulose. No separation of cellulose into two or more isomerides results even after prolonged fractional crystallisation of the crystalline tri- and di-acetates, nor after fractional extraction with choloroform.

2. K. Hess and G. Schultze, Ann. 1926, **448**, 99; abst. C. A. 1926, **20**, 2663. They found that solutions of cellulose diacetates in acetic acid, when exposed to air, yield molecular weight figures (based on the depression of the freezing point) which sometimes start with a high value (e.g., 800) and fall during the course of 40-80 hours to values (about 130) slightly lower than that calculated for hexosane diacetate. In other cases, with warm solutions, the molecular weight figures rise during the first 15-20 hours and then fall. On the other hand, in the absence of air, the molecular weight figures first fall and then rise to infinity. This takes place in some cases and not in others. Similar effects are observed with cellulose triacetate and with lichenin triacetate. The authors hold the view that these cellulose derivatives can dissociate into the simplest hexosane derivatives and that these can re-associate to form bodies of very high molecular weight. In the second paper, the authors record similar effects with amorphous and fibrous cellulose triacetates.

a continuation of this work[1], it is shown that the amorphous triacetylcellulose and that prepared from ramie fiber show the same cryoscopic behavior in acetic acid as does the crystalline cellulose ester, change in optical activity of various cellulose acetates in pyridine being reported for periods varying from 0.5 to 72 hrs. The preparation of cellulose acetate crystals from ramie fibers[2] has been described, including reversible and irreversible lattice changes in cellulose triacetate[3].

In preparing laminated glass[4], a sheet of cellulose acetate is interposed, while immersed in a softening liquid as triacetin, between glass sheets, and the compound sheet pressed, rolled and finally united by steam pressure. The edges of the sheet may be treated with rubber solution, before the steam treatment. It has been found that when

1. K. Hess and G. Schultze, Ann. 1927, **455**, 81; abst. C. A. 1927, **21**, 2982.

2. *Ibid.* Ann. 1927, **456**, 55. On treating purified china grass fibers with acetic anhydride in benzene with dilute sulfuric acid as catalyst, a cellulose acetate is obtained which dissolves in acetic acid or chloroform, leaving undissolved about 15% of needle crystals (0.05 to 0.1 mm. in length). It is considered that these crystals pre exist in the fibers and that the acetylation and extraction remove amorphous intercrystallite cellulose. Elementary analysis of the crystals gives values agreeing with those of cellulose. No attempt has been made to determine whether they contain acetyl, which would not readily be disclosed by elementary analysis. On treatment with acetic anhydride in benzene in the presence of dilute sulfuric acid a yield of cellulose triacetate indistinguishable from that obtained from the intercrystallite substance is obtained.

3. K. Hess and C. Trogus, Z. physik. Chem. Abt. B. 1928, **5**, 161; abst. C. A. 1930, **24**, 2287. It was found that when fibrous cellulose triacetate is allowed to swell in cyclohexanone, methyl alcohol, benzene, pyridine or a chloroform-methyl alcohol mixture, an expansion of the lattice at right angles to the fiber is observed, and the original dimensions are regained when the solvent is removed by drying or displacement. If, however, the material is completely dispersed in choloroform the lattice is destroyed, and on reprecipitation with methyl alcohol a different lattice is formed. The change in the lattice structure corresponds with a marked difference in external properties, the reprecipitated material consisting of doubly refracting crystallization needles, possessing when swollen a lower elastic limit, and incapable of forming a film on drying. The lattice of this second form remains unchanged when the substance is moistened with organic liquids. The nature of the process of solution is discussed in the light of the observations.

4. G. Heyl and M. Greenhill, D. R. P. 519028; abst. C. A. 1931, **25**, 2827. Belg. P. 354051.

cotton dyed with indigo has slightly faded[1], the isatin extracted from it dyes cellulose acetate yellow.

In plasticizing acetated cellulose[2], ethers or thio ethers of glycollic esters have been brought forward, particular mention having been made as to the suitability of diamyl and cyclohexanol thioglycollates and diglycollates. The "dry-process" stencil sheet of E. Hill[3], intended for duplicating purposes, comprises a cellulose ester in solution, a non-volatile oil, a tempering agent (castor oil, oleic or stearic acid), and a plasticizer (acetanilid, chlornaphthalene). Cellulose ester surfaces may be smoothed, leveled and polished by subjecting the surface simultaneously to an abrasive and softening action, using ethyl acetate or lactate, diacetone alcohol, cresyl phosphate, glyceryl or benzyl benzoate, diphenyl ether or anisole[4].

In a British process[5], gases containing relatively small proportions of acetylene are used for acetaldehyde production, by washing in counter-current with a catalytic medium such as a liquor containing acid mercury and iron sulfates. In the manufacture of non-static photographic film to minimise the tendency to static discharges of electricity when the film is run through the camera[6], an electrolyte soluble in cellulose acetate dissolvants (sodium or ammonium acetate, ammonium iodide, nitrate or thiocyanate, potassium or cadmium iodide, calcium or nickel nitrate) is incorporated with the ester in amounts of 0.005-2% of the weight of the film.

When an aminoazo compound is condensed with phtha-

1. E. Hibbert, J. Soc. Dyers Col. 1928, **44**, 300; abst. C. A. 1929, **23**, 280.

2. M. Schmidt and J. Voss, D. R. P. 434640; abst. Chem. Zentr. 1927, I, 380.

3. U. S. P. 1608742; abst. Pulp & Paper Mag. 1927, **25**, #38, 1197.

4. J. Hirsh and A. Robson, U. S. P. 1621780.

5. H. Hirst and Imperial Chemical Ind., Ltd., E. P. 302515; abst. C. A. 1929, **23**, 4231.

6. H. Hoffman, U. S. P. 1570062.

lic acid to give a phthalamide[1], acetate silk dyes result. Examples, phthalic acid and aminoazobenzeneazodiphenylamine (orange), or aminoazobenzene (yellow); and from tetrachlorphthalic acid[2] and *p*-nitrobenzeneazo-*b*-naphthylamine (orange). Cellulose acetate dyes also result by condensing 1-chlor-2.4-dinitrobenzene-6-sulfonic acid or 1-chlor-2.6-dinitrobenzene-4-sulfonic acid with aniline. Temperature of dyeing about 75°.

Acetic acid, or a mixture of acetic acid and anhydride is formed when ethyl acetate vapor is passed through a quartz tube charged with a catalyst (copper, silver or their phosphates) at 600°, 98% or 99% acetic acid being obtained[3]. Contact with iron compounds are to be avoided. If aqueous acetic acid is vaporized and caused to react with sodium or potassium acetates[4] capable of combining with the acid to form an acid salt, the latter may be directly used for ester manufacture. In the catalytic oxidation of ethyl alcohol to produce acetaldehyde[5], the reaction products are dehydrated by cooling, then treated with anhydrous aldehyde solvent. Addition of a small amount of acid and distilling, then yields diethyl acetal.

Butyro- and valero-lactones have been introduced as cellulose acetate solvents and softening agents[6]. Acetic acid may be crystallized from dilute solutions[7] by combining with an acid capable of forming a solid acid salt as sodium acetate, and then distilling under reduced pressure.

1. L. Holliday & Co., Ltd., and C. Shaw, E. P. 298098; abst. C. A. 1929, **23**, 2832; J. S. C. I. 1928, **47**, 888-B.
2. L. Holliday & Co., Ltd., and A. Young, E. P. 244936; abst. C. A. 1927, **21**, 330; J. S. C. I. 1926, **45**, 154-B.
3. Holzverkohlungs-Ind. A.-G., E. P. 274076; abst. C. A. 1928, **22**, 1980; J. S. C. I. 1928, **47**, 886-B. D. R. P. 508256; abst. C. A. 1931, **25**, 714. Can. P. 285930. F. P. 636781; abst. C. A. 1929, **23**, 605.
4. *Ibid.* E. P. 291433, 291434; abst. C. A. 1929, **23**, 1141. D. R. P. 509936; abst. C. A. 1931, **25**, 713. Can. P. 285928, 285929.
5. Holzverkohlungs-Ind. A.-G. and O. Fuchs, E. P. 294037; abst. C. A. 1929, **23**, 1650; J. S. C. I. 1928, **47**, 703-B.
6. Holzverkolungs-Ind. A. G. and J. Seib, E. P. 295275. D. R. P. 501889; abst. C. A. 1930, **24**, 4931. F. P. 657812.
7. Holzverkohlungs-Ind. A. G., E. P. 302268, 302269, Addn. to 291433; abst. C. A. 1929, **23**, 4230.

L. Hooley[1] has discussed the anthraquinone colors (Celatene dyes) for dyeing acetylcellulose, and has given several dyeing recipes. In making laminated glass[2], polymerized dialkyl (dimethyl, diethyl, dipropyl) itaconates which form glass-like masses of high refractive index, are used as a cement to unite cellulose acetate sheets with glass. As ordinary glass contains an alkaline base exhibiting anticatalytic action, small amounts of pyridine are added to the composition.

A series of patents has been issued to S. Horii for the production of stencils and stencil sheets for duplicating manuscript and typewritten documents, in which cellulose acetate, mannan acetate and starch acetate dissolved in a volatile solvent are used with such softening agents as methylene-, ethylene- or propylene-glycol oleate or ricinoleate[3]; starch stearate or aluminum tannate[4]; naphthene alcohol obtained by reducing naphthenic alkyl esters by means of Na.[5]; chlornaphthalene, stearine or castor oil[6]; naphthenic acids[7]; Japan wax[8]; glyceryl naphthenates (naphthenic acid glycerides)[9]; and certain cellulose ester nonsolvents and fatty bodies as emollients and softeners, as the

1. L. Hooley, Color Trade J. 1925, **16**, 93; abst. C. A. 1925, **19**, 2415.

2. E. Hope, U. S. P. 1644131; abst. C. A. 1927, **21**, 4040. Cites R. Anshuetz, Ber. 1881, **14**, 2784. R. Fittig, Ann. 1903, **331**, 174. H. Stobbe and A. Lippold, J. Pr. Chem. 1914, **90**, 336.

3. S. Horii, E. P. 310181; abst. C. A. 1930, **24**, 699.

4. *Ibid.* U. S. P. 1753204, 1753205; abst. C. A. 1930, **24**, 2563.

5. *Ibid.* E. P. 289511; abst. C. A. 1929, **23**, 680. U. S. P. 1664777; abst. C. A. 1928, **22**, 1832; J. S. C. I. 1928, **47**, 364-B; Pulp & Paper Mag., Feb. 28, 1929, 323.

6. *Ibid.* U. S. P. 1645141; abst. C. A. 1927, **21**, 4036; Pulp & Paper Mag., Feb. 28, 1929, 323. E. P. 275747; abst. C. A. 1928, **22**, 2446.

7. *Ibid.* U. S. P. 1799793; abst. C. A. 1931, **25**, 3139. Cf. U. S. P. 1792095.

8. *Ibid.* E. P. 261203; abst. C. A. 1927, **21**, 3459; Pulp & Paper Mag., Nov. 22, 1928, 1682. U. S. P. 1594525; abst. C. A. 1926, **20**, 3217. Jap. P. 44216; abst. C. A. 1924, **18**, 752.

9. *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; Pulp & Paper Mag., 1927, **25**, 2567. U. S. P. 1587954; Re. 17267; abst. C. A. 1926, **20**, 2567. Cf. U. S. P. 1790987.

fatty acids of tsubaki and sasanqua oils[1]; quince oil[2]; Funori, solid soaps and glycerol[3]; liquid wax[4]; stearin and castor oil[5]; squalene (spinacene), a componet of shark oil[6]; and dolphin oil[7]. The Yoshino which is coated with the above may be colored by chrome yellow, toluidine red or Bismark Brown lakes which absorb the ultra-violet rays of sunlight[8], or a backing sheet may be used[9], the latter being of a firm, stiff paper treated with a coating composition including a non-drying oil and a waxy hardening material[10]. The Yoshino or Japanese paper is made by subjecting bast fibers to the wet beating process until hydration and incipient agglutination takes place[11].

Beech wood treated with acetic anhydride containing 0.25% sulfuric acid[12] gives an acetylated wood (150%) possessing unchanged woody structure and, apart from a yellow color, resembles externally the original wood, 90% of the lignin being acetylated. The W. Hoskins film[13] is prepared by pouring an acetylcellulose solution upon an endless film of gelatin hardened with formaldehyde or hexamethylenetetramine, and after dissipation of the acetate solvent, stripping off the ester film. The preferred method of preparing the gelatin sheet film has been described[14].

1. S. Horii, E. P. 278956; abst. C. A. 1928, **22**, 2819. U. S. P. 1664033; abst. C. A. 1928, **22**, 1660; Pulp & Paper Mag., Feb. 28, 1929, 323. E. P. 274241; abst. C. A. 1928, **22**, 2037.
2. *Ibid.* U. S. P. 1729072; abst. C. A. 1929, **23**, 5285.
3. *Ibid.* U. S. P. 1608881; abst. C. A. 1927, **21**, 308. E. P. 259808; abst. Chem. Zentr. 1927, I, 1109.
4. *Ibid.* U. S. P. 1770697; abst. C. A. 1930, **24**, 4598.
5. *Ibid.* U. S. P. 1698705; abst. C. A. 1929, **23**, 1228. Cf. E. P. 289511.
6. *Ibid.* U. S. P. 1679034; abst. C. A. 1928, **22**, 3748. Cf. E. P. 278956.
7. *Ibid.* U. S. P. 1790987; abst. C. A. 1931, **25**, 1646. Cf. E. P. 310126, 310181; U. S. P. 1770697, 1785260.
8. *Ibid.* U. S. P. 1785260; abst. C. A. 1931, **25**, 567. Cf. U. S. P. 1780391.
9. *Ibid.* E. P. 310126; abst. C. A. 1930, **24**, 699.
10. *Ibid.* U. S. P. 1780391; abst. C. A. 1931, **25**, 178.
11. *Ibid.* E. P. 299520; abst. C. A. 1929, **23**, 3344. Cf. U. S. P. 1698705.
12. O. Horn, Ber. 1928, **61**, 2542. See W. Fuchs, Ber. 1928, **61**-B, 948. H. Suida and H. Titsch, Ber. 1928, **61**-B, 1599.
13. W. Hoskins, U. S. P. 1524133; abst. C. A. 1925, **19**, 1055.
14. *Ibid.* U. S. P. 1582605; abst. C. A. 1926, **20**, 2091.

The edges of laminated glass sheets may be sealed by applying a liquid to the edges which will convert the layer of colloidal reinforcing material into a gel for the required depth, removing the gel, and introducing sealing material as cellulose acetate into the groove so formed[1]. An interesting paper has appeared by H. Hoz[2] describing the beautiful effects producible on mixed acetate and natural silk goods by differential dyeings, he having discovered[3] that many dyestuffs which by themselves have only a weak affinity for acetylcellulose, have strong tinctorial properties in the presence of aryl-carboxylic anions. Examples, Auramine with sodium *o*-cresotinate; Martius yellow with benzoic acid; Malachite green with 2-oxy*iso*naphthalic acid. A. Hutin[4] has given details of the manufacture of the cellulose acetate plastics called Rhodoide, Sicoid, Plastin, Bernite, Cervinite, Isoloid, Oyocetyle, Cellutite, Satolite, Amzylolithe, Novolithe, Aceloide, Zellon and Cellone.

In the manufacture of mixed dopes from cellulose acetate and rubber[5], it has been demonstrated that, in general, cellulose acetate solvents are non-solvents for rubber, and conversely. Cellulose acetate is dissolved by the mono-alkyl ethers of ethylene, propylene or butyl glycol (see p. 183, n. 2) (excepting glycol monoethyl ether) as methyl (or ethyl, *iso*propyl, butyl, amyl) ether of ethylene (or propylene, butylene) glycol, these fifteen solvents being heavy liquids of slow evaporative tendency[6]. The corresponding 15 dialkyl ethers[7] have also been recommended.

1. F. Howe and M. Misener, E. P. 290144. D. R. P. 491726; abst. C. A. 1930, **24**, 2567. Can. P. 285240; abst. C. A. 1929, **23**, 682.
2. Melliand Textilber. 1927, **8**, 252; abst. C. A. 1927, **21**, 2069; Chem. Zentr. 1927, I, 2776.
3. H. Hoz, W. Bernoulli and A. Link, U. S. P. 1650275; abst. C. A. 1928, **22**, 503; J. S. C. I. 1928, **47**, 12-B. E. P. 231897; abst. J. S. C. I. 1925, **44**, 588-B.
4. Rev. des Produits Chimiques, 1921, **24**, 524; Rev. gen. mat. plastiques, 1925, **1**, 6; Kunst. 1925, **15**, #7, 116; abst. Plastic, 1925, **1**, 11.
5. A. Hutin, Rev. gen. mat. plastiques, 1926, **2**, 208; abst. C. A. 1926, **20**, 3089.
6. I. G. Farbenindustrie Akt. Ges., E. P. 252203; abst. C. A. 1927, **21**, 1556. Can. P. 285360; abst. C. A. 1929, **23**, 704.
7. *Ibid.* E.P. 256229; abst. C.A. 1927, **21**, 2985. Swiss P. 133200.

In order to facilitate esterification, cellulose may be given a preliminary treatment with formic acid[1], or lactic acid[2]. Acetylene in gas mixtures containing it[3], is converted into acetaldehyde by treating the mixture in a very finely divided condition with acid solutions containing mercury salts. Solutions of acetylcellulose which may contain natural or artificial resins are produced by means of ethyleneglycol monomethyl formate, acetate or phthalate[4]. Cellulose phosphate or sulfate may be made by esterifying cotton (preferably after swelling in NaOH solution) with phosphorous oxychloride or sulfuryl chloride[5]. Cellulose acetates and other cellulose esters may be prepared by treating cellulose with 0.5-1% sulfuric acid in the presence of acetic acid as a diluent, then adding acetic anhydride to effect partial esterization, and subsequently adding more sulfuric acid to complete the reaction to the solubility point desired[6].

Cellulose acetonitrates (nitracetates) are made by esterifying cellulose by means of an organic acid anhydride and adding nitric acid[7], or by pretreating cellulose with a mixture of nitric acid and a catalyst (sulfuric acid), then acetylating in the usual way. Anhydrous acetic acid is produced from its aqueous solutions by distilling 40% acetic

1. I. G. Farbenindustrie, A.-G., E. P. 263128; abst. C. A. 1928, **22**, 164; Plastics, 1928, **4**, 386. Ital. P. 254530. Can. P. 283366; see also Can. P. 273515; C. A. 1927, **21**, 3742; 1928, **22**, 4246.

2. *Ibid.* E. P. 268289; abst. C. A. 1928, **22**, 1237; J. S. C. I. 1928, **47**, 444-B; Plastics, 1928, **4**, 323.

3. *Ibid.* E. P. 278324; abst. C. A. 1928, **22**, 2573; J. S. C. I. 1928, **47**, 397-B. F. P. 641406; abst. C. A. 1929, **23**, 1142.

4. *Ibid.* E. P. 279771; abst .C. A. 1928, **22**, 3044. Ital. P. 256719. Cf. E. P. 278735; abst. C. A. 1928, **22**, 2663.

5. *Ibid.* E. P. 279796; abst. C. A. 1928, **22**, 3044. F. P. 635963; abst. C. A. 1928, **22**, 4815. Ital. P. 260874.

6. *Ibid.* E. P. 281927; abst. C. A. 1928, **22**, 3777; J. S. C. I. 1928, **47**, 258-B; Silk J. 1928, **4**, #47, 68.

7. *Ibid.* E. P. 283595; abst. C. A. 1928, **22**, 4246; J. S. C. I. 1929, **48**, 750-B; Silk J. 1928, **4**, #48, 64. Belg. P. 347095. See E. P. 19330, 1905. F. Becker, U. S. P. 1783771; abst. C. A. 1931, **25**, 414; J. S. C. I. 1931, **50**, 154-B; Plastics, 1931, **7**, #3, 177. Or, the cellulose may be treated in the presence of a diluent, with a mixture of nitric acid and a catalyst, and then acetified.

acid with ethyl acetate[1]. An azeotropic mixture of ester and water distils at 69-70° and separates in the receiver, the ester being returned to the dilute acid until all water has been removed. The ester is then distilled off, leaving glacial acetic acid. Or[2], a solvent (benzene, dichlorbenzene, or quinoline) is introduced at the top (as liquid) and at the lower portion (as vapor) of a fractionating column through which the acetic anhydride vapors are passed.

Cellulose propionate or butyrate may be prepared by warming cellulose for several hours with a halogenated acetic anhydride, the higher fatty acid and a catalyst (monochloracetic or sulfuric acids). The ester is then precipitated by water in the usual way[3]. Acetic anhydride can be made in mixing glacial acetic acid with dry sodium acetate in a closed vessel and adding silicon tetrachloride while stirring. Tetrachlorides of tin or titanium may also be used[4].

In acidylation of cellulose or its converstion products into the acetic ester[5], thionyl chloride with zinc chloride or cuprous chloride as catalyst has been recommended, or[6], the cellulose may be treated with acetyl chloride in the presence of pyridine and an indifferent medium as chlorbenzene which at least partially dissolves the addition product of acid halide and organic base formed in the esterifi-

1. I. G. Farbenindustrie, A.-G., E. P. 284588; abst. C. A. 1928, **22**, 4539; J. S. C. I. 1929, **48**, 671-B. E. P. 294626, Addn. to 284588; abst. C. A. 1929, **23**, 1909; J. S. C. I. 1929, **48**, 671-B. F. P. 647682; abst. C. A. 1929, **23**, 2449. See also F. P. 633817; abst. C. A. 1928, **22**, 3669.

2. *Ibid.* E. P. 285090; abst. C. A. 1928, **22**, 4539; J. S. C. I. 1929, **48**, 671-B. E. P. 300563, Addn. to 285090; abst. C. A. 1929, **23**, 3932; J. S. C. I. 1930, **49**, 452-B. D. R. P. 486953; abst. C. A. 1930, **24**, 1393. F. P. 652820; abst. C. A. 1929, **23**, 3716. Norw. P. 45355.

3. *Ibid.* E. P. 285858; abst. C. A. 1929, **23**, 277; J. S. C. I. 1929, **48**, 594-B; Pastics, 1929, **5**, 336; Silk J. 1928, **5**, #49, 78. F. P. 649576; abst. C. A. 1929, **23**, 3098.

4. *Ibid.* E. P. 289959; abst. C. A. 1929, **23**, 850; J. S. C. I. 1928, **47**, 515-B.

5. *Ibid.* E. P. 289973; abst. C. A. 1929, **23**, 980; J. S. C. I. 1928, **47**, 520-B; Silk J. 1928, **5**, #51, 76; Plastics, 1929, **5**, 693.

6. *Ibid.* E. P. 291360; abst. C. A. 1929, **23**, 1267; J. S. C. I. 1928, **47**, 853-B. Ital. P. 260690. Belg. P. 351169. Can. P. 285918.

cation mixture, but which is not a solvent of the cellulose ester produced. A fibrous acetylcellulose results. Cork meal may be esterified by suspending in chlorbenzene and treating with acetic anhydride, or lauryl chloride in presence of pyridine or phosphorous oxychloride. The esters, cork acetate or laurate, while insoluble in the solvents usually used in plastic masses, are plastic under pressure and when heated[1].

Acetic acid may be concentrated by extraction with an organic base not attacked by concentrated acetic acid (quinoline, quinaldine, dimethyl- or diethyl-aniline), the concentrated acid being then recovered by distillation[2]. Visible reproducible inscriptions may be impressed on raw film material by the use of a dyestuff in a slowly evaporating solvent, or the dyestuff used in the colloidal printing solution may be substituted by a solution of acetylcellulose in glycol acetate[3]. Tendency to swell of cellulose and cellulose hydrate is minimised by treatment with solutions of resinous condensation products, which are afterwards treated with heat or formaldehyde[4].

1.1.2-Trichlorethane[5] may be obtained by direct addition of vinyl chloride and chlorine gas without the use of a solvent, by a suitable application of light or heat energy, a yield of 93% of theory being obtained. In producing acetaldehyde from acetylene with use of solution of a mercury salt[6], the reaction chamber is lined with an alloy of steel containing Cr. 19-20, Ni. 7-8, Mo. 2-3%. Chloracetaldehyde[7] is producible without use of a catalyst by intro-

1. I. G. Farbenindustrie, A.-G., E. P. 291773. Belg. P. 351137.
2. I. G. Farbenindustrie Akt. Ges., G. Schwaebel and F. Schleicher, E. P. 295238; abst. C. A. 1929, **23**, 2190; J. S. C. I. 1928, **47**, 746-B. F. P. 633817; abst. C. A. 1928, **22**, 3669. Swiss P. 126819; abst. C. A. 1929, **23**, 850. U. S. P. 1766404; abst. C. A. 1930, **24**, 4052; J. S. C. I. 1930, **49**, 754-B.
3. I. G. Farbenindustrie Akt.-Ges., E. P. 295383, Addn. to 287124; abst. C. A. 1929, **23**, 2113.
4. *Ibid.* E. P. 297463. Belg. P. 351088.
5. *Ibid.* E. P. 298084.
6. *Ibid.* E. P. 299234; abst. C. A. 1929, **23**, 3235; J. S. C. I. 1928, **47**, 921-B.
7. *Ibid.* E. P. 299319; abst. C. A. 1929, **23**, 3235.

ducing chlorine gas and vinyl chloride into water and preferably keeping the temperature at 0-40° to avoid formation of by-products. If light is not excluded, 1.1.2-trichlorethane is formed.

A method of stabilization of cellulose acetate has been published[1] in which, after precipitating the acylcellulose from its crude solution and washing, it is heated up to 100° with dilute aqueous or alcoholic sulfuric acid, under such conditions that the solubility in a specific solvent is not altered, a difficult thing to do. A method for continuous acetylation of cellulose[2] comprises pretreating paper in sheet form or rolls with glacial acetic acid, which are rolled up again and then fed continuously into the acetylation chamber. Acetic acid may be separated from water by use of a halogenized hydrocarbon (trichlorethylene)as entraining liquid[3].

For film identification purposes[4], one or each margin is treated with a dye solution, as ultramarine 5, cellulose acetate 2, glycol acetate 100. Esterification of cellulose with a carboxylic acid anhydride and/or acid halide is carried out in presence of liquid sulfur dioxide, with or without the usual catalysts[5]. Water vapor is separated by diffusion (as through a heated graphite tube within a quartz tube)[6] from a mixture containing acetic anhydride such as may be produced by heating acetic acid, and after diffusion separations, the anhydride and associated acid are obtained by distillation.

1. I. G. Farbenindustrie, A.-G., E. P. 299326; abst. C. A. 1929, **23**, 3343; J. S. C. I. 1930, **49**, 457-B; Silk J. 1929, **5**, #57, 72.
2. *Ibid.* E. P. 299511, 299512; abst. C. A. 1929, **23**, 3343; J. S. C. I. 1929, **48**, 13-B. U. S. P. 1675498, 1675499. F. P. 639119; abst. C. A. 1929, **23**, 703; Plastics, 1929, **5**, 637.
3. *Ibid.* E. P. 300923; abst. C. A. 1929, **23**, 3932; J. S. C. I. 1930, **49**, 452-B.
4. *Ibid.* E. P. 300991; abst. J. S. C. I. 1930, **49**, 168-B.
5. *Ibid.* E. P. 301036; abst. C. A. 1929, **23**, 4071; J. S. C. I. 1930, **49**, 504-B; Silk J. 1929, **5**, #58, 76. Belg. P. 356130.
6. *Ibid.* E. P. 301562; abst. C. A. 1929, **23**, 4231; J. S. C. I. 1929, **48**, 122-B. F. P. 640721; abst. C. A. 1929, **23**, 850. See E. P. 285090, 300563.

For the manufacture of cellulose acetate[1], particularly the acetone-soluble ester, there is employed as catalyst zinc chloride, sulfuric and hydrochloric acids in the proportion 6:4:0.5 by weight, the product of esterification being hydrolyzed by known methods. In the extraction method for concentrating aqueous acetic acid[2], a secondary liquid (light petroleum, benzene, tetrahydronaphthalene, trichlorethylene) is used so that less water is extracted, and on subsequent distillation of the extract all remaining water is carried over the secondary liquid.

In the manufacture of dope materials for producing non-transparent dopes[3], cellulose acetate with a gelatinizing agent and castor oil at least equal to the quantity of cellulose ester with coloring matter is thoroughly subdivided under rollers and a small amount of alcohol added. The material is said to be capable of withstanding pressures of 200 atms. without separation of its constituents, and is soluble in the usual solvents to produce a lustrous varnish. To render lacquers uninflammable[4], methylene chloride is advised as the solvent, and to increase their plasticity[5], dibutyl or diamyl phthalate (see p. 268, n. 2), or ethylene, propylene or butylene glycol dibenzoate[6] have been recommended.

In a method for preparing acetate filaments[7], the solution is spun into a bath of calcium chloride solution containing a swelling agent for the ester (acetone or formaldehyde). As a mouth piece for cigarette holders (see p. 296,

1. I. G. Farbenindustrie, A.-G., E. P. 301755; abst. C. A. 1929, **23**, 4342; J. S. C. I. 1930, **49**, 674-B; Silk J. 1929, **5**, #58, 78.
2. *Ibid.* E. P. 302174; abst. C. A. 1929, **23**, 4230; J. S. C. I. 1930, **49**, 500-B.
3. *Ibid.* E. P. 302280; abst. C. A. 1929, **23**, 4356. See Belg. P. 350232.
4. *Ibid.* Belg. P. 350722; abst. Chem. Zentr. 1929, I, 1625.
5. *Ibid.* Belg. P. 330723. Ital. P. 254252, 254253; Addns. to Ital. P. 244959. See Belg. P. 354736.
6. Can. P. 285919; abst. C. A. 1929, **23**, 1267.
7. I. G. Farbenindustrie A.-G., E. Hubert, L. Lock and O. Leuchs, U. S. P. 1766822; abst. C. A. 1930, **24**, 4391; J. S. C. I. 1930, **49**, 761-B; Plastics, 1930, **6**, 671. Swiss P. 115676; abst. J. S. C. I. 1927, **46**, 296-B; Chem. Zentr. 1926, II, 2856.

n. 5; 367, n. 2; 425, n. 6) acetylcellulose in the softened condition is mixed with an equal volume of tobacco powder and molded into the shape desired[1]. Acetaldehyde is prepared by passing acetylene, or gases containing it, with steam over a contact mass containing boric or phosphoric acids, or their copper, nickel or zinc salts[2]. The working temperature is 200-300°. Silver or tin vanadate may also be used[3]. Or[4], the gases containing acetylene may be treated with a solution of alkali bisulfate with a mercury compound. Ethylene chlorhydrin[5] may be made by reacting upon gas mixtures containing ethylene with hypochlorous acid.

A series of patents has been granted the I. G. Farbenindustrie and investigators connected therewith, for the dyeing and printing of cellulose esters, primarily cellulose acetate. In one method[6] water-soluble sulfamic acids derived from colored amino compounds which are not dyestuffs in a usual sense are employed, as sodium 1.4-diaminoanthraquinonesulfamate (giving reddish violet), sodium 4.8-dihydroxyanthraquinone-1.5-disulfamate (reddish blue), and sodium 1-amino-4-methoxyanthraquinonesulfamate (bluish red). The acetate silk may also be directly dyed or developed on the fiber, if used in aqueous colloidal suspension containing a compound which catalyzes the hydrolysis of fats and oils[7], as a naphthenic acid, naphthalenesulfonic acid, or *iso*propyl or butyl -naphthalene or

1. I. G. Farbenindustrie A.-G. and E. Schnabel, D. R. P. 473701; abst. C. A. 1929, **23**, 3099; Chem. Zentr. 1929, II, 2282.
2. I. G. Farbenindustrie A.-G., M. Luther and H. Soenksen, D. R. P. 489360; abst. C. A. 1930, **24**, 2145.
3. I. G. Farbenindustrie A.-G., F. P. 645967; abst. C. A. 1929, **23**, 1910. D. R. P. 509020; abst. C. A. 1931, **25**, 714.
4. I. G. Farbenindustrie A.-G., O. Eisenhut and A. Auerhahn, D. R. P. 489283; abst. C. A. 1930, **24**, 2145. F. P. 657027; abst. C. A. 1929, **23**, 4231. E. P. 312716.
5. *Ibid.* Can. P. 285920.
6. I. G. Farbenindustrie, A.-G., and R. Metzger, U. S. P. 1602695; abst. C. A. 1926, **20**, 3822; J. S. C. I. 1927, **46**, 9-B. E. P. 267695; abst. C. A. 1928, **22**, 1243. F. P. 610539; abst. J. S. C. I. 1927, **46**, 407-B.
7. *Ibid.* U. S. P. 1610961; abst. J. S. C. I. 1927, **46**, 249-B.

-naphthalenesulfonic acid. Example, 3-aminobenzanthrone, fluorescent yellow; *Bz*-1-aminobenzanthrone, red; 5-nitro-1.4-diaminoanthraquinone with di-*iso*-propylnaphthalene sulfonic acid, violet.

Molasses or concentrated sulfite cellulose waste liquor may be used with aminoazobenzene, dinitrodiphenylamine or other organic substances capable of producing dyeings in full, deep shades on acetated cellulose, but not sufficiently soluble in water to permit use of its simple aqueous solution[1]. By the use of ammonium formate, acetate or sulfate (see p. 123, n. 1) to the dyebath[2], acetate silk may be readily dyed with such colors as Malachite green, Dianil yellow R, Fast red O, and Azoyellow to shades of considerable permanency. If the bath contains pyridine or homologues[3], basic dyes as Diamond fuchsine, or China Green, may be employed. Pyridine may be substituted by hydrogenated pyridines (dipiperidyl, *o*-toluidine methanesulfonic acid, guanidine) with equally satisfactory results[4].

In the printing and fixing of basic dyes on acetate silk[5], clear prints are obtained by the use of phenols (phenol, naphthols, resorcinols, cresolsulfonic acids) in printing or fixing pastes. Addition of tannin followed by tartar emetic is unnecessary. *b*-Naphthylamine carbonic acids possess a strong affinity for acetate silk[6], 2.3-naphthylaminecarbonic acid being an example. Acetate yarn may be dyed

1. I. G. Farbenindustrie, A.-G., and R. Metzger, U. S. P. 1666715; abst. C. A. 1928, **22**, 2067; J. S. C. I. 1928, **47**, 365-B. E. P. 271550; abst. J. S. C. I. 1927, **46**, 552-B; C. A. 1928, **22**, 1693.

2. I. G. Farbenindustrie, A.-G., E. Mueller and A. Schaeffer, D. R. P. 438378; abst. Silk J. 1928, **5**, #52, 53; J. S. C. I. 1927, **46**, 964-B. Cites D. R. P. 198008, 355533. G. Schultz, Farbstofftabellen, **6**, 26, 141, 161, 424, 495.

3. I. G. Farbenindustrie, A.-G., and P. Rabe, D. R. P. 439004. E. P. 215373; abst. J. S. C. I. 1925, **44**, 281-B; Chem. Zentr. 1924, II, 2789. U. S. P. 1517581; abst. J. S. C. I. 1925, **44**, 69-B. D. R. P. 445979, Addn. to 439004; abst. C. A. 1930, **24**, 1521. See D. R. P. 486696.

4. P. Rabe, U. S. P. 1622122; abst. C. A. 1927, **21**, 1553; J. S. C. I. 1927, **46**, 407-B. E. P. 215783; abst. J. S. C. I. 1925, **44**, 801-B.

5. I. G. Farbenindustrie, A.-G., and A. Schneevoigt, D. R. P. 441327; abst. J. S. C. I. 1927, **46**, 905-B.

6. I. G. Farbenindustrie, A.-G., D. R. P. 446220; abst. Die Kunstseide, 1927, #8, 421.

with weakly basic, difficultly soluble organic compounds (usually nitroarylamines)[1], if dissolved in formic acid, Turkey red oil or other suitable solvent. Benz-1-aminobenzanthrone gives red; *N*-methyl-4-anilidoanthrapyridine, blood-red; aminoacridine, fluorescent, light yellow; diaminophenanthraquinone, violet.

In acetate silk dyeing the color may be produced on the fiber by padding with a diazotizable amino compound (aminoazobenzene, 2-oxynaphthalin), diazotizing and coupling in the usual manner[2]. Or[3], by coupling a nonsulfonated diazo compound with *b*-naphthylamine- or *b*-naphthol-8-sulfonic acid; e.g. 2.5-dimethoxyaniline with crocein acid (yellow); 5-nitro-*o*-anisidine with phenyl-*b*-naphthylamine-8-sulfonic acid (seal-red); *o*-chloraniline with phenyl acid (reddish yellow); 2.5-dimethoxyaniline with crocein acid (pink).

R. Metzger has found[4] that acetylcellulose may be dyed with azo dyestuffs as *p*-aminophenoxyacetic acids and *b*-naphthol or with *m*-phenylenediamine in aqueous solution, if ammonia and a soap be present. In piece goods dyeing containing effect threads of acetate silk or partially esterified cotton[5], clearer effects are obtained by adding to the dyebath an organic mordant for basic dyes as Katanol. Or, cotton threads may be impregnated with Katanol before esterification or dyeing.

Triarylmethane dyes are made by condensing an *o*-halogenated aromatic aldehyde with a primary aromatic amine, and oxidizing the leuco base thus obtained[6]. An example

1. I. G. Farbenindustrie, A.-G., D. R. P. 446539, Addn. to 428176; abst. Rayon, 1927, **5**, #5, 24; Die Kunstseide, 1927, #7, 375.
2. *Ibid.* D. R. P. 451231, Addn. to 446541; abst. Rayon, 1927, **5**, #12, 48; Die Kunstseide, 1927, #11, 567. F. P. 603710.
3. I. G. Farbenindustrie, A.-G., and F. Weber, D. R. P. 452213; abst. J. S. C. I. 1929, **48**, 15-B; Die Kunstseide, 1928, #1, 15.
4. I. G. Farbenindustrie, A.-G., D. R. P. 457957; abst. Die Kunstseide, 1928, #6, 252.
5. I. G. Farbenindustrie, A.-G., A. Kiesewetter and E. Franz, D. R. P. 481253; abst. C. A. 1930, **24**, 248. See also E. P. 306876; abst. C. A. 1929, **23**, 5330.
6. I. G. Farbenindustrie, A.-G., and K. Schmidt, D. R. P. 487458; abst. C. A. 1930, **24**, 2302. Ital. P. 251367.

is given in which the initial materials are *o*-chlorbenzaldehyde and aniline, dyeing tannin-mordanted acetate silk red-blue to green-blue shades. To produce discharge effects[1], dyed cellulose acetate fabric is printed with zinc salts of formaldehyde-sulfoxylic acid (Hyraldite Z or Decroline), then steamed and treated in the usual manner. Or[2], coloring may be carried out with unsulfonated dyes derived from diazotized *b*-hydroxyethyl ethers of aminophenols, as 4-*b*-hydroxyethoxyaniline diazotized and coupled with acetated aniline (yellow), with 1.7-aminonaphthol (red), with 2.7-aminonaphthol (orange red); 2-*b*-hydroxyethoxyaniline with *b*-naphthol (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). *p*-Aminobenzeneazosalicylic acid diazotized and coupled with naphthol on the fiber gives a red color[3].

Anthraquinonylalanines are obtained by condensing aminoanthraquinones with a halogen propionic acid, or condensing a halogen anthraquinone with alanine[4]. The alkali salts of the products dye acetate silk, and may serve as intermediates for making other dyes. Or[5], azo dyes obtained by the development process may be used in the presence of a compound of the urea group (urea and formaldehyde). A full red is obtained with 2.3-hydroxynaphthyl-aminohydroquinone-dimethyl ether developed with diazotized 4-chlor-2-toluidine, or yellowish red with *p*-nitroaniline with *b*-naphthol. When *p*-nitrodiazobenzene is

1. I. G. Farbenindustrie, A.-G., and A. Fischesser, D. R. P. 461753; abst. J. S. C. I. 1930, **49**, 762-B. U. S. P. 1747540; abst. J. S. C. I. 1930, **49**, 987-B; C. A. 1930, **24**, 1750. Cites E. P. 2573, 1904.

2. I. G. Farbenindustrie, A.-G., O. Spengler and W. Mueller, D. R. P. 495619; abst. C. A. 1930, **24**, 3656. F. P. 619329; abst. J. S. C. I. 1928, **47**, 86-B.

3. *Ibid.* F. P. 639818; abst. C. A. 1929, **23**, 713.

4. *Ibid.* E. P. 246840; abst. C. A. 1927, **21**, 500.

5. *Ibid.* E. P. 262830; abst. C. A. 1927, **21**, 4068; J. S. C. I. 1927, **46**, 936-B.

coupled with 4-nitro-*m*-phenylenediamine, the product gives non-phototropic fast golden-yellow shades on acetate silk[1].

If amino- or mono- or di-alkylamine groups are introduced into the 4 positions of 1-amino-2-alkylhydroxyanthraquinone, the products may be used as pigments for coloring acetylcellulose[2]. Acetate silk may be dyed with unsulfonated azo dyes containing a di(hydroxyethyl)amino-group. Thus di(*b*-hydroxyethyl)aniline is coupled with diazotized *p*-nitroaniline (yellow) or 3.4-trichloraniline (orange); di(*b*-hydroxyethyl)-*m*-toluidine with diazotized *p*-nitroaniline (dark yellowish-red), or 2.4-dinitroaniline (bluish-bordeaux)[3]. An aminonaphthoic acid may be used as diazo or coupling component for azo dyes for acetate silk either in substance or on the fiber[4]. Examples, 4-nitro-*o*-anisidine with 2.3-aminonaphthoic acid (red-violet); 2.6-aminonaphthoic acid and 2.3-hydroxynaphthoic acid with *b*-naphthol (ruby); 2.3-aminonaphthoic acid with *b*-naphthylamine (brown); 2.6-dimethoxyaniline with 2.6-aminonaphthoic acid (yellow); 33 other couplings are detailed.

Acid or basic dyes may be fixed on cellulose acetate by attaching phosphotungstic, phosphotungsticmolybdic[5] or phosphomolybdic acids on the fiber, and then coloring with the dyestuff from tetramethyldiaminobenzhydrol and bibenzylanilinedisulfo acid (violet); or ethylbenzyl-*m*-toluidine and *p*-diethylaminobenzaldehyde (blue). For fast dyeings on acetate textiles[6], it is recommended to pad the

1. I. G. Farbenindustrie, A.-G., O. Spengler and W. Mueller, E. P. 270352; abst. J. S. C. I. 1928, **47**, 8-B. F. P. 633812; abst. C. A. 1928, **22**, 3785.
2. *Ibid.* E. P. 272469; abst. C. A. 1928, **22**, 1859. See E. P. 147001, 267163, 267164.
3. *Ibid.* E. P. 274823; abst. C. A. 1928, **22**, 2279; J. S. C. I. 1928, **47**, 601-B. F. P. 634036; abst. C. A. 1928, **22**, 3787. U. S. P. 1673301; abst. C. A. 1928, **22**, 2846. D. R. P. 479343; abst. C. A. 1929, **23**, 4831; Chem. Zentr. 1929, II, 2506.
4. *Ibid.* E. P. 275307; abst. C. A. 1928, **22**, 2279; J. S. C. I. 1927, **46**, 776-B. D. R. P. 446220. See E. P. 202157.
5. I. G. Farbenindustrie, A.-G., P. Rabe, H. Stoetter, B. Wenk and W. Schepss, E. P. 283281; abst. C. A. 1928, **22**, 3996; Chem. Zentr. 1928, I, 2006. U. S. P. 1694562; abst. C. A .1929, **23**, 718. See Ber. 1894, **27**, 1405. D. R. P. 287003.
6. I. G. Farbenindustrie, A.-G., E. P. 287651, Addn. to 262537; abst. C. A. 1929, **23**, 524; J. S. C. I. 1928, **47**, 401-B.

goods with a mixture of a coupling component, an arylamine and a nitrite, the bath being then acidified to develop the shade.

Hydroxyalkylated aminoanthraquinones are prepared by condensing a chlor-, nitro-, or methoxy-anthraquinone, or a 1.4-dihydroxyanthraquinone with hydroxylated alkylamines, (*b*-aminoethyl alcohol)[1]. Examples, 1-*b*-hydroxyethylaminoanthraquinone, 1.4-di-(*b*-hydroxyethylamino) anthraquinone and its 5-hydroxy derivatives (blue on acetate silk); and the product from *leuco*-1.4.5.8-tetrahydroxyanthraquinone (bluish-green). Monoazo dyes giving bluish violet to blue shades on acetate silk are formed by coupling diazotized picramide or its homologues with the sulfonic acid of a *N*-aralkyl-, or *N*-alkylaralkyl-aniline as *N*-ethyl-*N*-sulfobenzyl-3-toluidine[2].

In forming azo dyes on acetate silk[3], the fabric is printed with a paste containing a solution of an amine and coupling component in an organic solvent (2-naphthylamine and resorcinol in thiodiglycol, 1-methoxy-2-chlor-4-aminobenzene and 2.3-hydroxynaphthoic acid in cyclohexyldiethanolamine, or dianisidine and 2.3-hydroxynaphthoic acid) and the print developed in an acid bath containing a nitrite. If mixed fabrics are to be colored[4], they 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. Examples, Zambesi black D, *a*-naphthylamine and sodium butylnaphthalenesulfonate on wool-acetate fabric, diazotized and developed with 2.3-hydroxynaphthoic acid for deep black; Diamine black BH, dianisidine and wetting agent for dark blue.

1. I. G. Farbenindustrie, A.-G., F. Baumann, H. Friedrich and L. Zeh, E. P. 289807; abst. J. S. C. I. 1929, **48**, 845-B. D. R. P. 499965; abst. C. A. 1930, **24**, 4639.
2. I. G. Farbenindustrie, A.-G., E. P. 295237; abst. C. A. 1929, **23**, 2301. F. P. 634620; abst. Chem. Zentr. 1928, I, 3117. D. R. P. 481265; abst. C. A. 1930, **24**, 245.
3. *Ibid.* E. P. 297374; abst. C. A. 1929, **23**, 2837.
4. *Ibid.* E. P. 299787; abst. C. A. 1929, **23**, 3584; J. S. C. I. 1930, **49**, 416-B.

A process for acetate filament formation has been described[1] in which the dispersed particles in the solution to be used for filament formation are caused to arrange themselves in chain formation, by the action of the electric field produced by a high voltage electric discharge.

Designs may be formed on cotton or other fabrics with cellulose acetate[2], and the fabric thus prepared dyed with a dye which has a selective affinity for either the ester or the vegetable fiber. W. Jaeck[3] in 1927 gave a brief portrayal of acetate silk dyeing with details of the developing dyes (Azanile, Azonine, Acedronol, Azole, Ionamine), the suspension dyes (Cibacet, Imacol, Sedacyl), and the Cellacet, Duranol and Celanese dyestuffs. Cellulose acetate may be treated to render it suitable for molding purposes as for relief or surface printing[4], by first boiling in a hot solution of alkali hypochlorite containing some caustic alkali, then immersed in a bath of mineral oil or fat in which has been dissolved colophony and sulfur.

W. Jancke[5] (see p. 71, n. 3) has examined technical acetylcellulose under the roentgenograph, and has reported that it seems to be made up of microcrystal structure with static axial arrangement along the length of the filament. It showed weak equatorial interference bands in this direction. D. Jones[6] has detailed the properties of acetic anhydride, and its miscibility relations[7]. Phonograph disc records are formed under pressure from one or more porous

1. T. Iwasaki and K. Hagiwara, E. P. 288655; abst. C. A. 1929, **23**, 705.

2. R. Jacoby, U. S. P. 1610786; abst. C. A. 1927, **21**, 502.

3. Melliand Textilber, 1927, **8**, 254; abst. C. A. 1927, **21**, 2069; Chem. Zentr. 1927, I, 2776.

4. G. Jakowa-Mertui and J. Poggioli, E. P. 291765; J. S. C. I. 1930, **49**, 158-B.

5. Kolloid Z. 1927, **42**, 186; abst. C. A. 1927, **21**, 3128; J. S. C. I. 1927, **46**, 715-A.

6. J. C. S. 1928, **131**, 1193; abst. C. A. 1928, **22**, 3078; J. S. C. I. 1928, **47**, 697-A.

7. D. Jones and H. Betts, J. C. S. 1928, **131**, 1177; abst. C. A. 1928, **22**, 3077; J. S. C. I. 1928, **47**, 699-A.

discs of gelatinized cellulose acetate, acaroid resin, barium sulfate, silica and lamp black[1].

As a composition for blocks for traffic markings[2], cellulose acetate has been patented used with a nonvolatile solvent as *p*-toluenesulfonanilide, phenyl or tolyl-urethane, or diethyldiphenylurea, with fillers as lithopone or mica. The mixture is kneaded or rolled, hot pressed in molds and laid in grooves formed in the road. A comprehensive series of articles appeared in 1928 on practical operating directions for desizing, washing, bleaching and dyeing of cellulose acetate[3], and the struggle for supremacy of acetate silk over filaments produced by other processes[4].

In the covering of gauze[5], a wide-meshed wire gauze is dipped into acetylcellulosee lacquer, and when dry, into aqueous alcohol as swelling agent. The operations are repeated until the required thickness is attained. Benzene or phenol may be used instead of aqueous alcohol. The finished product may be rendered weatherproof by a coating of 2-3% tricresyl phosphate. Acetic acid is obtained by passing acetylene and oxygen into glacial acetic acid containing a mercury salt and cellulose fibers, sawdust, shavings or straw, best yields being obtained when only the quantity of water required for the hydration of the acetylene is present, and this is preferably added in the form of dilute acetic acid[6]. Better yields are obtained if the cellulose is activated by heating in a current of nitrogen[7].

In the oxidation of acetylene[8], the latter and the acid absorption medium are separately maintained in circulation systems having in common a reaction chamber in which the absorption medium falls in coherent thin streams. The

1. F. Jones, U. S. P. 1558175; abst. C. A. 1926, **20**, 98.
2. *Ibid.* E. P. 270025; abst. C. A. 1928, **22**, 1455.
3. Jorre, Tiba, 1928, **6**, 279; 1929, **7**, 13. Russa, 1928, **3**, 147; 1929, **4**, 35; abst. C. A. 1929, **23**, 3811.
4. Jtg., Die Kunstseide, 1928, #3, 100.
5. Kalle & Co., A.-G., and A. Dulitz, D. R. P. 515531.
6. J. Karpati and M. Hubsch, E. P. 287135; abst. C. A. 1929, **23**, 396; J. S. C. I. 1929, **48**, 708-B.
7. *Ibid.* E. P. 294226; abst. C. A. 1929, **23**, 1910.
8. *Ibid.* E. P. 294227; abst. C. A. 1929, **23**, 1910.

water-resisting properties and sheen of acetate silk are augmented without impairment of softness and dyeing properties[1], by simultaneous or successive treatment with formaldehyde and the sodium, potassium or ammonium salts of lactic, acetic, formic, oxalic, tartaric, citric, boric, phosphoric or silicic acids.

Difficulties in dyeing acetate silk are primarily due to its impermeability to water[2], but it is far from porous and exhibits no crystalline structure. It may be regarded as a solid colloid possessing a negative electrostatic discharge, which however, does not appear to enter into the mechanism of dyeing. The purity of the dyes is very essential[3]. The rate of increase of color with time of cellulose acetate has been found[4]. A theory of dyeing cellulose acetate has been promulgated[5], in which it was determined that the partition coefficients of a number of dyes between the fiber and water and between water and ethyl acetate are of the same general order of magnitude, indicating that dyeing proceeds by a process of solution. In 1928 was published a detailed study of the dyeing of cellulose acetate silk by 15 water-insoluble anthraquinone derivatives[6]. H. Kay[7] has discussed methods and dyes used for producing three-color effects on fabrics containing acetate silk.

In recovering acetic acid from cellulose acetate solutions[8], the latter with the catalyst (H_2SO_4 usually) is treated with sodium acetate to neutralize the catalyst, and

1. H. Karplus, E. P. 234618; abst. C. A. 1926, **20**, 830.
2. V. Kartaschoff, Helv. chim. acta, 1925, **8**, 928; abst. C. A. 1926, **20**, 1719; J. S. C. I. 1926, **45**, 49-B.
3. *Ibid.* Helv. chim. acta, 1926, **9**, 152; abst. J. S. C. I. 1926, **45**, 188-B.
4. *Ibid.* Rev. gen. mat. color. 1926, **30**, 162.
5. *Ibid.* Textilber. 1926, **7**, 28; abst. C. A. 1926, **20**, 1719; Chem. Zentr. 1926, I, 2062.
6. V. Kartaschoff and G. Farine, Helv. chim. acta, 1928, **11**, 813; abst. C. A. 1929, **23**, 1272; J. S. C. I. 1928, **47**, 812-B; Chem. Zentr. 1929, II, 1272; Bull. Soc. Chim. 1929, **46**, 348.
7. Dyer & Calico Printer, 1926, **56**, 25; abst. C. A. 1926, **20**, 3282.
8. J. Kessler, U. S. P. 1546902; abst. C. A. 1925, **19**, 2878; J. S. C. I. 1925, **44**, 753-B.

the resulting mixture subjected to film evaporation on a heated surface until at least most of the acetic acid in the film has dissipated, which is condensed and removed. To produce acetic anhydride[1], ketene is passed into acetic acid to produce the anhydride without secondary products. By additional supply of ketene, a solution of ketene in the anhydride is obtained, glacial acetic acid being used.

A process for cellulose esterification has been evolved[2], whereby cellulose is treated with ketene in the presence of a neutral liquid (ether or benzene), in which the ketene is soluble, in order to effect esterification. The catalysts recommended are zinc chloride, benzenesulfonic acid or chlorosulfonic acid. C. Keyworth[3] has published tables showing the reactions and identification of 220 dyestuffs used for coloring cellulose acetate silk. The commercial possibilities of ethylene dichloride have been detailed, including the manufacture of the cellulose acetate solvent glycol diacetate[4], and catalysis in the hydration of acetic anhydride[5], in which the velocity constant for the hydration of acetic anhydride has been determined at 0° by means of a dilatometer, which is described. P. King in 1927 contributed an article on the uses of artificial silk in the textile industries[6], with special reference to cellulose acetate.

In an investigation on the tenacity and elongation of acetate silks[7] under conditions set forth in the original

1. Ketoid Co., E. P. 237573, 237575; abst. C. A. 1926, **20**, 1415; J. S. C. I. 1925, **44**, 863-B; Chem. Zentr. 1926, I, 228. Can. P. 257831; abst. C. A. 1926, **20**, 2333. Holl. P. 16356. Dan. P. 37042.
2. *Ibid.* E. P. 237591; abst. C. A. 1926, **20**, 1522; J. S. C. I. 1925, **44**, 843-B; Jour. Soc. Dyers, 1926, **42**, #2, 69. Belg. P. 327433. Holl. P. 16355. Swiss P. 61035. Ital. P. 240671, 242239. Dan. P. 36092. Norw. P. 42722. Can. P. 261560. D. Nightingale, U. S. P. 1604471; abst. C. A. 1927, **21**, 176; J. S. C. I. 1927, **46**, 59-B.
3. J. Soc. Dyers and Col. 1927, **43**, 343; abst. C. A. 1928, **22**, 320; J. S. C. I. 1927, **46**, 932-B.
4. D. Killeffer, Ind. Eng. Chem. 1927, **19**, 636; abst. C. A. 1927, **21**, 1961.
5. M. Kilpatrick, J. A. C. S. 1928, **50**, 2891; abst. C. A. 1929, **23**, 1044; J. S. C. I. 1929, **48**, 151-A.
6. P. King, J. Soc. Dyers Col. 1927, **43**, 219; abst. Chem. Zentr. 1927, II, 2525.
7. P. King and E. Johnson, J. Soc. Dyers Col. 1928, **44**, 346.

article, the tenacity was less than viscose rayon in the dry condition, but about equal to it in the wet, increase in extensibility of acetate silk in the wet state being considerable (about 30%). T. King[1] in 1927 contributed methods and formulas for dyeing acetate filaments, and L. Kirkberger[2] recipes and affixed samples for dyeing acetate silk. A series of papers appeared in 1928 on the physical constants of acetate films and fibers[3], the generalizations being that acetylcellulose obtained at 25° gave weaker films than those obtained at lower temperatures. It not always follows that acetylcellulose of higher viscosity gives the weaker film. In film manufacture the optimum pressure prevailing during evaporation of the solvent is about 70 cm. of mercury, the optimum concentration in acetone being about 12%. Cellulose naphthenates[4] were first described

1. Proc. Am. Assoc. Textile Chem. Colorists, 1927, 156; Am. Dyestuff Rept. **16**, 494; abst. C. A. 1927, **21**, 3272; Chem. Zentr. 1927, II, 2366.

2. Melliand Textilber. 1927, **8**, 261; abst. C. A. 1927, **21**, 2069.

3. G, Kita, G. Kanno, T. Uematsu and S. Masuda, J. S. C. I. Japan, 1928, **31**, 730; abst. C. A. 1929, **23**, 3082; J. S. C. I. 1929, **48**, 319-B.

4. G. Kita, T. Mazume, T. Nakashima and I. Sakurada, Cellulose Ind. Tokyo, 1926, **2**, 31; abst. C. A. 1926, **20**, 3079; J. S. C. I. 1926, **45**, 400-B; Kunstoffe, 1926, **16**, 167; Chem. Zentr. 1926, II, 2426. See Ber. 1926, 45. G. Kita, J. Sakrada, T. Mazume and T. Nakashima, Kunstoffe, 1926, **16**, 167, 199; abst. C. A. 1927, **21**, 320. Naphthenic acid fractions having acid values between 199 and 250, and prepared free from hydrocarbons by suitable treatment of petroleum fractions, were used in the forms of acid anhydrides and acid chlorides. Cellulose esters are obtained with the naphthenic acid anhydrides but the degree of esterification is low. With the acid chlorides in the presence of pyridine, esters containing up to 2.5 mols. of naphthenic acid to 1 mol. of cellulose are produced; unmodified cellulose reacts less readily than hydrocellulose. The esters resemble those produced with the higher fatty acids; those with high naphthenic acid content show definite melting points. Naphthenic esters of unmodified cellulose are substantially insoluble, although a portion is soluble in benzene; the solubility depends not only on the naphthenic acid content but also on the condition of the cellulose. The di-naphthenic ester prepared from hydrocellulose is completely soluble in benzene, chloroform, carbon tetrachloride and ether. The originally insoluble ester also becomes soluble in these media after fusion. Naphthenic esters containing up to 1 mol. of naphthenic acid to 4 mols. of cellulose are obtained by treating alkalicellulose with the acid chlorides.

in 1926. In the esterification of alkalicellulose[1], it has been found that the presence of sodium chloride results in lower yields of the ester, sodium carbonate being without influence (probably on account of immediate neutralization by the acid in the esterizing bath). In the presence of alcohol, the alkali is absorbed both physically and chemically. Cellulose benzenesulfonates and toluenesulfonates, of possible industrial importance, have been prepared[2].

The acetone-solubility of various types of cellulose esters obtained by the partial saponification of the acetone-insoluble triacetate has been reported upon[3], variation, being due not entirely to degradation in the cellulose molecule and being shown by the acetone-insoluble triacetate, is found over a wide range of acetyl content. That it is due but partially to degradation of the cellulose molecule is

1. G. Kita, T. Mazume, I. Sakurada and T. Nakashima, Cellulosechemie, 1926, **7**, 130; abst. Can. Pulp & Paper Mag. 1927, **25**, #10, 314. G. Kita, I. Sakurada and T. Nakashima, Cellulosechemie, 1927, **8**, 105.

2. G. Kita, T. Nakashima and I. Sakurada, Cellulose Industry, Tokyo, 1926, **2**, 405; abst. C. A. 1928, **22**, 1038; J. S. C. I. 1927, **46**, 163-B; Kunstoffe, 1927, **17**, 269; abst. C. A. 1928, **22**, 684. The acid content of the cellulose ester formed by the action of *p*-toluene sulfonyl chloride on alkalicellulose is uninfluenced by the temperature of the reaction between 8° and 30°, but at 30-80° the product contains a lower proportion of acid. Addition of excess of acid chloride has no effect on the composition of the ester, but reduces the time necessary for reaction. The esterification proceeds further in the presence of an excess of alkali, but, with given concentrations of alkali and toluenesulfonyl chloride, a definite maximum esterification is reached. In this behaviour, and in the fact that there is no sudden liberation of heat, the reaction differs from those between alkalicellulose and carboxylic acid chlorides. Alkalicellulose prepared by the action of a 15-35% (by vol.) alkali solution yields with toluenesulfonyl chloride an ester containing 1 mol. of acid to 2 mols. of cellulose. If an excess of alkali is added before esterification, the product consists principally of the monoester, and if the esterification is repeated 5 times the acid content of the product corresponds with that of a mixture of the mono- and the di-esters. An ester with a higher acid content is difficult to obtain even by esterification in presence of pyridine, under which conditions carboxylic acid chlorides give di- and tri-esters. An ester with a higher acid content than is required for the monoester is more stable towards heat than one of lower acid content. Similar results to the above were also obtained with benzenesulfonyl chloride.

3. *Ibid.* Cellulosechemie, 1928, **9**, 13; abst. C. A. 1928, **22**, 2271; J. S. C. I. 1928, **47**, 230-A. Cellulose Ind., Toyko, 1926, **2**, 30; abst. C. A. 1927, **21**, 3457; J. S. C. I. 1926, **45**, 944-B.

shown by the acetone insolubility of re-acetylated acetates of all types, and from this the conclusion is drawn that the acetone-insolubility of cellulose acetate is properly ascribable to physical conditions, probably correlated with differences in the distribution of groups in the molecule.

It has been determined that without continuous stirring[1], saponification of acetylcellulose with aqueous NaOH is a mono-molecular reaction until 50% has been saponified; with continuous stirring the reaction is mono-molecular until 90% complete; while with alcoholic aqueous KOH of somewhat high concentration with stirring, the reaction is bi-molecular, differences being ascribed to diffusion of the medium into acetylcellulose and of sodium acetate produced by saponification into the medium. It has been found that acetate filaments like natural silk may be dyed with Tartrazine by immersion in a warm liquor containing the components from which this dyestuff is usually prepared[2]. For example, acetate silk may be dyed to a full yellow shade by immersion for 20 minutes in a liquor at 50° containing 0.75% sodium dihydroxytartrate and 1.3% phenylhydrazine together with a mineral acid; an orange shade is produced similarly by use of *p*-nitrophenylhydrazine, and a terracotta shade by immersion in a bath containing acetic acid, *m*-tolylenediamine and "nitrosamine."

In the conversion of carbohydrates into esters[3], cellulose is mixed with HCl in one container, then transferred to another container and treated with gaseous HCl, then heated, access of air being avoided. R. Kölliker[4] has described the fire-retarding effect of Cellon, and detailed the history and patents in connection with the development of the cellulose acetate industry[5], together with recipes for

1. G. Kita, T. Nakashima and I. Sakurada, Cellulose Ind. Tokyo, 1927, **3**, 9-A, 61; abst. C. A. 1928, **22**, 1038; Chem. Zentr. 1927, II, 193; J. S. C. I. 1927, **46**, 526-A.
2. E. Knecht, J. Soc. Dyers Col. 1925, **47**, 97; abst. C. A. 1925, **19**, 1780; J. S. C. I. 1925, **44**, 313-B.
3. R. Kocher, U. S. P. 1670727; abst. J. S. C. I. 1928, **47**, 520-B.
4. R. Koelliker, Papierfabr. 1925, **23**, 162; abst. C. A. 1925, **19**, 3017.
5. Kunstseide, 1928, **10**, 409.

its proper dyeing[1]. A process has been delineated for bleaching of cellulose acetate during the esterification stage, comprising introducing hypochlorites or peroxides in the esterizing bath and continuing the process[2]. Viscosity of 9.22%, 9.95% and 10.58% solutions of acetic acid have been determined at temperatures of 11.78-30.50°, from which values the apparent molecular heat of aqueous solutions of acetic acid has been calculated to be 41, indicating the acid is not hydrated in solution[3]. P. Krais[4] has published stability tests for cellulose acetate fibers.

The E. Krause acetaldehyde process of manufacture[5] comprises passing ethyl alcohol and air over silver gauze. Krüger has described the various methods of manufacture of cellulose acetonitrate[6] with the object of combining the desirable plastic properties of the nitrate and the slow-burning properties of the acetate, and A. Kunze[7] has contributed data on the desizing, degreasing and bleaching of acetate filaments, with practical operating hints on the dyeing of union fabrics containing acetylcellulose threads[8].

In tinting cellulose acetate[9], the dye (benzeneazophenylmethylpyrazolone, hexahydroxyanthraquinone, Algol Brilliant Violet 2B) is dissolved (using trichlorethylene, tetra- or penta-chlorethane, chlorbenzene, chlortoluene, turpentine, tetralin, decalin), with addition of soap, and poured into boiling soap solution. The mixture, after sieving, constitutes the dye-bath. In the production of hollow filaments[10], cellulose acetate dissolved in acetone and al-

1. R. Koellicker, Die Kunstseide, 1927, **9**, 415; abst. C. A. 1928, **22**, 2469; Chem. Zentr. 1927, II, 2366. Die Kunstseide, 1928, **10**, 244.
2. Koln-Rottweil, Akt-Ges., Belg. P. 329332.
3. N. de Kolosovskii, J. Chim. Phys. 1925, **22**, 321; abst. C. A. 1926, **20**, 2610.
4. Monatschr. Textil-Ind. 1928, **43**, 257; abst. C. A. 1928, **22**, 4828.
5. U. S. P. 1581641. See E. P. 178842.
6. Phot. Ind. 1928, **26**, 690.
7. Russa, 1928, **3**, 745; abst. C. A. 1928, **22**, 3987.
8. Russa, 1928, **3**, 1149; abst. C. A. 1929, **23**, 987.
9. G. Lacroix, F. P. 603123; abst. J. S. C. I. 1927, **46**, 964-B.
10. J. Lahousse and Societe pour la Fabrication de la soie Rhodiaseta, U. S. P. 1652206; abst. C. A. 1928, **22**, 868; J. S. C. I. 1928, **47**, 85-B. E. P. 267187; abst. J. S. C. I. 1927, **46**, 361-B.

cohol is spun into a cell containing air at a temperature substantially higher than the boiling point of the solvent used, a comparatively high rate of flow of this air being maintained in order to produce an active superficial evaporation from the filaments as they emerge from the nozzle.

A flexible enameled fabric having a smooth and glossy surface has been described[1] suitable for the body-work of motor vehicles, comprising a base of acetylcellulose, a coating of 400-800 gms. per square meter being necessary. A plurality of coats is required for automobile upholstery. Complete degumming of natural silk yarn in the presence of cellulose acetate[2] may be obtained with proteolytic enzymes (pepsin and trypsin) in presence of 1% sodium sulfate or sodium ammonium phosphate at 35-40° as with the ordinary alkali soap boiling. A protective composition has been patented[3] comprising cellulose acetate and acid butyl tartrate used together for marking on a paper base, which are releasable by the action of heat and may be used as transfers for protecting markings.

A process for the continuous rectification of acetic acid has been evolved[4], in which the purification is carried out in such a way as to have crystallizable acid at the base of the rectifier, while the minute particles of water at the top are rectified again for recuperating the acid lost, and sending it to the rectifier. *n*-Butyl alcohol may be deydrogenated into *n*-butyraldehyde and *n*-butyl butyrate[5] by passing the alcohol in the vapor phase over copper as catalyst at 260-320°, and separating by fractionation.

Acetylcellulose is colorable by dinitro-derivatives of aromatic amines in which both nitro-groups are in the *o*-position to the amino group, as 3.5-dinitro-*p*-toluidine and

1. G. Langverte et Cie, E. P. 298982; abst. C. A. 1929, **23**, 3111.
2. G. Lardy, Russa, 1928, **3**, 737; Tiba, 1928, **6**, 757; abst. C. A. 1928, **22**, 3993.
3. W. Lawrence, U. S. P. 1596545; abst. C. A. 1926, **20**, 3349; Plastics, 1927, **3**, #5, 218.
4. G. Legendre, Can. P. 258628; abst. C. A. 1926, **20**, 3459.
5. D. Legg and C. Bogin, U. S. P. 1580143. See U. S. P. 1401117.

2.6-dinitro-*p*-chloraniline[1]. Animal and vegetable fibers and cellulose acetate may be simultaneously colored with vat dyes in a hydrosulfite vat if an alkali salt of a higher fatty acid be used (sodium stearate, potassium palmitate) together with sodium carbonate or ammonia[2]. Indigo derivatives as Bromindigo FB, Ciba Bordeaux B or Ciba Scarlet G, Algol Black RO and Leucole Yellow G are examples of appropriate dyestuffs which may be employed for this purpose.

The G. Leonard stencil sheet for duplicating purposes (see p. 57, n. 2; 164, n. 1; 224, n. 1)[3] comprises cellulose acetate 8, dissolved in acetanilid 16, glycerol 8, diethyl phthalate 30, denatured ethyl alcohol 40, and acetone or methyl acetone 100. A mannose pentacetate (pentacetylmannose), m. pt. 64°, has been described[4]. Cellulose may be esterified with the usual mixture of acetic anhydride and acetic acid without the use of sulfuric acid as catalyst, by the employment of chromium salts (sulfate, nitrate, acetate, butyrate, benzenesulfonate, naphthalenesulfonate) or chromium oxide[5], or by the use of the sulfate of chromium, vanadium, nickel or cobalt[6]. In order to produce a more

1. J. Leitch & Co., Ltd., and A. Everest, E. P. 261822; abst. C. A. 1927, **21**, 3752; J. S. C. I. 1927, **46**, 105-B; Rayon, 1927, **5**, #11, 24. See also F. Weber, D. R. P. 446220. K. Meyer and H. Hopff, D. R. P. 446539; abst. Rayon, 1927, **5**, #11, 24.

2. J. Leitch & Co., Ltd., A. Everest and J. Wallwork, E. P. 274550; abst. Rayon, 1927, **5**, #11, 24.

3. U. S. P. 1607090; abst. C. A. 1927, **21**, 308; Pulp & Paper Mag. 1927, **25**, #38, 1197.

4. P. Levene and I. Bencowitz, J. Biol. Chem. 1927, **172**, 627; abst. J. S. C. I. 1927, **46**, 649-A. C. Hudson and J. Dale, J. A. C. S. 1915, **37**, 1280.

5. L. Levy, O. Silberrad and Apex (British) Artificial Silk, Ltd., U. S. P. 1652024; abst. C. A. 1928, **22**, 868; J. S. C. I. 1928, **47**, 155-B. E. P. 265267; abst. C. A. 1928, **22**, 317; J. S. C. I. 1927, **46**, 296-B; Plastics, 1928, **4**, 446. India P. 12668. E. P. 251680. Can. P. 279966.

6. L. Levy, U. S. P. 1655870; abst. C. A. 1928, **22**, 1040. E. P. 240624; abst. C. A. 1926, **20**, 2248; J. S. C. I. 1926, **45**, 10-B; J. Soc. Dyers Col. 1926, **42**, 99. F. P. 603712; abst. Caout. et Guttap. 1927, **24**, 13425. Belg. P. 329337. Can. P. 259328; abst. C. A. 1926, **20**, 2584. India P. 11753. Ital. P. 242937. Norw. P. 43407. Swiss P. 120810. Holl. P. 17997.

uniform color, the dye may be dissolved in a cellulose acetate solution which is then subjected to dry spinning[1].

In improvements relating to thermionic valves or electron discharge tubes[2], the complete base consists of a member of insulating composition consisting of a tubular part intended to receive the neck of the bulb and a lower part in which the valve pins are molded and have apertures through which the leading-in conductors pass to be connected to the pins by soldering. As a suitable solder is claimed cellulose acetate containing *p*-toluenesulfonanilid as plasticizer. A fluorescent screen has been described[3] comprising a thin sheet of acetylcellulose with which fluorescent material is incorporated, with an adhering backing sheet of celluloid. Metaldehyde which burns practically free from soot and ash[4] is manufactured by treating acetic acid with ammonium salts or other inorganic ammonium derivatives as catalysts. In the concentration of acetic acid[5], the dilute solution is treated with anhydrous aluminum ammonium sulfate (ammonia alum), ethyl alcohol, and an esterification catalyst, and the mixture heated to 90° to give ethyl acetate and the hydrated salt.

As a fire-resisting coating[6], airplane wings or other fabric are first impregnated with ammonium phosphate and then coated with acetylcellulose composition containing another inflammability-reducing agent as tricresyl phosphate. Aluminum fluoride[7], ammonium aluminum fluoride, calcium sulfate or tartrate may be added[8]. In the grease-

1. L. Levy, E. P. 227146; abst. C. A. 1925, **19**, 2751; J. S. C. I. 1925, **44**, 264-B.
2. *Ibid.* E. P. 234576.
3. L. Levy and J. Mason, E. P. 232696; abst. C. A. 1926, **20**, 154.
4. T. Lichtenhahn, E. Luscher and H. Steiger, Can. P. 257424.
5. F. Lichtenthaeler, U. S. P. 1660756; abst. C. A. 1928, **22**, 1365; J. S. C. I. 1928, **47**, 360-B. See also U. S. P. 1492717; abst. J. S. C. I. 1924, **43**, 671-B.
6. W. Lindsay, U. S. P. 1523813, 1523814; abst. C. A. 1925, **19**, 900.
7. U. S. P. 1534651. Can. P. 260844; abst. C. A. 1926, **20**, 2584.
8. L'Oyonnazienne, Belg. P. 325277, 325278, 325279, 325280. For cellulose acetate rayon see M. Luft, Kunstseide, 1927, **9**, 387; abst. C. A. 1928, **22**, 2269; Rayon, 1927, **5**, #6, 24; Chem. Zentr. 1927, II, 2366.

proofing of boots and shoes with cellulose acetate[1], the uppers or other parts of boots and shoes are coated with an acetylcellulose solution which is removed by a solvent as acetone when the article is completely fabricated.

In electric condenser manufacture, condensers having a dielectric in the form of a film or sheet of acetylcellulose are first made without the aid of plasticizers, thereby removing a source of dielectric loss introduced as foreign matter by the plasticizer[2]. The ester is dissolved in acetone and a film produced in the usual manner. The H. Mallabar process of acylation produces a cellulose acetate soluble in acetone, free from sulfuric acid residues, and which does not char when heated[3], prepared by acetylating cellulose in the absence of sulfuric acid, but after pretreatment with a mixture of sulfuric and acetic acids, the sulfuric acid is neutralized before acetylation proper commences. Zinc chloride is the catalyst used during acetation.

Composite sheets of glass and cellulose acetate are prepared by first coating the surfaces with a thin layer of gelatin, which when dry is softened and the sheets then united by pressure. A blue dye must be used to neutralize the yellow tint of the cellulose acetate[4]. "Violet methyl extra B"[5] is recommended for this purpose[6]. In the acylation of cellulose by the C. Malm process[7], perchlorates (aluminum, copper, methylamine, manganese, magnesium, calcium, barium, quinoline, lead, pyridine) are used as cat-

1. D. Macdonald, E. P. 259930; abst. C. A. 1927, **21**, 1029.
2. D. Macdonald and Dubilier Condenser Co., E. P. 259131; abst. C. A. 1927, **21**, 3165.
3. H. Mallabar, U. S. P. 1652573; abst. C. A. 1928, **22**, 868; J. S. C. I. 1928, **47**, 85-B. E. P. 258020; abst. C. A. 1927, **21**, 3128; J. S. C. I. 1926, **45**, 975-B. Can. P. 274567. Ital. P. 240432, 265012. E. P. 293724; abst. C. A. 1929, **23**, 1750; J. S. C. I. 1928, **47**, 706-B.
4. H. Mallabar and Non-Inflammable Film Co., Ltd., E. P. 288782; abst. C. A. 1929, **23**, 679; Plastics, 1929, 636. F. P. 645111; abst. C. A. 1929, **23**, 2006.
5. H. Mallabar, F. P. 645110; abst. Chem. Zentr. 1929, I, 592.
6. H. Mallabar, Discovery, 1927, **8**, 91.
7. U. S. P. 1645915; abst. C. A. 1928, **22**, 164; J. S. C. I. 1928, **47**, 121-B; Plastics, 1928, 24.

alyzers. A cellulose acetate composition has been described[1] the novelty of which lies in the use of castor oil combined with material that prevents the oil from making the film cloudy, and is made by combining acetylcellulose with castor oil and a transparency-inducing substance which also diminishes the combustibility (tetrachlorethane, methyl salicylate, tricresyl phosphate).

In a study of the influence of plasticization on the mechanical-elastic properties of artificial and natural plastic substances[2], investigation of cellulose acetate, Cellon, Rhodoid, shows that the elastic properties of plastic substances are, apart from factors such as temperature and the nature of the initial material, functions of the work of plasticizing, e.g. the total mechanical and chemical work required to bring about the changes of disaggregation and re-aggregation leading to the formation of a moldable mass. With diminishing work of plasticization, the elasticity modulus rises. A description of the dyeing[3], bleaching and finishing of the variety of acetate silk produced by the Lustron Co. was given in 1925.

An antistatic photographic film has been evolved[4] comprising a film support one face of which is coated with sensitive emulsion, and the other with cellulose acetonitrate. The A. Marlier shoe polish[5] is composed of cellulose acetate, acetone, amyl acetate, methyl alcohol, shellac and celluloid with coloring matter. In the piece-dyeing of wool, viscose and cellulose acetate mixed fabrics[6], on account of the staining of wool by SRA dyes, it is difficult

1. 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, 287.
2. O. Manfred and J. Obrist, Kolloid Zts. 1927, **43**, 41; abst. J. S. C. I. 1927, **46**, 838-B; Rev. gen. mat. Plas. 1928, **4**, 335. See also Kolloid Zts. 1927, **41**, 348; **42**, 174; abst. J. S. C. I. 1927, **46**, 514-A; 563-B.
3. A. March, Am. Dyestuff Rept. 1925, **14**, 37; abst. C. A. 1925, **19**, 1057.
4. J. Marette, U. S. P. 1635681.
5. A. Marlier, Belg. P. 347831; abst. C. A. 1929, **23**, 2002.
6. K. Marsden, Tex. Recorder, 1927, **45**, #537, 61, 56; abst. C. A. 1928, **22**, 1855.

to dye wool-acetylcellulose mixtures so that they will not rub. Best results are said to be obtained by dyeing all three fibers in one bath with Union Dark-blue R (Sandoz) and Imacol Blue R and Black CG with only sodium sulfate. This may be shaded with Xylene Fast Violet 4 RN, Chloramine Fast Violet R, Erica B and SRA Red V for navy blue.

If 1.5% phosphoric acid be added slowly to boiling ethylidene diacetate[1], decomposition to acetic anhydride and acetaldehyde ensues, the reaction proceeding smoothly with but little formation of acetic acid. Ethylidene diacetate 1000 treated in this manner yields acetaldehyde 238, acetic anhydride 555, acetic acid 71 and unchanged ethylidene diacetate 126. Natural cellulose yarns in mixed fabrics containing cellulose acetate[3] may be mercerized by treatment at not above 15° with NaOH solution of sp. gr. 1.24-1.30, and these fabrics subsequently squeezed, washed and stretched. The cellulose acetate yarn exhibits little or no contraction or loss of luster, and very little diminution in weight as the result of the treatment, while its dyeing properties are not materially affected. R. Martin[3] in 1928 contributed a review on the finishing of modern aircraft with acetyl- and nitro-cellulose dopes and finishes, and C. Marx[4] detailed progress in the cellulose ester art in connection with plastics manufacture and molding possibilities of acetylcellulose[5].

Compound transparent sheets are formed by joining glass sheets by the intermediary of an acetylcellulose plastic film[6], by virtue of the interposition between the three sheets of an adhesive containing caoutchouc with or with-

1. M. Marshall and G. Shaw, U. S. P. 1578454; abst. C. A. 1926, **20**, 1630; J. S. C. I. 1926, **45**, 513-B.
2. M. Marshall, E. P. 210484; abst. J. S. C. I. 1924, **43**, 290-B.
3. Chem. Met. Eng. 1928, **35**, 404; abst. C. A. 1928, **22**, 3306.
4. C. Marx, Plastics, 1928, **4**, 129. See U. S. P. 1516225, 1641411, 1641412, 1641413, 1652024, 1652573, 1655677, 1655870, 1658368, 1658725.
5. C. Marx, Plastics, 1928, **4**, 156.
6. M. Mattingley and A. Rea, E. P. 298423; abst. C. A. 1929, **23**, 2797.

out mastic or dammar, gradually increasing heat and pressure until a unitary-appearing layer results. The acetate sheet is 0.1-0.4 inch thick. The paper product of J. McIntosh[1] involves adding cellulose acetate or nitrate to paper pulp in the beater, then sheeting on a Fourdrinier machine, the paper being processed in the usual manner, parchmentized and then subjected to heat and pressure to cause increased permeation of the cellulose ester in the mass. It is claimed this material is useful for making gears, pulleys, electrical insulators, switchboards, veneer and radio panels, the paper being thermoplastic. T. Meisenheimer has pointed out the necessity for cleanliness in the cross-dyeing of cotton, wool, silk with cellulose acetate[2], the presence of traces of oil and grease on the fibers accompanying acetate silk causing a staining of the animal fibers due to the mordanting action of the oils for the acetate silk dyestuffs.

It is claimed the reaction of acetic anhydride with water is accelerated by concentrated acids (nitric, hydrochloric or sulfuric acids) for all solutions. To obtain anhydrous salts as sulfates or chlorides, the crystallized salt is mixed with acetic acid, the reaction taking place with heat evolution[3]. In the production of formic acid[4], methyl butyrate is used as the aqueous layer to retain the esters in solution, and is then passed to a small column, the vapor of which is passed to the cooler and thereby concentrated.

In the acetolysis of cellulose with a mixture of acetyl bromide and hydrogen bromide[5], it has been found that cellulose acetate on standing in the cold with the acetyl

1. U. S. P. 1631750; abst. C. A. 1927, **21**, 2559; Plastics, 1927, **3**, 529.
2. Textile World, 1928, **73**, 2007, 2015; Amer. Dyestuffs Rep. 1928, **17**, 300; abst. C. A. 1928, **22**, 1855, 2467; 1929, **23**, 519; Rayon, 1928, **6**, #12, 16; Chem. Zentr. 1928, II, 494.
3. J. Menke, Chem. Weekblad, 1926, **23**, 552; abst. C. A. 1927, **21**, 848; J. C. S. 1927, **132**, 27.
4. K. Meyer and J. Mueller, U. S. P. 1522257; abst. J. S. C. I. 1925, **44**, 338-B. E. P. 217467; abst. J. S. C. I. 1924, **43**, 731.
5. F. Micheel, Ann. Chem. 1927, **456**, 69; abst. C. A. 1927, **21**, 4061.

bromide saturated with hydrogen bromide, yields a small proportion of crystalline acetobromocellobiose, the non-crystalline portion appearing to contain acetobromoglucose. In the acetylation of carbohydrates[1], especially in the production of cellulose acetate, ketene is brought into contact with the carbohydrate suspended in glacial acetic acid containing sulfuric acid (1.5%) to form the chloroform soluble cellulose acetate (see p. 441, n. 2).

According to G. Miles and C. Dreyfus[2], clear and transparent solutions are obtained by treating cotton linters with sulfuric acid (75 to 100%) at a temperature between freezing point and 22°, aliphatic acids or alcohols being added to the sulfuric acid, the solutions thus formed being used for the manufacture of artificial silks or producing cellulose esters or ethers. Nitrocellulose may be prepared in a similar manner[3], preferably by the use of both ortho- and meta-phosphoric acid.

In 1928 appeared a statement by G. Miles and E. Worden in respect to the Dreyfus patents with the opinion that in their entirety at that time they substantially controlled the production of cellulose acetate most suitable for the manufacture of artificial filaments[4]. W. Milne[5] in 1926 gave a resume with directions for the printing and discharging of colors on Celanese.

In the production of multi-ply material containing cellulose esters[6], plasticized cellulose acetate is superficially treated with a pigment, subjected to pressure and heat and then formed into sheets by cutting. Foil such as tinfoil may be interposed between the sheets thus formed, and the superposed sheets of foil and cellulose ester composition

1. E. Middleton, U. S. P. 1685220; abst. C. A. 1928, **22**, 4536; J. S. C. I. 1929, **48**, 242-B.
2. G. Miles and C. Dreyfus, E. P. 263810; abst. C. A. 1928, **22**, 164.
3. E. P. 269529, 269530; abst. C. A. 1928, **22**, 1473; Plastics, 1928, 446.
4. Rayon, 1928, **6**, #2, 23, 26.
5. Proc. Amer. Assoc. Textile Chem. Col. 1926, 288; Amer. Dyestuff Rept. **15**, 886; abst. C. A. 1927, **21**, 652.
6. K. Monroe, U. S. P. 1657172; abst. C. A. 1928, **22**, 1041.

transformed into a homogeneous block by heat and pressure to produce a material suitable for the manufacture of such articles as buttons and toilet requisites. It has been found[1] that non-hydroxylated nitrodiazo compounds (e.g., those prepared from *m*-nitroaniline, 2.4-dinitroaniline or 2.6-dichloro-4-nitroaniline) are combined with ethylbenzylanilinesulfonic acid and 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. The dyes formed are orange to violet blue and greenish black powders which yield on acetylcellulose when dyed in a dilute acid or neutral bath, yellow to bluish-red and brown tints of good fastness to washing and not fugitive to light. In the coating and polishing of wood, metals or other surfaces[2], a coating of cellulose acetate is applied and then rubbed down after it is dry, with a "mild" solvent of cellulose acetate, a fine grit and a liquid lubricant such as a mixture of paraffin oil or Vienna chalk and turpentine. In the acetylation of cellulose by the G. Morden process[3], cellulose is treated with sulfuryl chloride, glacial acetic acid and acetic anhydride, hydrolyzed, the acetylation being subsequently completed in a second stage by treatment with acetic anhydride and sulfuric acid. The cellulose acetate formed is hydrolyzed to the point of solubility in pure acetone. In the impregnation of fabric for use in the stiffening of shoes[4] (see p. 525, n. 4), cellulose acetate is admixed with copal, benzene, alcohol, triphenyl phosphate, abietic acid or zinc oxide and compounded by a combination of heat and pressure. In the preparation of artificial filaments from acetyl cellulose[5], a solution of the ester, tet-

1. G. de Montmollin and G. Bonhote, U. S. P. 1534506; abst. C. A. 1926, **20**, 508.

2. M. Moore, E. P. 249726; abst. C. A. 1927, **21**, 1021.

3. E. P. 294415; abst. C. A. 1929, **23**, 2033; J. S. C. I. 1928, **47**, 810-B. Belg. P. 355452. Ital. P. 273313. See E. P. 24382, 24980, 1910; 29882, 1913; 21016, 1914; 145525, 203599, 258020.

4. M. Morle, E. P. 275575; abst. C. A. 1928, **22**, 2272. Swiss P. 127231; abst. C. A. 1929, **23**, 1231.

5. H. Mork and C. Coffin, U. S. P. 1551112; abst. C. A. 1926, **20**, 115; J. S. C. I. 1925, **44**, 915-B; Caout. et Gutta. 1926, **23**, 13315.

rachlorethane, alcohol and kerosene is coagulated in a bath which also contains an aliphatic hydrocarbon such as kerosene 90%, together with tetrachlorethane 10%. The esters may be stabilized[1] by the addition thereto of about 2% of sodium or potassium acetate, oleate, salicylate or benzoate. L. Mostny[2] has proposed to produce artificial sponges (see p. 425, n. 5) by mixing a solution of cellulose esters as acetylcellulose using a pore-forming material, treating the mixture with steam and separating the water-soluble components.

A series of papers were published in 1925 giving a list of precautions and recipes for the dyeing of acetate silk[3], and a description of the "soluble vat" dyestuffs for the coloring of acetylcellulose silk[4], with formulas and methods used in dyeing both acetate silk and union materials containing the same, including[5] a discussion of the constitution, physics, chemistry, textile and general dyeing properties, manufacture and identification of cellulose acetate artificial filaments, including the theory, application and properties of the dispersol dyes in general, and the S. R. A. dyes in particular, as affecting the coloring of acetyl cellulose silk[6]. Descriptions have also been given for the cross dyeing of Celanese at the temperature approaching boiling water, either alone or in conjunction with other fibers[7], and the staining properties of the direct

1. H. Mork, U. S. P. 1607474; abst. C. A. 1927, **21**, 1322; Plastics, 1927, **3**, 279; J. S. C. I. 1927, **46**, 71-B.

2. U. S. P. 1611056. E. P. 245049; abst. Oil, Paint, Drug Rep. 1926, **109**, #12, 68; J. S. C. I. 1926, **45**, 122-B. Can. P. 270288.

3. C. Mullin, Amer. Dyestuff Rept. 1925, **14**, 173, 214, 237, 243, 279, 315, 345, 350, 379, 410, 420, 462, 482, 510, 517, 554, 577, 588, 622, 653, 694, 747, 765, 787, 849, 893; 1926, **15**, 1, 38, 43, 69, 81, 139, 153, 181, 191, 223, 285; abst. C. A. 1925, **19**, 2748; 1926, **20**, 113, 506, 1718, 2076.

4. C. Mullin, Amer. Dyestuff Rept. 1927, **16**, 575; abst. C. A. 1927, **21**, 3748.

5. C. Mullin, Can. Col. & Tex. Proc. 1925, **5**, 260, 298, 324; 1926, **6**, 4, 12, 36, 68, 81, 132, 198, 200, 213, 228, 262, 268, 276; abst. C. A. 1926, **20**, 506, 1325, 2076, 2585, 2908, 3087, 3817.

6. C. Mullin, Can. Col. & Tex. Proc. 1926, **6**, 329, 339, 365; 1927, **7**, 6, 14; abst. C. A. 1927, **21**, 177, 1014, 1358.

7. C. Mullin, Can. Col. & Tex. Proc. 1927, **7**, 78, 94; abst. C. A. 1927, **21**, 2801.

cotton dyes when applied to acetate silk[1], including methods of dyeing of acetate silk and wool combinations, showing the staining properties of the wool dyestuffs[2], and the general difficulties encountered in the dyeing of various brands of acetate silk[3]. Types of apparatus and machines are described and illustrated, together with formula used in applying the vat dyes to combinations of cotton and acetate silk, both for white and two-color effects in unions[4]. In 1927 appeared a comprehensive resume by C. Mullin[5] on the physical and chemical properties of acetate silk[6] and methods for the manufacture of the same[7], including their general properties.

A fabric suitable for the production of towels, tablecloths and handkerchiefs is produced by passing a number of layers of cellulose, cotton or wadding or of soft strong paper through goffering rollers and then impregnating with a solution of acetylcellulose, with or without the addition of such hardening agents as formaldehyde, or softening agents as glycerol[8].

Cellulose may be formylated by treatment at zero or under, for 48 hours with 96% formic acid containing 4% hydrochloric acid[9]. The viscous solution it is claimed can

1. C. Mullin, Can. Col. & Tex. Proc. 1927, **7**, 80, 94; abst. C. A. 1927, **21**, 2800.
2. C. Mullin, Can. Col. & Tex. Proc. 1927, **7**, 114; abst. C. A. 1927, **21**, 3131.
3. C. Mullin, Can. Col. & Tex. Proc. 1927, **7**, 154; abst. C. A. 1927, **21**, 3131. Can. Col. & Tex. Proc. 1927, **7**, 156; abst. C. A. 1927, **21**, 3272.
4. C. Mullin, Can. Col. & Tex. Proc. 1927, **7**, 190; abst. C. A. 1927, **21**, 4072.
5. Silk J. 1926, **3**, #29, 64; #32, 58; 1927, **4**, #38, 40; #39, 51; abst. C. A. 1928, **22**, 873.
6. C. Mullin, Silk J. 1928, **4**, #46, 49; #58, 50; #50, 51; abst. C. A. 1929, **23**, 1265.
7. C. Mullin, Silk J. July 1927, 49; Dec. 1928, 59. Text. Col. 1926, **48**, 459, 739, 813; 1927, **49**, 21, 101, 173, 178, 305, 377, 454, 460, 466; 1928, **50**, 17; abst. C. A. 1926, **20**, 3818; 1927, **21**, 648, 2191, 3272; 1928, **22**, 872, 1044, 1240; 1929, **23**, 1272. Text. J. Australia, 1927, **2**, 268, 324, 380; abst. C. A. 1928, **22**, 872.
8. E. Munktell, E. P. 252719; abst. C. A. 1927, **21**, 2388.
9. N. V. Fabriek van Chem. Producten, Holl. P. 16073; abst. C. A. 1927, **21**, 1883. Ital. P. 270612. Cites D. R. P. 189836, 189837. F. P. 424621.

be spun directly, after neutralization of the hydrochloric acid by means of sodium formate in a formate bath. The product is equivalent in properties to the acetate, having a fracture length dry of 15 km., and wet of 5 km., the formic acid content being 41%. The preferred method of spinning formylcellulose combines extruding downwardly into a slowly ascending medium, the temperature of which gradually increases in an upward direction[1]. Diminished luster may be imparted to acetylcellulose silk by the introducing of water vapor as such, into the spinning cell[2]. Alternatively, the silk may be spun in the usual manner, and before the threads have been wholly deprived of solvent, are passed into a second cell to which water vapor is supplied. The degree to which the silk is delustered is dependent on the amount and temperature of water vapor introduced. The hydrolysis of cellulose triacetate is said to be best effected by the use of sulfuric acid at 20°, the hydrolysis being prolonged to a point of desired solubility[3]. Acetate filaments may be sized by the dry spinning method while avoiding an after treatment of the same[4] by adding to the spinning solution a small portion of fats or oils, particularly those which have a melting point range of 20-40°, suitable oils and fats are olive, olein, cocoanut oil, butter fat, beef suet, lard, bone oil or peanut oil. An X-ray study of cellulose acetate or cellulose nitrate was published in 1928 by the phase shift through various stages of cellulose esterification. The fundamental units for cellulose acetate were found to be 13.3 ± 0.4 Å.U

1. N. V. Nederlandsche Kunstzijdefabriek, A.-G., E .P. 282326; abst. Rayon, 1928, **6**, #11, 26.

2. *Ibid.* E. P. 291067; abst. C. A. 1929, **23**, 1505; J. S. C. I. 1929, **48**, 126-B; Silk J. 1928, **5**, #51, 76. Belg. P. 354883.

3. *Ibid.* E. P. 292398; abst. C. A, 1929, **23**, 1504; J. S. C. I. 1928, **47**, 637-B; Silk J. 1928, **5**, #52, 80. F. P. 642909; abst. C. A. 1929, **23**, 1504. Belg. P. 354884. Swiss P. 126588; abst. C. A. 1929, **23**, 703. S. Vles, U. S. P. 1782796; abst. C. A. 1931, **25**, 414; J. S. C. I. 1931, **50**, 154-B; Cellulose, 1930, **1**, #11, 294; Plastics, 1931, **7**, #3, 175. Refer to E. P. 19330, 1905; 20977, 1911; 20852, 1912; 207562.

4. *Ibid.* E. P. 301017; abst. C. A. 1929, **23**, 4072; J. S. C. I. 1930, **49**, 370-B; Silk J. 1929, **5**, #58, 76. Holl. P. 22568. Cites E. P. 20979, 1911. U. S. P. 1551112.

in diameter[1]. The diagrams infer this degree of esterification, since a well defined lattice is only obtained with a completed substituted product.

In the thermal and catalytic decomposition of 99.9% pure, almost anhydrous formic acid, it is passed through tubes of silica, pyrex, porcelain, or copper at 350° to 550°, carbon dioxide and hydrogen being chiefly found with varying amounts of water, formaldehyde and carbon monoxide[2]. At 450° decomposition is 90% or more. Pyrex is least, and copper most active. W. von Neuenstein[3] has found that cellulose nitrate and acetate solutions become less viscous with age, but subsequent mechanical treatment augments the viscosity. The diminution is assumed to be primarily due to the arrangement of the rod-like micelles to form secondary particles which in turn are broken up by mechanical treatment into an irregular structure of higher viscosity. He has reported upon the colloid-chemical relationship of solutions of various esters[4], finding that Ostwald's "peptization rule" applies also to the dispersion of cellulose acetate in chloroform and in ethyl acetate. Small-scale laboratory tests on the production of pulverulent cellulose, chlorinated cellulose and cellulose acetate[5] were made in 1926.

1. St. v. Náray-Szabó and G. Susich, Z. physik. Chem. 1928, **134**, 264; abst. C. A. 1928, **22**, 3043; J. S. C. I. 1928, **47**, 818-A.

2. W. Nelson and C. Engelder, J. Phys. Chem. 1926, **30**, 470; abst. C. A. 1926, **20**, 2445.

3. Kolloid-Zeit. 1926, **39**, 88; abst. J. S. C. I. 1926, **45**, 677-A.

4. Kolloid-Zeit. 1927, **41**, 183; abst. C. A. 1928, **22**, 1472; Plastics, 1928, **4**, 323; J. S. C. I. 1927, **46**, 327-B. Refers to W. Ostwald, Kolloid-Zeit. 1927, **41**, 163; abst. C. A. 1928, **22**, 897.

5. C. de Neyman, Chim. et Ind. 1926, **15**, 349; abst. C. A. 1926, **20**, 2070; Pulp & Paper Mag. 1926, **24**, 1042. Powdered cellulose can be obtained by the action of sulfuric acid in aqueous solution, the time of reaction and strength of acid required increasing with decrease in temperature. A minimum of 500 parts of liquid to 100 of cellulose is required, and the quantity of acid solution used above this minimum is without effect. Optimum results are obtained with 5 to 7 degrees Bé. acid at 100° for about 2-2½ hours. The time can be reduced by 20-30% (according to the temperature of the reaction and the intensity of beating) by proper mechanical action, and the cellulose can be thus reduced to a powder passing through a 200-mesh sieve. Hydrochloric acid gives practically the same results as sulfuric acid.

A softener for cellulose ester compositions is prepared by treating cocoanut oil under such conditions that one or more glycerides of the oil acids and acetic, formic, and propionic acids are produced[1]. For example, the product obtained by heating and purifying a mixture of glycerol, acetic and cocoanut oil acids with a small amount of sulfuric acid, and which comprises acetyl-laurin, acetyl-palmitin and acetyl-myristin, used with cellulose esters and a volatile solvent to produce a coating composition. In 1927 A. Noll[2] reviewed the newer cellulose ester solvents and plasticizers, especially the properties and applications of cyclohexanone acetate and methylhexalin acetate; also[3] adronol acetates, the methylhexalin acetates, the 1.4-dioxans, and the Δ_2-

Other acids or acid salts can be used in certain cases; but when ferric chloride is used, it imparts a dark color, which cannot be completely removed, even by prolonged washing. Different kinds of pulp possess different reactivities, esparto being particularly easily hydrolized. Complete chlorination of cellulose with chlorine gas, hydrolyzes the cellulose and also gives an unstable chlorine-absorption compound, which can very readily be esterified. In the acetylation of the chlorinated hydrocellulose, the action of acetic anhydride alone is too drastic; it partially burns the cellulose, so that glacial acetic acid must be added as solvent and diluent. The minimum amounts of reagents for 100 chlorinated powdered cellulose at 40-50° are 150 acetic anhydride and 150 glacial acetic acid. Attempts to treat the hydrocellulose with other gases than chlorine (hydrochloric acid), nitrogen peroxide, nitric acid, carbon dioxide, iodine vapors) were unsuccessful. The acetic acid can be replaced by a neutral liquid (e.g., gasolene or kerosene), but the acetic anhydride must be increased to 200 parts, and the diluent to 700 per 100 of cellulose; owing to the increase in volume, the mixture must be treated to keep the temperature at 40-45° during the reaction. The acetate obtained from chloro-hydrocellulose gives films with good transparency, but lacking in strength. Chlorination of cotton for 2-3 hours at 40-45° or for 6-12 hours at room temperature, causes but little or no hydrolysis of the cellulose. The resultant chloro-cellulose can be acetylated at not over 45° with the following minimum proportions of reagents (per 100 parts of cotton); sulfuric acid, 5-7; acetic acid, 250; acetic anhydride, 250; as compared with the usual proportions which are: sulfuric acid, 20; acetic acid, 400; acetic anhydride, 400. Acetylation tests carried out on chemical pulp and on white rag pulps gave results similar to those obtained with partially hydrolyzed cotton.

1. Nobel Industries, Ltd., E. P. 300157; abst. C. A. 1929, **23**, 3573. G. Schwartz, U. S. P. 1558299.

2. Papierfabr. 1927, **25**, 65; abst. C. A. 1928, **22**, 4795; Chem. Zentr. 1927, I, 3160. Cf. Chem. Ztg. 1927, **51**, 546; abst. C. A. 1928, **22**, 867.

3. Farben-Ztg. 1927, **32**, 1553; abst. C. A. 1928, **22**, 499; Chem. Zentr. 1927, I, 3160.

cyclohexan-1-on, the butanol acetate, the butanols, Tamasol J., Anon and Methylanon, methyl and ethyl acetate and formate, the various Palatinols, Erganol and Ergol, triphenylphosphates, the New-Camphrosals, adipic acid cyclohexyl esters, the Mannols, Camphol, Agent AEP and Mollit I[1].

Sheets or films having a matte surface are prepared by casting cellulose acetate solutions on a sheet or band having a rough surface prepared by coating with a layer of gelatin impregnated with starch, barium sulfate or kieselguhr. The surfaces so prepared are said to be non-hygroscopic and can be readily worked, especially with washes of color. Example, the polished metal band upon which the acetate solution is to be cast is coated with a mixture of gelatin, water, alcohol and barium sulfate[2]. Fluorescent colors seen with a screened mercury arc are valuable for rapid identification of fibers and textile chemicals[3], acetate rayon appearing distinctly blue-violet. Details on the preliminary treatment and dyeing of acetate silk[4] were published in 1927 with bibliographical references. In the coating of wood, metal or leather with "Zellon" (plasticized cellulose acetate)[5], the surface to be coated is ground and a plastic acetylcellulose applied, being pressed by a hollow plate having a polished surface.

S. Ohsaka[6] recommends adding to the spinning solution of cellulose acetate for film production a vegetable or animal protein and the fatty oils occurring naturally therewith, the resistance and elasticity of the thread being thereby increased. Technical applications of Celanese (cellulose

1. Seide, 1928, **33**, 404; abst. C. A. 1929, **23**, 3572; Chem. Zentr. 1929, I, 1288. Compare Papierfabr. 1927, **25**, 497; abst. C. A. 1928, **22**, 4792.
2. 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.
3. M. Nopitsch, Melliand's Textilber. 1928, **9**, 136; abst. C. A. 1928, **22**, 3049; Die Kunst. 1928, **10**, 321; abst. J. S. C. I. 1928, **47**, 705-B; Chem. Zentr. 1928, IV, 1507.
4. Novosilk, Kunstseide, 1927, **9**, 599; abst. C. A. 1928, **22**, 2843.
5. R. Ochschim, E. P. 231129; abst. C. A. 1925, **19**, 3606.
6. F. P. 636396; abst. C. A. 1929, **23**, 278. Swiss P. 129842.

acetate) in textile development was pointed out by B. Oliver[1] in 1926. Acetic acid may be purified[2] by adding acetic anhydride equivalent to the water present in the acid, together with 2% chromium oxide which, upon distillation yields an acetic acid of m. pt. 16.2-16.4°, the distillate containing not more than 5 parts acetic acid per 100,000 parts. A new *iso*cellotriose has been described by H. Ost[3], obtained by the action of acetic anhydride or sulfuric acid upon cellulose. Upon hydrolysis with barium sulfide it yields an *iso*triose readily soluble in water, nearly insoluble in alcohol; acetylation gives a mixture of isomeric hendeka-acetates. Whereas earlier studies of cellulose acetate by means of the X-ray spectograph led to conclusions that the material was amorphous[4], more recent work seems to prove that carefully prepared triacetate has at least feebly marked crystalline structure, exhibiting distinct although more sharp interference rings on X-ray analysis. E. Ott[5] claims priority in discovery of the crystalline structure of cellulose triacetate. Non-conducting films of acetyl cellulose may be given a coating of metal by covering them with metal salt and reducing[6]. Thus an alcoholic pyrogallol solution of silver nitrate is spread on a film, which, by reduction, becomes coated with silver.

Details of the preparation of cellulose acetate, borate, phosphate, formate, propionate, butyrate and benzoate were described in 1928[7], together with their physical properties.

1. B. Oliver, Rayon, 1926, **3**, #11, 28; abst. Pulp & Paper Mag. 1928, June 7, 770.
2. K. Orton and A. Bradfield, J. C. S. 1927, **130**, 983; abst. C. A. 1927, **21**, 2661; J. S. C. I. 1927, **46**, 645-A.
3. Zts. ang. Chem. 1928, **41**, 696.
4. E. Ott, Helv. Chim. Acta, 1926, **9**-B, 378; abst. C. A. 1926, **20**, 3079; Plastics, 1926, **2**, 440. Cites P. Karrer, Polymere Kohlenhydrate, 1925, 176.
5. Helv. Chim. Acta, 1926, **9**, 633; abst. C. A. 1927, **21**, 1707; J. S. C. I. 1926, **45**, 782-A; Chem. Zentr. 1926, II, 1731. Cf. R. Herzog, Helv. Chim. Acta, 1926, **9**, 631; abst. C. A. 1926, **20**, 3348; Chem. Zentr. 1926, II, 1731.
6. M. Ow, D. R. P. 492621; abst. C. A. 1930, **24**, 2562.
7. Paint & Varnish Mfr. Assoc. Circular No. 338, 1928, p. 657; abst. Plastics, 1929, **5**, 339.

In the varnishing of leather according to the J. Paisseau process[1], formic, lactic, tartaric or oxalic acid is applied to the leather to modify its surface so that acetylcellulose lacquer subsequently applied thereto will give better adhesion. Gelatin may be applied and rendered insoluble by tannin. C. Palmer[2] has considered the properties of cellulose acetate and cotton, especially in relation to weaving[3]. Crepe effects due to shrinkage are producible in artificial threads of acetylcellulose[4] by treatment with nitric acid of 30-50° Tw. at not to exceed 50°. In the case of a cotton warp and cellulose acetate weft, the treatment produces a material having the appearance of crepe-de-chine.

"Tro" and "Curacit"[5] are recommended as retarding agents in the application of vat dyes to mixtures of viscose and acetylcellulose, the latter being best scoured by means of a mixture of "Sucloughene" or "Solvolene" 5, soap 1.2, and "Tro" 2-5 per 1000 parts of water. The P. Pascal[6] method of synthetic alcohol and acetic acid manufacture depends upon the conversion of acetylene into aldehyde by a continuous process, discontinuously polymerizing the latter to paraldehyde, which is electrolytically reduced to alcohol in an acid bath after autodepolymerization. For the conversion of acetylene into alcohol, a solution is used containing 2% of mercury sulfate at 60-65°.

R. Patchett[7] has detailed methods of winding, warping and weaving of acetylcellulose fabrics, and the sizing of the same with aqueous gelatin mixtures. In the packing

1. E. P. 255803; abst. C. A. 1927, **21**, 2997.
2. C. Palmer, Textile Recorder, 1926, **44**, #520, 85; abst. C. A. 1926, **20**, 3820.
3. F. Palmer, Textile Mfr. **57**, 428; abst. Rayon, 1928, **6**, #7, 36.
4. C. Parker, W. Kershaw, F. Barrett and Bleacher's Assoc., Ltd., E. P. 274584; abst. C. A. 1928, **22**, 2279; Rayon, 1927, **5**, #9, 24.
5. G. Parker, Chemicals, 1927, **27**, #1, 21; abst. C. A. 1927, **21**, 1014.
6. Mem. poud. 1926, **22**, 1; abst. C. A. 1927, **21**, 564. Rev. Gen. des Matieres plastiques, Dec. 1928, 745; abst. Chem. Met. Eng. 1928, **35**, 112.
7. Textile Recorder, 1926, **44**, #522, 77; abst. C. A. 1926, **20**, 3820.

of photographic films and plates[1], sheets of cellulose acetate or gelatin are interposed between sensitized coatings and wrappings of paper. Plastic compounds are fabricated by incorporating with cellulose acetate a mixture of triphenyl and tricresyl phosphates with the assistance of a solvent[2], suitable proportions being acetylcellulose 100, triphenyl phosphate 15, tricresyl phosphate 12, the use of the above mixture avoiding the extrusion of crystals on the one hand and oily globules on the other. As desirable acetylcellulose solvent combinations[3] are recommended mixtures of absolute ethyl alcohol with acetone (20:80).

In the preparation of films sensitive to electrical action[4], nitrocellulose films are coated on one side with photographic emulsion, and on the other with a mixture of cellulose acetonitrate and benzoate. In the production of cellobiose from the octoacetate[5], 10 gm. of the latter, finely ground, are incorporated during 1 hr. with stirring, with 85 cc. 10% sodium methoxide in 95% alcohol. Yield 95% of theory. In 1926 appeared an exhaustive resume of work already published on the velocities of esterification of primary, secondary and tertiary alcohols[6].

In metal coating[7], the surface of an acetylcellulose sheet is slightly saponified as by treatment with 2% NaOH, and a copper or silver salt in solution contacted with the treated sheet to cause precipitation of reduced metal thereon. Insulating layers of acetylcellulose are formed by soak-

1. Pathe Cinema Anciens Etablissements Pathe Freres, E. P. 232604; abst. C. A. 1926, **20**, 155.
2. *Ibid.* E. P. 237900; abst. J. S. C. I. 1926, **45**, 661-B; Kunst. 1926, **16**, 204.
3. *Ibid.* F. P. 601546, 601547; abst. J. S. C. I. 1926, **45**, 533-B.
4. *Ibid.* F. P. 611136, 611137; abst. J. S. C. I. 1927, **46**, 362-B.
5. F. Peterson and C. Spencer, J. A. C. S. 1927, **49**, 2822; abst. J. S. C. I. 1928, **47**, 48-A.
6. P. Petrenko-Kritschenko, V. Bogatsky and N. Loubman, J. Russ. Phys. Chem. Soc. 1926, **58**, 215; abst. J. S. C. I. 1927, **46**, 116-A. Cites Z. physikal Chem. 1925, **115**, 289; abst. J. C. S. 1925, **128**, ii, 556. A. Michael, Ber. 1909, **42**, 310; abst. J. C. S. 1909, **96**, ii, 219.
7. E. Pfiffner, U. S. P. 1529712; abst. C. A. 1925, **19**, 1629; J. S. C. I. 1925, **44**, 351-B. E. P. 182780; abst. J. S. C. I. 1923, **42**, 317-A.

ing them in the absence of air[1], drying, and then allowing atmospheric oxygen to oxidize the oil. In an investigation made to determine whether or not the falling sphere viscosimeter could be used as a plastometer, cellulose acetate solutions were used[2], the conclusion being that the falling sphere method can be used to determine plasticity where present at low rates of shear.

E. Pitman[3] has described the manufacture of a nonstatic photographic film comprising cellulose acetate, acetic acid, glycerol and ammonium acetate, or[4], the acetylcellulose may be replaced by acetated starch. In increasing the durability of lacquers and threads of acetylcellulose[5], resins or rubber or rubber latex are incorporated therewith.

In the formation of insoluble colors on cellulose acetate silk[6], J. Pokorny devised various processes which were made the subject of sealed communications. Acoustic plates are prepared from mixtures of acetylcellulose, triphenyl phosphate, triacetin, and ethyl lactate, which are mixed with fillers and ground, then re-formed to the shape desired[7]. In a theoretical investigation of jellies of cellulose acetate in relation to their physical structure and chemical equilibria[8], the rigid material in cellulose acetate jelly is considered to have a sponge-like or fibrillary structure because the load-strain curve bends continuously toward the load axis, the elasticity of acetylcellulose jellies of various concentrations in a benzyl alcohol-water medium varying approximately as the square of the concentration.

1. E. Pfiffner, Swiss P. 126658; abst. C. A. 1929, **23**, 703.
2. H. Phipps, Colloid Symposium Monograph, 1927, **5**, 259.
3. E. Pitman, U. S. P. 1570077. See U. S. P. 1535438, 1570076, 1570078.
4. *Ibid.* U. S. P. 1570079.
5. P. le Play, F. P. 595208; abst. J. S. C. I. 1926, **45**, 401-B.
6. J. Pokorny, J. Soc. Dyers and Col. 1926, **42**, 345; abst. C. A. 1927, **21**, 326; J. S. C. I. 1926, **45**, 1010-B. The process was originally described in J. S. C. I. 1894, **13**, 388.
7. Polyphonwerke A.-G., F. P. 633790; abst. Brit. Plastics, 1930, **1**, #11, 499.
8. H. Poole, J. S. C. I. 1926, **45**, 165. Trans. Farad. Soc. 1926, **22**, 82; abst. J. S. C. I. 1926, **45**, 353-A; J. S. C. I. 1926, **45**, 794-A.

H. Price[1] has given a list of suitable colors for use with cellulose acetate, with details of the dyeing process[2].

Cellulose acetates of relatively high molecular weight may be depolymerized without hydrolysis[3] by heating in inert liquids as naphthalene or tetrahydronaphthalene at 208°. The solubility is improved and the viscosity characteristics lowered.

In a dissertation upon the state of division of acetylcellulose[4], H. Pringsheim has determined that conversion of primary to secondary acetate is accompanied by disintegration of the micelle, this distintegration being increased by heating in indifferent media as naphthalene. Reduction of micelle size was studied by the action of heating in vacuum and treating with 50% NaOH. In an investigation of the state of aggregation of cellulose acetate[5], acetylation with zinc chloride as catalyst is accompanied by a decrease in particle size, this decrease being least when the reaction takes place in inert liquids as benzene. The conversion of primary triacetate into an acetone-soluble secondary acetate involves loss of acetyl (from 40.-43.3% to 36.5-40.6%) and is accompanied by further disaggregation. The percentage yield and solubility in acetone of the product obtained by heating the primary acetate with tetralin[6], vary with the time and temperature of heating, the product being a crumbly mass. The secondary acetate is produced by shaking the primary substance in the cold with benzenesulfonic acid, keeping for several days in the cold, then heating. Polysaccharide triacetates have been described[7],

1. H. Price, Am. Dyestuff Rept. 1927, **16**, 275; abst. C. A. 1927, **21**, 2191; Chem. Zentr. 1927, II, 329.
2. *Ibid.* Proc. Am. Assoc., Textile Chem. Colorists, 1927, 89; Am. Dyestuff Rept. **16**, 213; abst. C. A. 1927, **21**, 1713.
3. H. Pringsheim, E. P. 267569; abst. C. A. 1928, **22**, 1237.
4. Chem. Ztg. 1928, **52**, 11.
5. H. Pringsheim, W. Kusenack and K. Weinreb, Cellulosechemie, 1928, **9**, 48; Papier-Fabr. 1927, **25**, 785; abst. J. S. C. I. 1928, **47**, 84-B; C. A. 1928, **22**, 2837; Rayon, 1928, **6**, #9, 30.
6. H. Pringsheim and E. Shapiro, Cellulosechemie 1928, **9**, 80; abst. C. A. 1929, **23**, 5571; J. S. C. I. 1928, **47**, 743-B.
7. H. Pringsheim, K. Weinreb and E. Kasten, Ber. 1928, **61-B**, 2025; abst. J. S. C. I. 1928, **47**, 1227-A.

obtained from the cellulose of white cabbage. Acetic anhydride is producible from acetylene in the usual manner[1], except that as catalyst, mercury reduced by iron oxide is used. Details of preparation of trimethylacetic acid[2] were published in 1928.

The R. Quait phonograph record[3] comprises a paper, cardboard or laminated paper core rendered waterproof, and a surface coating or coatings of cellulose acetate containing plastifying elements. Auxanin B is a violet-black, water-soluble crystalline powder which increases the fastness to light of cellulose acetate and cotton colored with basic dyes on a tannin or Katanol mordant[4]. Fastness to light of Malachite Green on cellulose acetate silk is greater than that on cotton mordanted with tannin. H. Ramsperger[5] has determined the vapor density of formic acid.

The F. Rawling process for obtaining acetic acid from wood involves heating the latter with a mixture of sodium sulfite and an alkali, thus forming alkaline acetates which are dissolved out, and from which acetic acid is obtained after acidification by distillation[6]. Alkyl phthalates (methylbutyl, ethylbutyl, propylbutyl, monobutyl and dibutyl) have been advanced as desirable nitro- and acetylcellulose high boiling solvents[7]. F. Reinthaler in 1927 set forth the properties and preparation of cellulose acetate,

1. Prod. Chimique Etablissements Maletra, Belg. P. 285557, 296272.
2. S. Puntambeker and E. Zoellner, Org. Syntheses, 1928 **8**, 104; abst. C. A. 1928, **22**, 1571; J. S. C. I. 1928, **47**, 617-A.
3. U. S. P. 1635862; abst. Plastics, 1927, **3**, 540.
4. R. Rabe, Textilber. 1928, **9**, 665. See E. P. 292253.
5. H. Ramsperger and C. Porter, J. A. C. S. 1928, **50**, 3036; abst. J. S. C. I. 1929, **48**, 128-A. Compare A. Coolidge, J. A. C. S. 1928, **50**, 2166; abst. J. S. C. I. 1928, **47**, 1084-A. H. Ramsperger and C. Porter, J. A. C. S. 1926, **48**, 1267; abst. J. S. C. I. 1926, **45**, 659-A.
6. F. Rawling, U. S. P. 1681684; abst. C. A. 1928, **22**, 3986; J. S. C. I. 1928, **47**, 886-B.
7. 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. Can. P. 271948; abst. C. A. 1927, **21**, 3742.

and artificial filament production therefrom[1], and H. Remaek[2] directions for dyeing the same. A tracing cloth has been described[3], finished in a known manner with starch and oil, which is treated with dissolved acetylcellulose to waterproof it, cellulose acetate 10 to methylglycol 31 at 50-80° being recommended. Nitrocellulose photographic films are backed with a composition comprising cellulose acetate and a protein (zein, gelatin, albumen, keratin)[4], or with a water-insoluble protein as casein in conjunction with acetylcellulose[5].

In the concentration of acetic acid[6], the dilute acid is esterified with methyl or ethyl alcohols to the corresponding ester which is separated by rectification, the ester being hydrolyzed with water and the liberated acetic acid regained by fractionation. J. Reynolds in 1927 contributed an article on general methods of dyeing acetate silk[7], and A. Rheiner[8] on the preparation of effect threads by acetylation of vegetable fibers with a mixture of acetic acid and anhydride, the esterification being advanced only to the stage of formation of cellulose mono- and di-acetate.

Cotton yarn may be finished by impregnating under tension with cellulose acetate[9], then drawn through sapphire dies or fluted rollers whereby excess of impregnating solution is removed and the tension on the yarn controlled. It is then dried and wound on bobbins. The E. Ricard acetic acid concentration process is effected in two stages[10]; the first being the use of a "withdrawal liquid" of relatively

1. Seide, **32**, 226; Chem. Zentr. 1927, II, 2525; abst. C. A. 1928, **22**, 4797.
2. Rayon J. 1926, **1**, #4, 29; abst. C. A. 1926, **20**, 2908.
3. M. Renker, E. P. 297993.
4. F. Renwick, U. S. P. 1680635; abst. C. A. 1928, **22**, 3595.
5. *Ibid.* U. S. P. 1680636; abst. C. A. 1928, **22**, 3595.
6. E. von Retze, U. S. P. 1647676; abst. C. A. 1928, **22**, 243; J. S. C. I. 1928, **47**, 45-B. Can. P. 266537; abst. C. A. 1927, **21**, 1007.
7. Textile Colorist, 1927, **49**, 687; abst. C. A. 1928, **22**, 1044.
8. Can. P. 278731; abst. C. A. 1928, **22**, 2847.
9. J. Rhodin and E. Westman, E. P. 257097; abst. J. S. C. I. 1926, **45**, 914-B.
10. U. S. P. 1668380; abst. C. A. 1928, **22**, 2170. E. P. 226822; abst. Chem. Zentr. 1927, II, 2111. F. P. 605208.

high boiling point which forms a binary mixture containing a large amount of water, and in the second stage a liquid is used which has a lower boiling point so that it can be more readily separated from the anhydrous acid produced.

For the coating or covering of articles with cellulose acetate[1], the latter is employed as a sheet, tube or other solid colloidal form, and after softening the material by treatment with aqueous acetone or alcohol, the softened ester is stretched over the article to be covered and allowed to dry, when the coating returns to its original condition while still retaining its polish. The physical properties of diethylene glycol have been given in great detail by W. Rinkenbach[2], and the dyeing of acetylcellulose with Azanile, Acedronole, Azonine, Azole and Ionamine colors by B. Roetel[3]. In 1928, J. Rossman[4] reviewed the U. S. patent literature upon the spinning of cellulose acetate.

Playing cards, dominoes, dice and counters may be prepared of cellulose acetate[5], cards being made of thin sheets of the material with pigment therein to produce opacity (see p. 203, n. 5; 292, n. 4), the design being printed thereon in either the ordinary way or by transference, and are preferably covered with a layer of varnish of the same material as the card. The invention is stated to be especially applicable to piano keys. Compound transparent sheets of high thermoplasticity are formed[6] by coating both sides of a sheet of celluloid with acetylcellulose, evaporating the solvent and compacting and polishing by the simultaneous application of heat and pressure. G. Roy[7] employs a halogenated zinc derivative as zinc chlo-

1. F. Ridley, E. P. 265257; abst. C. A. 1928, **22**, 317; J. S. C. I. 1927, **46**, 296-B; Plastics, 1928, **4**, 386. Compare D. R. P. 397919; abst. Plastics, 1925, **1**, 84.
2. I. E. C. 1927, **19**, 474; abst. C. A. 1927, **21**, 1964.
3. Melliand's Textilber. 1926, **7**, 43; Rayon J. 1927, **2**, #1, 30.
4. Rayon, 1928, **7**, #10, 20; #11, 16; abst. C. A. 1929, **23**, 1749.
5. L. Rottenberg, E. P. 285886.
6. J. Rowe, E. P. 298888; abst. C. A. 1929, **23**, 3066.
7. Soc. Chim. des Usines du Rhone, U. S. P. 1579248; abst. C. A. 1926, **20**, 1630. E. P. 238825; abst. C. A. 1926, **20**, 1995; J. S. C. I. 1925, **44**, 900-B. Can. P. 258028. Belg. P. 326722.

ride as a decomposition catalyst in the manufacture of acetic anhydride and acetaldehyde.

Blue, red and white effects in cotton-wool-cellulose acetate union fabrics are obtainable by dyeing the wool with a blue acid dye from an acid bath[1], the cotton with a red cotton dye at 50° in presence of 3% Katanol W (for retarding absorption of cotton dye by the wool), and leaving the cellulose acetate white. Many other combinations are contained in the original article. A description is also included of the I. G. Farbenindustrie, Cellit fast dyes, Celliton and Cellitazoles for acetylcellulose dyeing. Acetic anhydride is made by the action of sulfur trioxide on glacial acetic acid[2], partially converting mixtures being used directly in acetylating cellulose. Alkyl orthoacetates (trimethyl, triethyl, dimethylethyl, methyldiethyl, ethyldi-*n*-propyl, ethyldi-*n*-butyl) have been described[3], of possible value as cellulose ester solvents.

The spinning qualities of cellulose acetate are improved by treatment with precipitating agents as sulfuric acid or sodium sulfate solution[4] in presence of *b-iso*propylnaphthalenedisulfonate or *b*-naphthalenesulfonic acid, which lowers the surface tension. The rate of hydrolysis of cellulose acetate by aqueous alkali, to the extent of 50%, is in accordance with a unimolecular reaction[5]. After this point, the rate suddenly diminishes. In alcoholic alkali of different concentrations, without shaking, hydrolysis proceeds rapidly for a short time, then the rate markedly di-

1. G. Rudolph, Kunstseide, 1926, **8**, 13; 1928, **10**, 53; abst. C. A. 1928, **22**, 3533; J. S. C. I. 1926, **45**, 484-B.
2. C. Ruzicka, E. P. 283781; abst. C. A. 1928, **22**, 4133; J. S. C. I. 1928, **47**, 255-B.
3. P. Sah, J. A. C. S. 1928, **50**, 516; abst. J. S. C. I. 1928, **47**, 394-A.
4. R. Sajitz, F. Pospiech and Chemische Fabrik Pott & Co., U. S. P. 1689894; abst. C. A. 1929, **23**, 279; J. S. C. I. 1929, **48**, 14-B. E. P. 280608; abst. J. S. C. I. 1928, **47**, 85-B. F. P. 617600; abst. J. S. C. I. 1927, **46**, 963-B.
5. I. Sakurada, Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **8**, 42; abst. J. S. C. I. 1928, **47**, 598-A. Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **8**, 54; abst. J. S. C. I. 1928, **47**, 599-A.

minishes. Since cellulose acetates of different origin have, under the same conditions, different rates of hydrolysis, this may be used as a test of the quality of the ester. When cellulose is acetylated by treating alkalicellulose with acetic anhydride in benzene at room temperature[1], the product formed approximates to a combination of one molecule acetic acid plus 2 molecules cellulose. I. Sakurada[2] has deduced a mathematical formula for the hydrolysis velocity of mono-, di- and tri-acetylcellulose.

A scientific study of cellulose di- and tri-palmitate, -stearate and -laurate has been made[3], which are partly soluble in organic liquids, and prepared by the action of the corresponding acid chloride (palmityl, stearyl and lauryl chlorides) on cotton cellulose in a mixture of pyridine and benzene. By heating the insoluble portions of the stearic esters in naphthalene at 200°, they are rendered soluble. Since this process in no case is accompanied by hydrolysis, and since the cellulose regenerated from the esters corresponds in properties to the cellulose-A of Hess, the inference is drawn that the variation in solubility is associated with physical changes, probably in molecular arrangement. By acetylation of secondary cellulose acetate which is soluble in acetone, it becomes partly insoluble.

Printed transparent images suitable for projection purposes are produced by forming on a smooth surface[4], an opaque absorbent layer consisting of cellulose acetate, the layer being then printed, and afterwards rendered transparent by means of a second layer of either acetyl- or nitro-cellulose. Variation of conductivity with dilution of

1. I. Sakurada, Cellulose Ind. (Tokyo) 1928, **4**, 304; abst. C. A. 1929, **23**, 4062; J. S. C. I. 1929, **48**, 125-B.

2. *Ibid.* J. S. C. I. (Japan), 1928, **31**, 633; abst. J. S. C. I. 1929, **48**, 319-B.

3. I. Sakurada and T. Nakashima, Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **7**, 153, 165, 197, 213; abst. C. A. 1928, **22**, 1472; J. S. C. I. 1928, **47**, 124-A; Plastics, 1928, **4**, 322. Sci. Papers Inst. Phys. Chem. Research (Tokyo), 1927, **6**, 214; abst. C. A. 1928, **22**, 684.

acetic acid in acetone has been investigated[1] and the re sults fit an equation of the Ostwald form. Since the con stants of the equation give the high value 0.77 for the de gree of dissociation at 500 liters dilution, it appears tha the undissociated molecules also transport electricity.

M. Satoire[2] has investigated the details of swellin and deflocculation of cotton fiber in an endeavor to prov whether the theory of micellar complexity applies. P. Saw yer[3] proposes to protect paper currency and bonds fror wear and possible tampering by coating with a cellulos ester in solution. A patent has been granted[4] for a pro cess for cigarette and cigar manufacture (see p. 296, n. 5 367, n. 2; 384, n. 1; 425, n. 6), in which tobacco waste a cuttings and dust is mixed with acetylcellulose or other aci esters of cellulose and solvents for the latter, and forme into films, or made into a cake which can be sliced or com minuted for smoking. It is predicted the sales will not b large,—at least among tobacco connoisseurs.

Ethylene reacts with acyl halides in presence of alum inum chloride or bromide[5], to give *b*-halogenethyl ketones as methyl-*b*-bromethyl ketone and methyl-*b*-chlorethyl ke tone. The velocity of decomposition of formic acid by sul furic acid has been measured[6]. Esters of hydroaromati alcohols with an aliphatic dicarboxylic acid, excepting adipi acid[7], are valuable solvents and plasticizers for cellulos

1. N. Sata, Bull. Soc. Japan, 1926, **1**, 245; abst. C. A. 192 **21**, 1214; J. S. C. I. 1927, **46**, 113-A.
2. M. Satoire, Bull. Soc. Chim. Biol. 1928, **10**, 714; abst. Pul & Paper Mag. 1929, Jan. 3, 16.
3. P. Sawyer, U. S. P. 1575940.
4. A. Schaarschmidt and M. Popoff, E. P. 282369; abst. Chem Zentr. 1928, I, 1727.
5. Schering-Kahlbaum A.-G., E. P. 282412; abst. C. A. 192 **22**, 3669.
6. E. Schierz and T. Ward, J. A. C. S. 1928, **50**, 3240; abs C. A. 1929, **23**, 753. Cf. J. A. C. S. 1923, **45**, 447; abst. C. A. 192 **17**, 1422.
7. O. Schmidt, T. Eichler, K. Seydel and I. G. Farbenindustri Akt-Ges., U. S. P. 1600700; abst. C. A. 1926, **20**, 3567; J. S. C. I 1926, **45**, 1010-B.

acetate and nitrate, dicyclohexyl oxalate and succinate being examples.

Acetate silk may be printed with alkali vat color paste without loss of luster[1]. Anthraquinone colors, e.g. Yellow 3G, may be prepared with soluble oil, glycerol, *m*-nitrobenzenesulfonic acid (Ludigol) and thickeners, and fixed by steaming without pressure. The addition of resorcinol is beneficial to white sodium persulfate discharges. Azonine, Azanile, Silkone and Azole dyes are unsatisfactory for printing purposes, since in their subsequent development by diazotization and coupling, white effects are very easily stained.

A process for applying coatings of cellulose acetate or other cellulose derivatives to a fabric consists in coating a polished, matte or other surface with an acetylcellulose solution[2], drying the film thus produced, attaching the fabric or base to the film, and removing both base and film from the supporting surface. Sticky preparations for entangling insects and for caterpillar limes[3], are made by adding castor oil 3-9% to acetylcellulose dissolved in acetone. Attractive scents may be added (molasses for flies, beef extract for fleas). E. Schulke reported in 1926 that the wet strength of Celanese yarns tested but 57% of the dry strength[4]. G. Schultze and K. Hess[5] failed to confirm the "de-association" of cellulose acetates when heated in boiling naphthalene (see p. 704, n. 4), and "cellosan" is shown to

1. A. Schneevoigt, Melliand's Textilber. 1926, **7**, 354; abst. C. A. 1927, **21**, 2801; J. S. C. I. 1926, **45**, 662-B; Rayon J. 1926, **1**, #6, 34. Melliand's Textilber. 1926, **7**, 945; abst. Rayon J. 1926, **1**, #11, 15.

2. G. Schneider, E. P. 271425; abst. C. A. 1928, **22**, 1660. Can. P. 277598.

3. V. Scholz and B. Eibes, E. P. 281068; abst. C. A. 1928, **22**, 3499.

4. Melliand Textilber. 1926, **7**, 25; abst. C. A. 1926, **20**, 1719; C. A. 1927, **21**, 2796; J. S. C. I. 1926, **45**, 737-B.

5. Annalen, 1926, **450**, 65; abst. C. A. 1927, **21**, 172; J. S. C. I. 1927, **46**, 44-A. See also H. Pringsheim, J. Leibowitz, A. Schreiber and E. Kasten, Annalen 1926, **449**, 163; abst. J. S. C. I. 1926, **45**, 942-A.

have no relation to cellulose. H. Schupp[1] published in 1928 a comparative study of acetylcellulose silk in comparison to the rayons as to appearance, feel, water-resistance and typical dyeing properties.

Cellulose acetate 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 contains at least one other hydroxyl or halogen substituent in the molecule, but not those polyhydroxyanthraquinones which contain two hydroxyl groups in *o*-position to one another. Suitable dyestuffs are 1.5-dihydroxy- (yellow), 1-hydroxy-4-chlor- (yellow), 1.6-dihydroxy- (yellow), 1.6-dihydroxy-4-chlor- (yellow), 1.4-dihydroxy- (orange), leuco-1.4-dihydroxy- (reddish-yellow), 1.4.6-trihydroxy- (reddish-yellow), 1.4.6-trihydroxy-2-chlor-anthraquinone (reddish-yellow)[2].

Cellulose acetate may be dyed in greenish-blue to deep blue shades by immersion in a hot aqueous suspension containing hexa-aminodianthraquinonyl thioether or a dyestuff obtained by nitration of 1.5- or 1.8-diphthaliminoanthraquinone[3] and subsequent partial hydrolysis by alkali sulfide. Or[4] calcium hydrogen sulfide may be used. The V. Sease process for producing cellulose acetate[5] involves impregnating fibrous cellulose with a small percentage of water (calculated on the weight of the cellulose), acetic acid and anhydride, and then subjecting to the action of an acetylation catalyst, acetic acid and anhydride at 40-65°, reaction being continued until the solubility sought has been attained. Another process[6] treats cellulose 100, with

1. Kunstseide, 1928, **10**, 283; abst. C. A. 1929, **23**, 712.
2. E. Beckett, J. Thomas and Scottish Dyes, Ltd., E. P. 238936; abst. C. A. 1926, **20**, 2079; J. S. C. I. 1925, **44**, 845-B.
3. 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. Compare E. P. 214765.
4. *Ibid.* E. P. 253584, Addn. to 231260; abst. C. A. 1927, **21**, 2563; J. S. C. I. 1926, **45**, 703-B.
5. U. S. P. 1546679; abst. C. A. 1925, **19**, 2878; J. S. C. I. 1925, **44**, 753-B.
6. Seaton Syndicate, Ltd., Swiss P. 122361.

acetic acid 400 and sulfuric acid 2-5, for 24 hours at room temperature, then esterifies in the usual manner.

A series of three patents was granted to P. Seel in this period, the first for an intermediate product in the manufacture of cellulose acetate in the form of a powder, the separate grains of which do not coalesce when stored at room temperature and pressure, and which consists of a mixture of cellulose acetate and acetic acid residues[1]. The acetic acid may be recovered from an acetylcellulose mixture[2] by means of passing a current of warm air over the granular acetylcellulose-acetic acid mass in an apparatus which is illustrated in the patent. In order to obtain greater uniformity in esterification[3], a moist but self-sustaining pulp of cellulose fibers as cotton rag stock, is subjected to a picker action to form fiber aggregates which maintain, at least partially, their identity. The aggregates are then dried and subjected to esterification.

A flexible waterproof fabric is produced by impregnation with a plurality of coats, a cellulose acetate solution of low viscosity, or nitrocellulose which is ether-soluble[4], the flexibility of the coating being maintained by introducing into the formula semi-drying oils as castor or rapeseed. J. Shaw in 1926 gave a resume of the various preferred methods in use for the washing of artificial silks with the minimum detriment to the fibers[5]. The plastic properties of acetyl- and nitro-cellulose films have been recorded[6], and a modified Bingham plastometer described. Cellulose plastics resemble the metals in elastic properties[7], although the

1. P. Seel, U. S. P. 1536311; abst. C. A. 1925, **19**, 1948; J. S. C. I. 1925, **44**, 540-B. Cf. U. S. P. 1494816.
2. *Ibid.* U. S. P. 1536312; abst. C. A. 1925, **19**, 1948; J. S. C. I. 1925, **44**, 540-B.
3. *Ibid.* U. S. P. 1544944; abst. C. A. 1925, **19**, 2745; J. S. C. I. 1925, **44**, 707-B.
4. L. Seidell and G. Jack, U. S. P. 1676362; abst. C. A. 1928, **22**, 3305.
5. J. Shaw, Dyestuffs, 1926, **27**, #1, 12.
6. S. Sheppard and E. Carver, J. Phys. Chem. 1925, **29** ,1244; abst. C. A. 1926, **20**, 529; J. S. C. I. 1925, **44**, 912-B.
7. Faraday Soc., Jan. 15, 1923; May 14, 1923; J. S. C. I. 1923, **42**, 178-A, 649-A.

ultimate particles are more like those of rubber than are the metals. A fibrillar structure is suggested for these sols, the fibrils being chains of molecules held together by residual valences. On this view, E. Mardles "metastable phase" may consist of a brush-like structure of broken fibrils. In a determination of the time factor and yield value of cellulose esters[1], "films of cellulose esters are imperfectly elastic and flow slightly even under very small loads." The yield points, as obtained by ordinary stretch testing machines, depend largely on the speed at which the machine is run.

Benzyl esters of fatty acids containing ten or more atoms, e.g. benzyl stearate, m. pt. 45.8°, are prepared by treating the anhydrous sodium salt of the acid with benzyl chloride[2]. Aldol is made by gradual addition of acetaldehyde to a barium hydroxide sludge[3], while cooling, the reaction product neutralized by oxalic or acetic acid, the aldol distilled off and may be converted into crotonaldehyde.

The luster of textile materials, films and other cellulose acetate products[4] is preserved in processes as bleaching, dyeing, printing and steaming at temperatures above 85° by the presence of a 10-30% solution of sodium chloride, sulfite, sulfate, hydrosulfite, phosphate; magnesium chloride, sulfate; ammonium, calcium, potassium, barium, strontium chlorides or bromides. In the dyeing of acetylcellulose products in oxidation black shades[5], 2.4-diaminodiphenylamine is used in aqueous solution or suspension, and subsequent immersion in boiling solutions of oxidizing agents. Mixtures of 2.4-diaminodiphenylamine with

1. S. Sheppard, E. Carver and S. Sweet, I. E. C. 1926, **18**, 76; abst. C. A. 1926, **20**, 821; J. S. C. I. 1926, **45**, 187-B.
2. H. Shonle and P. Row, U. S. P. 1553271; abst. C. A. 1925, **19**, 3491; J. S. C. I. 1925, **44**, 943-B.
3. O. Silberrad, E. P. 273776; abst. C. A. 1928, **22**, 1982.
4. 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. Cites E. P. 176535.
5. Silver Springs Bleaching and Dyeing Co., Ltd., and A. Hall, E. P. 258699; abst. J. S. C. I. 1926, **45**, 976-B. U. S. P. 1657255; abst. C. A. 1928, **22**, 1050; J. S. C. I. 1928, **47**, 189-B.

aromatic amines as aniline, *o*-toluidine, *p*-phenylenediamine, and *p*-aminodiphenylamine may be used. Furs, skins and feathers may be similarly treated[1].

The resistance of acetate silk in the form of yarns, skeins and fabrics to hot aqueous solutions is increased by stretching the fully set and finished filaments beyond their elastic limit, the stretching being assisted by pre-treatment with swelling agents (acetone, alcohol, formaldehyde, glycerol). The threads so treated preserve their luster and do not become curly or wool-like in boiling water[2]. Woven fabrics with a raised or pile surface is printed or grained on one face to resemble leather[3], and then treated with a cellulose acetate composition coating, afterwards being embossed. A surface decoration or finish may be produced on (say) tennis racket handles or electric lamps[4], by placing on the surface a cellulose acetate yarn or fabric and then applying a solvent as ethyl acetate.

Potassium or other alkali acetate and acetic acid may be formed by leading methyl alcohol vapor under pressure in presence of hydrogen over molten alkali formate at[5] 200-300°. Acetic acid may be concentrated by extracting the aqueous solution with an acetic acid ester[6], and the mixture distilled to separate first an aqueous ester, then the balance of the ester, finally the anhydrous acid; a 10% acetic acid solution may be treated with ethyl acetate, or a 5% butyric acid solution with butyl acetate. Or[7], a hydrocar-

1. Silver Springs Bleaching and Dyeing Co., Ltd., and A. Hall, E. P. 270075; abst. J. S. C. I. 1927, **46**, 475-B.
2. *Ibid.* E. P. 277089; abst. C. A. 1928, **22**, 2465; J. S. C. I. 1927, **46**, 964-B; Silk J. 1927, **4**, #43, 66. See E. P. 206113, 246879.
3. C. Simpson, E. P. 291890; abst. C. A. 1929, **23**, 1304; J. S. C. I. 1928, **47**, 651-B.
4. M. Smith, E. P. 286006; abst. C. A. 1929, **23**, 277; Plastics, 1929, **5**, 336.
5. P. Smith and H. Smith, U. S. P. 1679994; abst. C. A. 1928, **22**, 3669; J. S. C. I. 1928, **47**, 740-B. E. P. 271589; abst. C. A. 1928, **22**, 1596; J. S. C. I. 1927, **46**, 571-B. Can. P. 273715; abst. C. A. 1927, **21**, 3906. Australian P. 6590. New Zealand P. 58177. Ital. P. 258713.
6. Soc. anon. des Distilleries des Deux-Sevres, E. P. 273744; abst. C. A. 1928, **22**, 1981.
7. *Ibid.* E. P. 290992; abst. C. A. 1929, **23**, 1419.

bon as toluene or xylene may be used for extracting. The acid may also be extracted from its aqueous solutions by a solvent having a boiling point above that of acetic acid[1] but below 150° as amyl acetate, which is insoluble in and does not form an azeotropic mixture with acetic acid, followed by dehydration of the extract by distilling with an entraining liquid as ethyl acetate[2]. If the acid solution contains mucilaginous substances which might hinder the separation in the extraction column[3], the acid is vaporized and led to the middle of the separating column to which the solvent is supplied. When acetaldehyde is aldolized with alkali at 5° and the product neutralized and distilled[4], aqueous crotonaldehyde passes over at 84-85° in 92% yield on unrecovered acetaldehyde.

In applying a printing process to cellulose acetate fabrics[5] with a natural silk or wool foundation, the fabric, after printing the acetylcellulose, is passed through a bath of potassium permanganate and then through a bath of sodium acid sulfate to remove all traces of color from the silk or wool foundation. Aromatic sulfonic or carboxylic acids or their salts may be added to the printing paste[6] of the acetylcellulose goods for impregnation, before being printed. A printing paste may be setoglausine, 2-naphthol-7-sulfonic acid, acetic acid and a gum thickener.

Cellulose acetate goods are dyed violet, green, blue and black shades with monoazo dyes containing one or more

1. Soc. Anon. des Distilleries des Deux-Sevres, E. P. 296974; abst. C. A. 1929, **23**, 2449; J. S. C. I. 1929, **48**, 349-B.
2. *Ibid.* E. P. 300246, Addn. to 296974; abst. C. A. 1929, **23**, 3478; J. S. C. I. 1929, **48**, 426-B.
3. *Ibid.* E. P. 301415; abst. C. A. 1929, **23**, 3932. Australian P. 15976.
4. F. P. 637517; abst. J. S. C. I. 1930, **49**, 807-B.
5. Soc. Anon. des Etablissements Petitdidier, Ancienne Maison Jolly-Belin, E. P. 270657, Addn. to 256238; abst. C. A. 1928, **22**, 1694; J. S. C. I. 1928, **47**, 260-B. See E. P. 256238.
6. Soc. Anon. J. R. Geigy, E. P. 231897; abst. C. A. 1925, **19**, 3599; J. S. C. I. 1925, **44**, 588-B. Compare E. P. 213593; abst. C. A. 1924, **18**, 2433.

diazotizable amino groups[1], the shades being diazotized and developed with alkyl- or aralkyl-*a*-naphthylamines. Dyes which readily disperse in water, especially in presence of a soap or sulfonated soap[2], and are thus suitable for dyeing acetate silk, are made by grinding a non-sulfonated dye with sulfite cellulose pitch (ligninsulfonic acid) and evaporating the dispersion so obtained. Diazotized aniline[3], coupled with 1-*o*-chlorphenyl-3-methyl-5-pyrazolone, gives a yellow dye for acetate silk. Fast blue to green tints are obtained by use of indophenols[4] made by joint oxidation of a halogenated *p*-aminophenol and an aromatic amine with free *p*-position. Examples are indophenols made by oxidation of 2-chlor-, 2.6-dichlor-, and 2.5.6-trichlor-*p*-aminophenols with dimethylaniline, diethylaniline, benzylmethylaniline, *N*-phenyl-*N*-ethylglycine, methyldiphenylamine, *o*-toluidine, *a*-naphthylamine. The di- and tri-chlor compounds are greener than the mono-chlor.

Sulfite cellulose solution may be used for converting into colloidal condition[5], insoluble dyes as azo dyes, quinophthalone, indophenols, anthraquinone derivatives and nitrodiarylamines. Acetate silk possessing the property of being dyed with ordinary dyes is obtained by spinning a mixture of cellulose acetate 5-20% with nitrocellulose and denitrating the resulting filaments[6] in a bath of at least 8% soluble hydrosulfite at above 50°. White or colored discharges on acetate silk are produced by printing the material with a paste comprising a zinc sulfoxylatealdehyde

1. Soc. anon. pour l'ind. Chim. a Bale, E. P. 231455; abst. C. A. 1925, **19**, 3599; J. S. C. I. 1925, **44**, 916-B.
2. 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. W. Jaeck and F. Felix, Can. P. 265027; abst. C. A. 1927, **21**, 1017.
3. *Ibid.* E. P. 256205; abst. J. S. C. I. 1927, **46**, 869-B.
4. *Ibid.* E. P. 261423; abst. C. A. 1927, **21**, 3469; J. S. C. I. 1928, **47**, 121-B. Swiss P. 122569; abst. J. S. C. I. 1929, **48**, 716-B.
5. *Ibid.* E. P. 263579; abst. C. A. 1928, **22**, 171; J. S. C. I. 1927, **46**, 186-B. U. S. P. 1796028, 1796029. Cf. E. P. 219349.
6. *Ibid.* E. P. 268363; abst. C. A. 1928, **22**, 1243; J. S. C. I. 1928, **47**, 706-B; Kunstseide, 1927, #8, 424; Chem. Zentr. 1927, II, 747. Swiss P. 121531.

compound[1] which may be used with an acid or alkali as required. Discharges containing Methylene blue D, Ciba blue 2 BD or Pyrogene blue 3 GL give blue effects on a red ground and Auramine, yellow effects on a red ground.

Methylaminoanthraquinone-ω-sulfonic acids[2], containing a further substituent in the methyl group are made by the action of a bisulfite compound of an aldehyde containing more than one C. atom. The products are suitable for acetylcellulose dyeing. Examples, condensation of 1-amino-4-hydroxyanthraquinone or 1.4.5.8-tetra-aminoanthraquinone (both) with sodium acid sulfate and benzaldehyde. Furfural, acetaldehyde and crotonaldehyde may be used with aminoanthraquinones. Dry solid preparations of dyes suitable for coloring acetylcellulose[3] are made by evaporating to dryness in the presence of sulfite cellulose liquor, a fine dispersion produced by stirring the dye with water in the presence of saponin or a formaldehyde-naphthalene sulfonic acid condensate. Acetate dyes are obtained by treating aminoanthraquinone or derivatives[4], with aldehyde and formic acid. When 1-amino-4-nitroanthraquinone is thus treated, a red dye results, which, when reduced to methyldiaminoanthraquinone with sodium sulfide, dyes acetate silk fast violet tones.

Azo dyes obtained by coupling non-sulfonated diazo compounds containing a nitro group *o*-to the diazo group with primary, secondary or tertiary amines, are useful acetate silk dyes. Diazotized *o*-chlornitro-, 4-chlor-2-nitroaniline or *m*-nitro-*p*-toluidine coupled with *o*-toluidine,

1. Soc. Chem. Ind. in Basle, E. P. 285973; abst. C. A. 1929, **23**, 289; J. S. C. I. 1928, **47**, 331-B.
2. *Ibid.* E. P. 295257; abst. C. A. 1929, **23**, 2300. Swiss P. 131100; abst. C. A. 1929, **23**, 3812.
3. *Ibid.* E. P. 300299; abst. C. A. 1929, **23**, 4083; J. S. C. I. 1929, **48**, 317-B.
4. *Ibid.* D. R. P. 489863; abst. C. A. 1930, **24**, 2301. E. P. 282853; abst. J. S. C. I. 1928, **47**, 153-B. E. P. 309087. Swiss P. 134943; abst. C. A. 1930, **24**, 2610. Swiss P. 136257; abst. C. A. 1930, **24**, 4400.

o-anisidine or *p*-xylidine produce shades of unusual fastness[1].

Dilute acetic acid is concentrated by mixing with butyl or amyl alcohols, mesitylene, methyl*iso*butyl ketone, or butyl acetate, which boils below 150°, which when mixed with more than 50% water boils below 95°, and has less than a 10% solubility in water[2]. A photographic plate has been described[3], the back of which is coated with a layer of cellulose acetate containing a plasticizer and a black aniline dye or lampblack. After evaporation of the solvent an easily strippable coating remains.

In the continuous manufacture of cellulose acetate[4], all the necessary operations are carried out in one or more inclined, tubular, reaction vessels rotating about their axes and preferably provided internally with mixing and circulating devices, the particular type of device being determined by the texture of the reaction mixture at the point at which it is to operate. The reagents are introduced at the end of the reaction vessel, temperature control being by means of sprays.

When a stream of acetylene mixed with air or oxygen is passed through an acid solution of ferrous sulfate in the presence of copper salts and mercury[5], acetaldehyde is produced. Dilute acetic acid from cellulose acetate manufacture is heated for several hours with sulfuric acid before

1. Soc. Chem. Ind. in Basle, F. P. 641675; abst. C. A. 1929, **23**, 1280.

2. Soc. Anon. Progil, F. P. 622680; abst. J. S. C. I. 1929, **48**, 199-B.

3. Soc. Anon. Union Photographique Industrielle, F. P. 619395; abst. J. S. C. I. 1928, **47**, 286-B.

4. Soc. Chimique des Usines du Rhone, E. P. 274814; abst. C. A. 1928, **22**, 2272; J. S. C. I. 1928, **47**, 744-B; Plastics, 1928, **4**, 508. D. R. P. 493102; abst. C. A. 1930, **24**, 2882. Swiss P. 126204; abst. C. A. 1929, **23**, 704. See also Swiss P. 113353, 124767. E. P. 270656; abst. C. A. 1928, **22**, 1685; J. S. C. I. 1928, **47**, 229-B; Plastics, 1928, **4**, 446. F. P. 615879; abst. J. S. C. I. 1927, **46**, 811-B. D. R. P. 493101; abst. C. A. 1930, **24**, 2882.

5. *Ibid.* E. P. 238520; abst. C. A. 1926, **20**, 1995; J. S. C. I. 1925, **44**, 972-B. Can. P. 257056. Ital. P. 239502. Belg. P. 326725. M. Ledru and E. Bachmann, U. S. P. 1532190; abst. C. A. 1925, **19**, 1575. Cites D. R. P. 292818, 293070, 299467, 305182, 360417, 360418. F. P. 491466. U. S. P. 1477957.

being treated with solvents for acetic acid extraction[1], in order to render the cellulose compounds soluble in the sulfuric acid and prevent their precipitation while the acetic acid is being removed. Absorption of acetylene in acetic acid in the presence of a mercury salt is effected in the presence also of a strong acid and of acetic anhydride for ethylidene diacetate production[2]. The mercury salts of sulfuric, sulfoacetic, benzenesulfonic and naphthalenesulfonic acids are preferred.

Plates or other cellulose acetate articles[3] are dried to remove the solvent used in their manufacture in an atmosphere laden with the vapors of the solvents, circulation being effected by a pump which draws the gases from the base of the chamber through a condenser and returns them through a heater at the top of the chamber. In producing decorative effects on cellulose acetate sheets[4], the material is treated with cold ethyl lactate, methyl alcohol and ethyl acetate in which pigments may have been incorporated, the pigmented layer being applied in the manner desired to obtain the effect required.

Acetic acid may be rectified by a continuous process by vaporizing and passing into a rectifying column from the base of which concentrated acid is obtained[5]. The weak acid from the top of the column is passed into a second

1. Soc. Chimique des Usines du Rhone, E. P. 266684; abst. C. A. 1928, **22**, 597; J. S. C. I. 1927, **46**, 963-B. D. R. P. 462994; abst. C. A. 1928, **22**, 4246. Ital. P. 256235.

2. *Ibid.* E. P. 252632; abst. C. A. 1927, **21**, 2274; J. S. C. I. 1926, **45**, 936-A. Can. P. 262826. M. Bouvier and L. Hougoniot, U. S. P. 1680760; abst. C. A. 1928, **22**, 3669. E. P. 252640; abst. C. A. 1927, **21**, 2274; J. S. C. I. 1926, **45**, 936-A. M. Ledru and E. Bachmann, U. S. P. 1672646; abst. C. A. 1928, **22**, 2573; J. S. C. I. 1928, **47**, 516-B. Can. P. 269818; abst. C. A. 1927, **21**, 2274. Compare F. P. 487402. D. R. P. 271381.

3. *Ibid.* Swiss P. 117569. F. P. 601221; abst. Chem. Zentr. 1926, I, 3110. Swiss P. 127542; abst. C. A. 1929, **23**, 1286. Swiss P. 127543; abst. C. A. 1929, **23**, 1267; Plastics, 1929, **5**, 390. See F. P. 520101, 569642. E. P. 241871; abst. Chem. Zentr. 1926, I, 1250.

4. Soc. des Brevets J. Paisseau, E. P. 293391; abst. C. A. 1929, **23**, 1750; J. S. C. I. 1929, **48**, 849-B.

5. Soc. des Etabl. Barbet, E. P. 238566; abst. C. A. 1926, **20**, 1995; J. S. C. I. 1925, **44**, 899-B. Belg. P. 328067. Can. P. 258628.

column and the concentrated acid from the base of this column supplied to the first column. In the partial saponification of acetylcellulose for hydrated film production[1], hygroscopic bodies as magnesium chloride is added to the pellicle to diminish its speed of drying out. Formic and acetic acids are concentrated[2] by adding to the aqueous solution a soluble formate or acetate (Na. or K. salt) and distilling under reduced pressure, first at a low temperature until all the water is removed, and then at a higher temperature. To render films non-flammable[3], a variation in cellulose acetate production[4] comprises in hydrolyzing the formed acetate by means of a mixture of formic and sulfuric acids, it being claimed that formation of cellulose sulfacetates are avoided, and increased stability and plasticity results. Acetylation may be facilitated by pre-treatment of cellulose with 80-90% formic acid[5] containing a small amount of either sulfuric acid or zinc chloride at room temperature for 2 hrs., then esterifying in the usual manner. In spinning such a solution, a small proportion of alcohol or glycerol is added to the spinning bath[6], the solution being heated before extrusion and a cold evaporating atmosphere introduced into the spinning cell adjacent the extrusion nozzles in such a manner that it moves in the same direction as the filaments[7].

Cellulose acetate silk is said to be delustered with perfect regularity without deleteriously affecting the strength,

1. Soc. Francaise des Crins Artificiels, Swiss P. 112214.
2. Soc. James Nelson, Ltd., F. P. 637389.
3. Soc. Industrielle Applications, F. P. 645358. E. P. 301879, 305653, Addn. to 301878. Swiss P. 138609.
4. Soc. Lyonnaise de Soie Artificielle and P. Chevalet, F. P. 621376; abst. Rayon, 1928, **6**, #1, 24.
5. *Ibid.* E. P. 264181; abst. C. A. 1928, **22**, 164; J. S. C. I. 1928, **47**, 258-B. Ital. P. 255774. Swiss P. 125216. D. R. P. 505674; abst. C. A. 1931, **25**, 591; Chem. Zentr. 1930, II, 2463. E. P. 266300; abst. C. A. 1928, **22**, 499; J. S. C. I. 1928, **47**, 520-B. D. R. P. 516462; abst. C. A. 1931, **25**, 1993; Chem. Zentr. 1931, I, 2141. Holl. P. 23779.
6. *Ibid.* F. P. 621377; abst. Rayon, 1928, **6**, #1, 24.
7. *Ibid.* E. P. 300672; abst. C. A. 1929, **23**, 4072; J. S. C. I. 1929, **48**, 50-B. D. R. P. 487242, Addn. to 428745; abst. C. A. 1930, **24**, 2292.

elasticity and other qualities of the fiber[1], by soaking the yarn or fabric for 2-24 hrs. at the ordinary temperature in a 10-30% aqueous solution of calcium, lithium or magnesium chloride, and treating the impregnated fabric in boiling, dilute acid (0.1-0.01*N*), boric, hydrochloric, benzoic, salicylic or naphthalenesulfonic acids being satisfactory. Luster may be restored by bringing the wetter acetylcellulose fabric in contact with a surface heated to 125-170°, under a 0.3-0.5 kg. per sq. cm. pressure[2].

In the lubrication of acetylcellulose fibers[3], semi-drying, oxidized animal or vegetable oils are used, especially rapeseed and cottonseed oils, singly or in conjunction with other lubricants. In the preparation of cellulose esters of the higher fatty acids[4], toluene, xylene and homologous higher hydrocarbons are introduced as diluents in the condensing step. Uses of Celanese in the broadsilk industry was detailed by W. Spafford[5] in 1927.

Cellulose acetate dyestuffs are produced by means of unsulfonated azo dyes, examples being[6]: 1-*b*-hydroxyethoxy-4-diazobenzene and acetoacetic acid anilid (dyes greenish-yellow), and with 1-amino-7-hydroxynaphthalene (dark claret), or with 2-amino-7-hydroxynaphthalene (brownish-red-orange), or with 2-hydroxynaphthalene (intense red). If cellulose acetate is treated in presence of ammonia and an oxidizing agent (hydrogen peroxide) with

1. Soc. Lyonnaise de Soie Artificielle and P. Chevrolet, E. P. 301335; abst. C. A. 1929, **23**, 4085; J. S. C. I. 1929, **48**, 126-B; Silk J. 1929, **5**, #58, 78. G. Lardy, U. S. P. 1778327; abst. C. A. 1930, **24**, 6035; J. S. C. I. 1930, **49**, 1107-B. F. P. 638795; abst. C. A. 1929, **23**, 530. D. R. P. 512637; abst. C. A. 1931, **25**, 1391; Chem. Zentr. 1931, I, 872.
2. *Ibid.* F. P. 646719; abst. C. A. 1929, **23**, 2306.
3. *Ibid.* Belg. P. 351419. F. P. 660352; abst. Chem. Zentr. 1929, II, 1754.
4. Soc. de Stearinerie et Savonnerie de Lyon, E. P. 233263, Addn. to 201510; abst. C. A. 1926, **20**, 666; J. S. C. I. 1925, **44**, 540-B.
5. Textile World, 1927, Sept. 24, p. 74.
6. O. Spengler and W. Mueller, U. S. P. 1770714; abst. C. A. 1930, **24**, 4642; J. S. C. I. 1930, **49**, 815-B. F. P. 619329; abst. J. S. C. I. 1928, **47**, 86-B. D. R. P. 495619; abst. C. A. 1930, **24**, 3656.

an arylamine (*p*-aminophenol)[1], a colored compound is formed. Examples, 4.4′-dihydroxy- (brownish-red), 3′-5′-dichlor-4′-hydroxy- (bluish-red), 4′-amino-4-hydroxy- (clear violet), and 4′-dimethylamino-4-hydroxy-diphenylamine (clear blue).

*Iso*propyl[2] and butyl acetates[3] have been described and methods for their formation from petroleum cracking fractions. E. Stern[4] has contributed an article on the micrography of cellulose ester films. In the dyeing of acetylcellulose and unions in which it is present[5], the vat dyes (Caledon Red BN, Indanthrene Orange 3R, Hydron Yellow 2G, Caledon Jade Green, Algol Blue K, Hydron Blue G, Indanthrene Brilliant Violet RR, Duranthrene Red, Violet 2RN) may be applied to cotton containing acetylcellulose effects by means of sodium phenolate. Real silk may be degummed in the presence of acetylcellulose by impregnating at 75° with a strong solution of Turkey red oil and sodium carbonate, silicate or borate.

Lacquers have been described[6] comprising combining cellulose acetate with Congo copal in the presence of triphenyl phosphate, a solvent of both. F. Sturtevant[7] in 1927 discussed the effect on acetate silk of such re-lusterants as acetic acid, phenol, benzyl alcohol, triacetin, cyclohexanone, ammonium thiocyanate and alcohol, the ornamenting of

1. O. Spengler, P. Virck and R. Weidenhagen, U. S. P. 1615242; abst. C. A. 1927, **21**, 826; J. S. C. I. 1927, **46**, 249-B. F. P. 605127; abst. Chem. Zentr. 1927, I, 1218. Cites D. R. P. 198008, F. P. 383636.

2. Standard Oil Co., Belg. P. 347679.

3. *Ibid.* Belg. P. 347680. See J. Steiert, Ital. P. 255097.

4. E. Stern, Farben-Ztg., 1926, **31**, 2129; abst. J. S. C. I. 1926, **45**, 638-B.

5. F. Stevenson, Dyer & Calico Printer, **55**, 86; Chemicals, 1926, **25**, #17, 19; abst. C. A. 1926, **20**, 2076.

6. Stockholms Superfosfat Fabriks A.-B., Swed. P. 62474; abst. C. A. 1927, **21**, 3906. D. R. P. 488986; abst. C. A. 1930, **24**, 2143. E. Thorin, U. S. P. 1601891; abst. J. S. C. I. 1927, **46**, 59-B. See E. de Stubner, E. P. 297679; abst. C. A. 1929, **23**, 2841.

7. F. Sturtevant, Textile World, 1927, Feb. 12, p. 20; Mar. 12, p. 47. See E .P. 259265, 259266.

cellulose acetate fabrics[1], and the production of artificial wool.

A series of processes have been granted patent protection to H. Suida in connection with the production and recovery of acetic acid. In producing anhydrous acid from weak solutions, cresol is used as the acetic acid solvent[2], or hydrogenated phenols and creosotes[3]. Best results are obtained by mixing the cresol with a solvent as trichlorethylene, chloroform, carbon tetrachloride or ethylene chloride[4], or by the use of acetic esters as the acetates of glycol, glycerol, amyl, or hexyl, or amyl butyrate[5]. In the extraction of acetic acid, dibutyl phthalate has also been recommended[6], as well as hexyl phthalate[7]. Suida in 1927 gave an exhaustive resume of methods of acetic acid concentration[8].

Powdered beech wood acetylated with boiling acetic anhydride followed by treatment with acetic anhydride and

1. F. Sturtevant, Textile World, 1927, Sept. 24, p. 99; 1928, Jan. 14, p. 206.

2. H. Suida, U. S. P. 1624812; abst. J. S. C. I. 1927, **46**, 541-B. Can. P. 259147; abst. C. A. 1926, **20**, 3460. Ital. P. 260529. Aust. P. 117858; abst. C. A. 1930, **24**, 4306. Aust. P. 119478, Addn. to 116727; abst. C. A. 1931, **25**, 714. Aust. P. 119481, Addn. to 117858; abst. C. A. 1931, **25**, 714. Compare E. P. 218271, 218272.

3. *Ibid.* E. P. 230447; abst. C. A. 1925, **19**, 3272; J. S. C. I. 1925, **44**, 827-B; Rev. Gen. Mat. Plast. 1927, #1, 46. U. S. P. 1621441; abst. C. A. 1927, **21**, 1464; J. S. C. I. 1927, **46**, 349-B. Aust. P. 121251; abst. C. A. 1931, **25**, 2440. Ital. P. 271945. Can. P. 259146.

4. *Ibid.* E. P. 255043, 255047; abst. C. A. 1927, **21**, 2704; J. S. C. I. 1927, **46**, 316-B. U. S. P. 1624810, 1624811, 1624812; abst. C. A. 1927, **21**, 1819. F. P. 634202; abst. C. A. 1928, **22**, 3773. Aust. P. 111566; abst. C. A. 1929, **23**, 1419. D. R. P. 469942; abst. C. A. 1929, **23**, 2190. Compare E. P. 230447.

5. *Ibid.* E. P. 280501; abst. C. A. 1928, **22**, 3170; J. S. C. I. 1928, **47**, 921-B. Can. P. 263555; abst. C. A. 1926, **20**, 3696. Can. P. 279952.

6. *Ibid.* E. P. 295641; abst. C. A. 1929, **23**, 2191; J. S. C. I. 1930, **49**, 275-B. F. P. 639112; abst. C. A. 1929, **23**, 608. Can. P. 264781.

7. *Ibid.* E. P. 296172, Addn. to 230447; abst. C. A. 1929, **23**, 2449; J. S. C. I. 1928, **47**, 808-B. F. P. 594925; abst. J. S. C. I. 1926, **45**, 421-B. Can. P. 268067. Aust. P. 120859; abst. C. A. 1931, **25**, 2440. Can. P. 274719; abst. C. A. 1927, **21**, 4061. Aust. P. 121998; abst. C. A. 1931, **25**, 3015.

8. *Ibid.* Oesterr. Chem. Ztg. 1927, **30**, 1; abst. C. A. 1927, **21**, 1445; J. S. C. I. 1927, **46**, 123-B.

pyridine[1] gave 37% acetyl in combination, the ester not reacting with aniline sulfate or phloroglucinol-HCl (see p. 166; n. 7; 252, n. 1). In the formation of acetylcellulose according to the A. Sulzer process[2], after esterification, the product is heated in a vacuum, acetic acid being removed from the reaction mixture at a temperature below that at which cellulose acetate is degraded.

A material for electrical insulation has been patented[3], as in the form of panel or board, comprises cellulose 40, oil 15, soap 2, gilsonite 43 and acaroid resin, the whole being protected by a plurality of acetylcellulose coats. By treating swollen cotton with aromatic sulfochlorides in presence of indifferent solvents, the fiber bundles are converted into a resistant sulfo-ester. Material produced in this way using *p*-toluene chloride is on the market as "Immune yarn" (Chem. Fabrik vorm. Sandoz, Basle)[4]. The chemical behavior of the material resembles acetyl silk, its affinity for substantive colors being greatly reduced while its affinity for basic colors remains the same or is increased. By "immunizing" dyed yarn the color is rendered faster.

Owing to the presence in cellulose acetate of traces of cellulose sulfuric esters[5], it is desirable to add a stabilizer such as calcium naphthenate which reacts with the cellulose esters yielding naphthenic acid which is an acetylcellulose gelatinizer and improves the mechanical properties of the film. Amount of stabilizer required 1-2%. Data on the physical properties of ethylene glycol have been collected and tabulated[6], including glycol diacetate[7].

1. H. Suida and H. Titsch, Ber. 1928, **61**-B, 1599; abst. C. A. 1928, **22**, 4807; J. S. C. I. 1928, **47**, 1227-A; Can. Pulp & Paper Mag. 1929, Aug. 1, p. 187. Compare W. Fuchs, Ber. 1928, **61**-B, 948; abst. J. S. C. I. 1928, **47**, 743-A. A. von Wacek, Ber. 1928, **61**-B, 1604; abst. J. S. C. I. 1928, **47**, 1227-A.
2. U. S. P. 1560620; abst. C. A. 1926, **20**, 111.
3. D. Sutherland, U. S. P. 1636491; abst. Plastics, 1927, **4**, 540.
4. G. Tagliani, Textilber. 1925, p. 425; abst. J. Soc. Dyers, 1926, **42**, #2, 69.
5. Y. Tanaka and K. Atsuki, J. S. C. I. (Japan) 1928, **31**, 416; abst. C. A. 1929, **23**, 511; J. S. C. I. 1928, **47**, 519-B.
6. C. Taylor and W. Rinkenbach, I. E. C. 1926, **18**, 676.
7. *Ibid.* J.A.C.S. 1926, **48**, 1305; abst. J.S.C.I. 1926, **45**, 710-A.

Coated fabrics for floor covering[1] comprise a felt base with flexible filling material coated with paint and then lacquered with cellulose acetate solution, asphalt[2] or asphaltum[3] being used to impregnate the filling material. The acetylcellulose outer film is preferably transparent to admit of painting a design upon the layer immediately underneath[4]. The future of the cellulose acetate process was discussed by D. Taylor[5] in 1926, and the properties of "Celta" artificial silk delineated by T. Taylor[6] the year previous.

Cellulose acetate is dyed by means of direct cotton dyestuffs after treatment for 15-120 min. at 50-70° in an aqueous solution containing 1% each barium hydroxide and chloride[7]. Acetate paints, varnishes and lacquers and their uses have been dealt with in a paper by H. Tenen[8] published in 1926. In the production of hollow textile fibers[9] (see pp. 209, 210, 213, 217, 251, 303), cellulose acetate dissolved in acetone and alcohol is spun into a cell containing air at a temperature substantially higher than the boiling point of the solvent used, a comparatively high rate of flow of this air being maintained in order to produce an active superficial evaporation from the filaments as they emerge from the nozzle.

E. Terlinck[10] in a series of articles published in 1928, has reviewed in detail the innovations and improvements in the manufacture of acetic acid and its derivatives, and

1. C. Taylor, E. P. 243614; abst. C. A. 1926, **20**, 3826. Can. P. 256979, 256980.
2. *Ibid.* Can. P. 256981.
3. *Ibid.* Can. P. 256982.
4. *Ibid.* Can. P. 256983.
5. D. Taylor, Rayon, 1926, **2**, #5, 13.
6. T. Taylor, Silk J. 1925, **2**, 19; abst. C. A. 1926, **20**, 2580. In this connection see also T. Taylor and L. Lehrman, J. Amer. Chem. Soc. 1926, **48**, 1739; abst. C. A. 1926, **20**, 2310.
7. Teinturerie de la Rize, F. P. 590738; abst. J. S. C. I. 1926, **45**, 154-B.
8. Chemicals, 1926, **25**, #19, 9.
9. W. Tennant, E. P. 267187; abst. J. S. C. I. 1927, **46**, 361-B. See E. P. 189973.
10. Chem. Ztg. 1928, **52**, 249; abst. C. A. 1928, **22**, 2738; J. S. C. I. 1928, **47**, 514-B.

E. Terry and J. Stieglitz[1], the coefficient of hydrolysis of ethyl acetate. A transparent dope suitable for covering aeroplane wings including specially prepared aluminum hydroxide has been published[2], comprising acetylcellulose, a camphor substitute as eugenol, benzyl alcohol or ethyl acetoacetate, and a high boiler as triacetin. As a camouflage airplane wing coating, a three layer composition has been advanced in which the acetylcellulose composition has embedded therein a multiplicity of small, very thin, aluminum flakes overlapping each other[3].

In the delustering process of M. Theumann[4], acetylcellulose 1, acetic acid 2, water 5, and a small amount of sulfuric acid is added gradually to barium chloride in a mixture of acetic acid and water, and the whole precipitated, washed and dried. This is then dissolved and used for spinning purposes. The filaments contain about 20% barium sulfate and 80% cellulose acetate. Printing plates, bands or belts for producing grainy half-tone or non-grainy full tone prints[5], are produced from separate partial negatives or from screen-plate negatives, and printing is effected according to the requirements of the process employed on strips of plain cellulose acetate 0.003 inch thick, or on an unsensitized colloid layer 0.001 inch thick, coated with acetylcellulose. W. Todd has published a general description of the physical and dyeing properties of acetate silk[6], and details of the application and properties of the Celatene dyes.

Pattern effects are obtainable on cellulose acetate fab-

1. J. A. C. S. 1927, **49**, 2216; abst. J. S. C. I. 1927, **46**, 1036-A.
2. T. Tesse, U. S. P. 1590782; abst. C. A. 1926, **20**, 3091. Cites U. S. P. 1426521, 1521055, 1521056.
3. *Ibid.* U. S. P. 1590783; abst. C. A. 1926, **20**, 3091.
4. M. Theumann and Soc. pour la fabrication de la soie Rhodiaseta, Can. P. 284275; abst. C. A. 1929, **23**, 705.
5. J. Thornton, E. P. 230965, Addn. to 224569. Compare E. P. 5100, 1915; 100629, 187638, 214934, 224571, 224572.
6. W. Todd, Dyer & Calico Printer, 1926, **55**, 112; abst. C. A. 1926, **20**, 2586.

rics[1], by treating selected areas with organic acids or phenols which are solvents or swelling agents, as acetic, lactic, mono- and tri-chloracetic or butyric acids, phenol or cresol. A mixture of lactic acid and feculose is printed on the fabric, and passed over heated surfaces. Products adapted for use as protective colloids or as intermediates in the manufacture of cellulose acetate and nitrate[2] are made by treating dry cellulose with sulfur trioxide until 50% of it has combined with the cellulose. Wood, straw, or starch may be similarly treated, and fuming sulfuric acid may be used. The sulfuric acid derivatives formed have low copper numbers, and give highly colloidal solution. Cellulose trisulfate A, a similar product[3], has been described. A general X-ray investigation of cellulose acetates has been made by J. Trillat[4] (see p. 232, n. 4). Cellulose acetates show the presence of well-defined crystals in an amorphous phase[5], the latter increasing at the expense of the former when the higher acetylated products are destroyed by hydrolysis. The structure of the haloes is dependent on the amount of acetyl radical present, and changes progressively as acetylation proceeds. M. Trimmer[6] has tabulated the properties of the plasticizers tricresyl phosphate, dibutyl, diamyl and diethyl phthalates, dibutyl tartrate, triacetin and camphor.

Hydrocellulose with anhydrous formic acid and sulfuric acid yields a product containing 22.9% formic acid (theory for monoformate 24.21%), while the product re-

1. Tootal Broadhurst Lee Co., Ltd., and R. Foulds, E. P. 263248; abst. C. A. 1928, **22**, 172; J. S. C. I. 1927, **46**, 185-B; Silk J. 1927, **4**, 35, 75.

2. W. Traube, E. P. 294572; abst. C. A. 1929, **23**, 2034; J. S. C. I. 1930, **49**, 99-B.

3. W. Traube, B. Blaser and C. Grunert, Ber. 1928, **61**-B, 754; abst. C. A. 1928, **22**, 4793; J. S. C. I. 1928, **47**, 621-A.

4. J. Trillat, Rev. gen. Colloides, 1928, **6**, 57; abst. C. A. 1928, **22**, 4244; C. A. 1929, **23**, 971. Rev. gen. Colloides, 1928, **6**, 177; abst. Pulp & Paper Mag. 1929, July 25, p. 151.

5. *Ibid.* Compt. rend. 1928, **186**, 859; abst. C. A. 1928, **22**, 3043; J. S. C. I. 1928, **47**, 466-A; Pulp & Paper Mag. 1929, Jan. 3, p. 16.

6. M. Trimmer, Chemicals, Aug. 30, 1926.

generated from viscose[1] contains 50.5% (cellulose triformate requires 56.9%). The ester is readily soluble in pyridine, only sparingly soluble in other solvents. In the catalytic hydration of propylene oxide or other organic oxides containing the olefinic oxide group to form glycols[2], just sufficient water is used to react with the oxide present. A hydrating catalyst as sulfuric acid may be used. In ester production[3], a mixture containing a constant boiling solution of ethyl acetate, water and alcohol is brought into contact with a body of water, thereby forming two layers of liquid containing respectively high and low percentage of ester. E. Valet and O. Funk[4] advocate prepared cellulose from cane sugar bagasse as suitable for esterification purposes.

As cellulose ester plastifying agents, benzyl lactate, tartrate, citrate; methylbenzyl or chlorbenzyl lactates or tolyl ricinoleate, are given as suitable examples of benzyl esters of hydroxy-aliphatic acids[5]. Benzyl lactate is an excellent blending agent for cellulose esters and certain alcohol-soluble resins. In acetic acid recovery in acetylcellulose manufacture[6], the residual acetic acid—without removing the cellulose acetate—is recovered by vacuum distillation of the mixture at temperatures ranging from 50-90°. The remaining solution of cellulose acetate is then precipitated with water to separate the cellulose ester. In

1. Y. Ueda and K. Hata, J. Cellulose Inst. Tokyo, 1928, **4**, 1; abst. C. A. 1928, **22**, 4792; J. S. C. I. 1928, **47**, 399-A. Cellulose Ind. Tokyo, 1928, **4**, 203; abst. C. A. 1929, **23**, 3081; J. S. C. I. 1928, **47**, 1226-A.
2. F. Untiedt, U. S. P. 1641710; abst. C. A. 1927, **21**, 3368.
3. U. S. Industrial Alcohol Co. and A. Backhaus, Can. P. 261187; abst. C. A. 1926, **20**, 2504.
4. E. P. 287461; abst. Silk J. 1928, **5**, #49, 80. See E. P. 277163.
5. R. Van Schaack, U. S. P. 1612669; abst. C. A. 1927, **21**, 649.
6. Verein f. Chemische Industrie A.-G., E. P. 268778; abst. C. A. 1928, **22**, 1473; J. S. C. I. 1928, **47**, 11-B; Plastics, 1928, **4**, 386. For developments in acetic anhydride manufacture in Belgium in 1927, see Belg. P. 348187, 348774, 350179, 350271, 351362, 351783, 352640, 352641, 352821, 352964, 353110, 353145, 353792, 354653, 355665.

another process[1] the precipitated acetylcellulose is pressed to remove acetic acid and then washed and pressed to remove wash water, the material being finally dried. From solutions of cellulose in acetic acid[2], the latter may be driven out and recovered with a current of steam or dilute acetic vapors at reduced pressure. Or[3], a solution of acetylcellulose containing acetic acid is mixed with a saturated solution of sodium or potassium acetate or magnesium sulfate to form a jelly, and this is then gently pressed to exude liquid rich in acetic acid. The jelly is repeatedly moistened and pressed to remove further amounts.

While viscose rayon stretched prior to dyeing, or under tension during the dyeing[4], tends to give lighter shades than the unstretched yarn with most dyestuffs, acetate silk does not show nearly as much difference in shade, with and without tension. Dilute acetic acid is concentrated by distillation with an acetic ester boiling between 105-135°, as butyl, *iso*butyl or *iso*amyl acetates[5]. In the preparation of acetone-soluble acetylcellulose[6], the acetic acid may be recovered by treating the acid liquid with mixture of hydrocarbons or their chlorine derivatives, which precipitate acetylcellulose but dissolve acetic acid, as dichlorethylene.

A clear acetylcellulose lacquer is obtained by dissolving the ester in a mixture of one or more chlorinated hydrocarbons with two or more alcohols[7], as di- or tetrachlor-ethylene with methyl or butyl alcohols or methyl acetate. A method of identification of acetylcellulose and other textile

1. Verein f. Chemische Industrie A.-G., E. P. 269543; abst. C. A. 1928, **22**, 1473; J. S. C. I. 1928, **47**, 228-B; Plastics, 1928, **4**, 146. Swiss P. 126410; abst. Plastics, 1929, **5**, 631; C. A. 1929, **23**, 704. Belg. P. 355389. F. P. 632619; abst. C. A. 1928, **22**, 2528.
2. Verein fur Chemische Industrie A.-G. and E. Loew, D. R. P. 463871; abst. C. A. 1928, **22**, 4246.
3. Vereinigte Glanzstoff-Fabriken A.-G., and F. Paschke, E. P. 235727; abst. C. A. 1926, **20**, 988; J. S. C. I. 1925, **44**, 986-B.
4. Viskex, Silk J. 1928, **5**, #52, 59; abst. C. A. 1929, **23**, 1753.
5. Wacker Ges. fur Elektrochemische Ind. Ges., E. P. 298137; abst. C. A. 1929, **23**, 2724; J. S. C. I. 1930, **49**, 95-B. Can. P. 245985.
6. *Ibid.* D. R. P. 473833; abst. C. A. 1929, **23**, 3098.
7. *Ibid.* D. R. P. 488989; abst. C. A. 1930, **24**, 2316. Belg. P. 354852.

fibers has been evolved[1], using Picrocarmin K in an aqueous solution of ammonium phosphate and sodium carbonate. Acetate silk is colored intense yellow-green, degummed silk, red; nitro-silk, viscose and cotton, rose; and copper-ammonia rayon, wine-red. The J. Watson cross-dyeing process for cellulose and cellulose esters[2] appeared in 1927.

A process for cellulose acetylation involving employment of phosphorous halides as catalytic material[3], comprises distributing red phosphorus homogeneously through an acetylating bath containing acetic acid and anhydride, and treating cellulose in the bath in the presence of chlorine until the degree of esterification desired has been arrived at. An artificial ebonite was patented in 1928, prepared by admixing acetylcellulose with fillers and softening agents, then malaxated and finally dried and reduced to fragments[4]. Articles are made from this mass by pressing in heated steel molds. The S. Wein light-sensitive electrical resistance device[5], comprises selenium in solution, which is spread upon a support as a glass sheet, the surface of which has been treated with acetylcellulose solution and the solvent then evaporated therefrom to leave a film on the surface which may be annealed, this preliminary surface treatment serving for the protection and uniformity of the film.

To prevent or minimize shrinking or crinkling in the developing baths of films of acetylcellulose, admixed with aryl phosphates, aryl ethers and alcohols[6], the film base is treated for six hours or longer, and before it is coated with sensitive gelatin emulsion, with water at a temperature not

1. W. Wagner, Melliand's Textil. 1927, **8**, 246; abst. Rayon, 1927, **5**, #7, 24; Chem. Zentr. 1927, I, 2695.
2. U. S. P. 1629769; abst. C. A. 1927, **21**, 2388. Cites U. S. P. 1448251, 1575958. D. R. P. 217477, 220173, 237262, 239314.
3. W. Webb and C. Malm, U. S. P. 1591590; abst. C. A. 1926, **20**, 3236; J. S. C. I. 1926, **45**, 783-B; Plastics, 1927, **4**, 38.
4. K. Wegner, F. P. 644011; abst. C. A. 1929, **23**, 2569.
5. S. Wein, U. S. P. 1601607; abst. C. A. 1926, **20**, 3654.
6. L. Weston, E. P. 293269.

exceeding 70°. The E. Wheeler wire conductor[1] is fireproofed by a covering consisting of finely divided selenium and cellulose acetate. In a study of organophile colloids[2], it developed that the cellulose esters of the higher acids are less polar than the cellulose acetates and nitrates, and are dissolved by the less polar solvents. G. Whitby[3] has given extensive physical data concerning *b*-butyryl, *b*-propionyl, *b*-palmityl and *b*-stearyl dichlorhydrin; methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *iso*amyl, benzyl and *n*-octyl stearates and palmitates; propionic, butyric, palmitic and stearic anhydrides; cetyl and stearyl palmitate and stearate; and butyro-, stearo-, and palmito-distearin and -dipalmitin.

In the manufacture of foils for cigarette mouthpieces[4] (see p. 296, n. 4; 367, n. 2; 384, n. 1; 425, n. 6), finely pulverized mica is mixed with acetylcellulose, and the mixture brought onto a width of paper or upon a transparent ribbon. Acetaldehyde results when ethyl alcohol vapor is passed over a copper alloy maintained at a high temperature below that at which it deteriorates rapidly, but above that at which the alloy is relatively inactive[5]. A stencil sheet has been described[6], comprising an acetylcellulose dissolved in acetone and another solvent, glycerol and resin being added and the whole digested to form a homogeneous impregnating substance.

Acetylcellulose paints have been brought forward[7], containing lead and other pigments very finely ground and

1. E. Wheeler, U. S. P. 1689311; abst. C. A. 1929, **23**, 223; J. S. C. I. 1929, **48**, 62-B; Plastics, 1929, **5**, 636.
2. G. Whitby, Can. Chem. Met. 1925, **9**, 265.
3. *Ibid.* J. C. S. 1926, **129**, 1458.
4. F. Wickel, E. P. 269194; abst. C. A. 1928, **22**, 1474; Chem. Zentr. 1927, II, 656.
5. C. Williams, U. S. P. 1555539; abst. C. A. 1925, **19**, 3490; J. S. C. I. 1925, **44**, 971-B.
6. D. Williams and J. Rowe, Can. P. 264211; abst. C. A. 1926, **20**, 3787. U. S. P. 1795461.
7. H. Wolff and R. Singer, E. P. 293732; abst. C. A. 1929, **23**, 1763.

incorporated therein, and containing small amounts of picric acid and fatty acids. In dyeing union goods containing acetylcellulose silk[1], 1.5% magnesium sulfate is added to the dyebath to conserve the luster. Thiocellobiose and thiocellobiosides have been described[2].

In preparing esters as ethyl acetate and butyl butyrate[3], anhydrous aldehyde is brought into contact with a catalyst comprising the aluminum alkoxy derivative of ethyleneglycol monoethyl ether. The preferred solvent for cellulose acetate of G. Young[4] is ethyleneglycol diacetate, excellent for preventing blushing in airplane dopes. He has detailed directions for acetylcellulose application in airplane dope manufacture[5]. Esters of furoylacetic acid (methyl, *n*-propyl, and *n*-butyl)[6], have a slight softening action upon some forms of cellulose acetate.

1. K. Wolfgang, Kunstseide, 1928, **10**, 117; abst. C. A. 1928, **22**, 4255; J. S. C. I. 1928, **47**, 744-B. See E. P. 246879.

2. F. Wrede and O. Hettche, Z. physiol. Chem. 1928, **172**, 169; abst. J. S. C. I. 1928, **47**, 621-A. Cellobiose bromide hepta-acetate in hot alcohol reacts with methyl-alcoholic potassium disulfide to give *dicellobiosyl disulfide tetradeca-acetate*, m. p. 271-273°, which is hydrolysed by methyl-alcoholic ammonia to *dicellobiosyl disulfide*, decomp. 165-170°, or is reduced and acetylated by zinc dust and acetic anhydride to *thiocellobiose octa-acetate*, m. p. 205°. *Thiocellobiose hepta-acetate*, m. p. 197°, obtained by reduction of the disulfide tetradeca-acetate in phenol by aluminum amalgam and aqueous-alcoholic acetic acid, gives by methylation with diazomethane the *methyl ether hepta-acetate*, m. p. 200°, from which *methylthiocellobioside*, m. p. 220°, is prepared by hydrolysis; the *ethyl ether hepta-acetate*, m. p. 193°, and *ethylthiocellobioside*, m. p. 219°, are similarly obtained. *Thiocellobiose*, $C_{12}H_{22}O_{10}S$, prepared from the octa-acetate and methyl-alcoholic ammonia, sinters about 110°; the *silver* salt gives, by treatment with methyl iodide followed by acetylation, the above methyl ether hepta-acetate.

3. C. Young, U. S. P. 1630593; abst. C. A. 1927, **21**, 2273. Can. P. 267894; abst. C. A. 1927, **21**, 1660.

4. G. Young, U. S. P. 1522852; abst. C. A. 1925, **19**, 894; J. S. C. I. 1925, **44**, 202-B.

5. *Ibid.* Aviation, April 23, 1928, p. 1149.

6. J. Zanetti and C. Beckmann, J. A. C. S. 1928, **50**, 1438; abst. J. S. C. I. 1928, **47**, 766-A.

Directly spinnable cellulose acetate acetylation solutions or mixtures are rendered stable as to viscosity by adding a stabilizer (water, methyl alcohol, ethyl alcohol, amyl alcohol, lactic or formic acids)[1] (see p. 590, n. 1). Solutions thus prepared remain in spinnable condition for several weeks. Or[2], the acetylation mixture may first be chlorinated, an ester containing 20-30% acetyl being obtained, the chlorine remaining in the solution being utilized by adding sulfur dioxide or trioxide or an oxide of phosphorous. Acetylation is completed by the addition of a very small quantity (0.01-0.1%) of sulfuric acid. Acetylcellulose solutions may be stabilized by the addition of tetrachlorethane[3]. To prevent development of undue stresses during the drying of the thread[4], freshly coagulated acetylcellulose filaments are wound on a resilient bobbin or spool, at the same time means is provided whereby the initial tension of winding is automatically increased slowly and continuously as the drying proceeds.

Directly spinnable acetylcellulose solutions result by treating cellulose with acetic anhydride until a disintegrated paste forms[5], which is then treated with a strong condensing agent. D. Zwartz[6] in 1927 detailed methods of cellulose acetate artificial filament manufacture.

1. J. Zdanowich, E. P. 227134; abst. C. A. 1925, **19**, 2751; J. S. C. I. 1925, **44**, 202-B; Rayon J. 1926, **1**, #1, 55. Can. P. 252565; abst. C. A. 1925, **19**, 3373. Cites E. P. 139232, 190732, 196641, 200186, 203599. Can. P. 261525.

2. *Ibid.* E. P. 244148; abst. C. A. 1927, **21**, 1321; J. S. C. I. 1926, **45**, 152-B; Caout. et Gutta. 1926, **23**, 13315. U. S. P. 1600159; abst. C. A. 1926, **20**, 3567; J. S. C. I. 1926, **45**, 1010-B. Can. P. 258763; abst. C. A. 1926, **20**, 2411. Swiss P. 121353.

3. *Ibid.* Can. P. 258765; abst. C. A. 1926, **20**, 2411; Rayon J. 1926, **1**, #3, 53. Aust. P. 105804; abst. Kunstseide, 1927, #6, 424.

4. *Ibid.* 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.

5. *Ibid.* Can. P. 258769; abst. C. A. 1926, **20**, 2412.

6. D. Zwartz, Indian Textile J. **37**, 266; Chem. Zentr. 1927, II, 1419; abst. C. A. 1928, **22**, 4797. See Swiss P. 70135.

Advancement in Acetylcellulose Art for the Year 1929. The year 1929 was especially prolific in the number and relative importance of contributions, both as to wideness of field embraced and their individual merit. H. Bassett and T. Banigan[1] take an acetylating solution containing acetylnitrocellulose and treat it with glacial or dilute acetic acid to reduce the consistency to a point just short of precipitation, using this to spin through a precipitating bath without removing it from the solution, for artificial filament formation.

C. Aberle[2] has contributed an article on the use of Celta, Glamat and Opago rayon in the knitting industry, while Aceta[3] describes the application of nitroacetylcellulose fibers with wool containing about 1-2% N and acid equivalent to about 54% acetic acid. It is said that such a mixture may be subjected to the ordinary hot vat treatments such as are used in wool dyeing, and to carbonization as with aluminum chloride, without damage.

The Acetex safety glass[4] comprises a composite sheet of a cellulose acetate derivative which is fixed between two sheets of glass by dampening the composite sheet with a plastifying agent or solvent of high boiling point, passing the sheets together by means of an inert gas under pressure followed by steam, the temperature of the latter being kept below the boiling point of the plastifying agent. The Aktiengesellschaft f. Stickstoffduenger[5] rapidly prepare acetic anhydride by treating acetic acid with carbonyl chloride in the presence of compounds of metals, the chlorides of which are transformed into acetates when boiled with acetic acid, examples being given of the use of aluminum chloride and magnesium acetate. R. Allgeier, W. Peterson

1. U. S. P. 1709513; abst. C. A. 1929, **23**, 2822; J. S. C. I. 1929, **48**, 774-B; Plastics, 1929, **5**, 390.
2. Jentgen's Rayon Review, 1929, **2**, 218.
3. E. P. 319354; abst. C. A. 1930, **24**, 2616; J. S. C. I. 1930, **49**, 943-B.
4. Acetex Safety Glass, Ltd., F. P. 677389; abst. C. A. 1930, **24**, 3095.
5. F. P. 669150; abst. C. A. 1930, **24**, 1652.

and E. Fred propose to produce acetic and lactic acids from mill sawdust[1].

The Alloy Welding Processes and E. Jones[2] provide the coating of a metallic arc-welding electrode with an impermeable film formed by dipping the coated electrode in a cellulose acetate varnish. The American Cyanamid Co. have described esters of aliphatic *a*-hydroxy *iso*-acids such as ethyl *a*-hydroxy*iso*butyrate with cellulose acetate in the formation of varnishes and lacquers, the esters being formed by reaction between a ketone and a cyanide or a ketone cyanohydrin and an alcohol[3].

Certain effects produced on commercial photographs, such as shadings and line backgrounds[4], and known as "Ben Day" effects, may be quickly created by the use of thin, transparent sheets of cellulose acetate on which a design is printed. The design is claimed to be quite stable with ordinary handling, yet may instantly be removed in whole or in part. It appears that union between a urea-aldehyde resin and a cellulose filling material such as wood flour may be obtained by incorporating with them a proportion of cellulose acetate stable at the temperature of moulding, a plastifier being also used as a dialkylester of an organic acid[5].

In the method of carbon paper manufacture as disclosed by M. Bandli[6], an acetone solution of cellulose acetate in admixture with suitable softening material and optionally containing undissolved cellulose in a fine state of subdivision, is used for applying the coloring medium to the paper. Results have been published[7] on the comparative

1. J. I. E. C. 1929, **21**, 1039; abst. C. A. 1930, **24**, 459.
2. E. P. 303996; abst. C. A. 1929, **23**, 4437. See Alloy Welding Processes, Ltd., and E. Clarke, E. P. 301221; abst. C. A. 1929, **23**, 3896.
3. American Cyanamid Co., E. P. 312469; abst. C. A. 1930, **24**, 961.
4. C. Anderson, Bull. Phot. Mar. 27, 1929, **44**, 389.
5. Bakelite Corp., F. P. 670841; abst. C. A. 1930, **24**, 1946. See L. Redman, U. S. P. 1732533; abst. C. A. 1930, **24**, 253.
6. E. P. 307714; abst. J. S. C. I. 1929, **48**, 470-B.
7. G. Baker, R. Edgar and K. Cranor, Rayon, 1929, **8**, #12, 7, 22; abst. C. A. 1929, **23**, 5324.

effects of laundering and dry cleaning rayons made from cellulose acetate, viscose and cuprammonium cellulose.

J. Beard[1] points out a new use for cellulose acetate plastics in the manufacture of molded tops for soda water syphons in the place of the metal ones usually employed. In producing colored photographs by the subtractive method[2], transparent, permeable cellulose acetate films are recommended, which are sensitized in the mass with substances producing colored images[3] or by the use of diazo compounds with coupling agents[4], but without the use of substances which produce an image with grains of opaque matter[5].

According to E. Beckett and J. Thomas[6] dyes are formed by nitrating a diphthalimidoanthraquinone such as 1.5-diphthalimidoanthraquinone, and then treating the product with an alkaline sulfide and a hydrolyzing agent such as sulfuric acid, the dyes obtained being suitable for producing blue shades on cellulose acetate. M. Bergmann and F. Koch[7] have described the preparation of mixed acetylated sugars, tribenzoyl-*b*-glucosan being converted into acetyltribenzoylglucose bromhydrin, and this into either 6-acetyl-2:3:4-tribenzoyl-*b*-methylglucoside or 1:6-diacetyl-2:3:4-tribenzoylglucoside. In the production of acetic anhydride from acetic acid, E. Berl[8] passes the latter in the vapor form over asbestos or pumice carrying copper or silver chloride, hydroxide or carbonate, which are capable of checking a too extensive decomposition of the acetic acid

1. Brit. Plastics, 1929, **1**, 250.
2. W. Becker, L. Oliver, H. Murray and Colour Photographs (British & Foreign), Ltd., E. P. 317911; abst. C. A. 1930, **23**, 2071. See L. Dufay, F. P. 651196; abst. C. A. 1929, **23**, 3176.
3. As described by M. Martinez, E. P. 280252; abst. C. A. 1928, **22**, 2891.
4. Kalle & Co., A. G., E. P. 234818; abst. C. A. 1926, **20**, 716. See Kalle & Co., A. G., E. P. 210862; abst. C. A. 1924, **18**, 1619.
5. W. Becker and L. Oliver, E. P. 317909; abst. C. A. 1930, **24**, 2071.
6. U. S. P. 1711873; abst. C. A. 1929, **23**, 3353.
7. Ber. 1929, **62B**, 311; abst. J. S. C. I. 1929, **48**, 428-A.
8. F. P. 670659; abst. C. A. 1930, 1869. E. P. 344482. Can. P. 295437.

molecule. J. Bert[1] has given a series of formulas for discharge and resist printing on celanese dyed with S. R. A. colors.

In the treatment of fabrics consisting of or containing acetyl silk, luster pattern effects are said to be obtained by completely delustering the fabric, and then embossing in the usual manner at about 150°, the fabric then being preferably wetted and lightly calendered whereby the embossing marks are removed[2]. In an extension of this process[3], the cellulose acetate fabrics are impregnated with a solvent such as ethyl acetate or lactate, lactic or acetic acids or ethylene glycol monoethyl ether, and then embossed. Two tone effects in dyeing may thus be obtained. C. Boehringer & Son[4] in order to obviate general or localized overheating in the acylation of cotton, while still retaining the fibrous structure, hold the temperature under 30°, and add a volatile substance such as sulfur dioxide or hydrocarbons, which does not react with cellulose but may act as a catalyst.

The H. Boehme A. G.[5] have patented a dressing and sizing preparation for artificial silk composed of a solution of methylated cellulose with suppleness-inducing agents. H. Bradshaw[6] coats the rear side of a cellulose film base with a layer of cellulose carbamate (cellulose phenylurethane) to overcome static electrical charges. H. Brandenburger has contributed a series of four articles on acetate

1. Dyer & Calico Printer, 1929, **61**, 75; abst. C. A. 1929, **23**, 2829.

2. Bleachers Assoc., Ltd., W. Kershaw, F. Barrett and R. Gaunt, E. P. 303286, Addn. E. P. 311306; abst. J. S. C. I. 1929, **48**, 204-B; C. A. 1929, **23**, 4581; Silk J. 1929, **5**, #59, 74. F. P. 660022; abst. C. A. 1930, **24**, 249. In this connection see their E. P. 301567, 301568; abst. J. S. C. I. 1929, **48**, 127-B.

3. 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.

4. E. P. 312242; abst. J. S. C. I. 1931, **50**, 108-B; C. A. 1930, **24**, 903. Belg. P. 371220.

5. F. P. 685994; abst. C. A. 1930, **24**, 6035. See also their F. P. 679185; abst. C. A. 1930, **24**, 3911.

6. U. S. P. 1703470; abst. J. S. C. I. 1929, **48**, 378-B.

silk[1], the dyeing of acetate rayon[2], the relative fastness to washing of dyed acetate rayon[3], and the use of Setacyl direct dyes in the acetate rayon art[4].

In the patented photographic film of K. Bratring[5], a supporting layer of cellulose hydrate is secured to the gelatin side of a film after it has passed through all of the baths, a cellulose ester base of reduced thickness being used for the taking and completion of the film. In a repetition of the work of K. Hess, H. Friese and F. Smith[6] on the acetates of rice and potato starch, and contrary to many of the conclusions of E. Peiser[7], it has been found by B. Brigl and R. Schinle[8] that when rice starch is swollen with hot water, precipitated by alcohol and dried, then heated with pyridine and acetic anhydride at 80° until a transparent jelly results, a starch triacetate is formed which is soluble in chloroform, *s*-tetrachlorethane and glacial acetic acid, giving solutions which are very viscous, even when dilute. The acetate apparently has a high molecular weight since it does not appreciably increase the boiling point of chloroform. In glacial acetic acid, the starch acetate does not dialyze under conditions whereby the acetates of dextrose, sucrose and maltose readily pass through the membrane.

A superior solution for coating of surfaces is claimed to result when a solution of a polyhydric phenol as resorcinol

1. Jentgen's Art. Silk Review, 1929, **2**, 115.
2. Kunstseide, 1929, **11**, 98, 144, 300, 338, 425; 1930, **12**, 51; abst. C. A. 1929, **23**, 4575; 1930, **24**, 1985. Melliand Textilber. 1929, **10**, 215; abst. C. A. 1929, **23**, 4575. Zts. ges. Textil-Ind. 1929, **32**, 356; abst. C. A. 1930, **23**, 6022. See also H. Brandenburger, Zts. ges. Textil-Ind. 1930, **33**, 151; abst. C. A. 1930, **23**, 5502.
3. Rayon, 1929, **8**, No. 8, 16, 39; abst. C. A. 1930, **24**, 242. Melliand Textilber. 1929, **10**, 227; abst. C. A. 1929, **23**, 4575.
4. Melliand Textilber. 1929, **10**, 869; abst. C. A. 1930, **24**, 3373.
5. E. P. 307431; abst. J. S. C. I. 1930, **49**, 840-B; Brit. Plastics, 1930, **2**, 17, 229. D. R. P. 489261; abst. C. A. 1930, **24**, 2073. K. Bratring and A. Giebmanns, D. R. P. 519137; abst. C. A. 1931, **25**, 2848.
6. Ber. 1928, **61B**, 1975; abst. J. S. C. I. 1928, **47**, 1225-A.
7. Zts. Physiol. Chem. 1927, **167**, 88; abst. J. S. C. I. 1927, **46**, 753-A.
8. Ber. 1929, **62B**, 99; abst. J. S. C. I. 1929, **48**, 299-A.

in furfural is combined with a plasticizer as triphenyl phosphate and a toughening agent as cellulose acetate[1].

By far the greater number of patented processes appeared during the year from the British Celanese, Ltd., and their interests. A summation of them is embraced in the subject matter constituting the succeeding 88 separate notes. In the production of coated articles, intimate pulverulent mixtures of finely divided cellulose acetates with plasticizers[2] as prepared according to specific directions[3], and in the absence of volatile solvents and water, are applied to sheets or other articles and caused to coalesce under a heat of 50-80° and a pressure of 300-500 lb. per sq. in. to form adherent coatings. To raise the ironing temperature of cellulose acetate textiles[4], the material is treated at 70-90° with a solution containing 0.3-0.7 gms. per liter of caustic soda, the alkalinity being maintained within these limits by addition of NaOH from time to time, whereby a regular and partial (not more than 6%) hydrolysis of the cellulose ester takes place.

Cellulose acetate sheets or articles may be coalesced[5], when ground with plasticizers in a finely divided state[6], by applying a combination of heat and pressure to the articles to be cemented. Carrying this idea out in the manufacture of laminated or splinterless glass[7], glass having a high quartz content and cellulose acetate, preferably using the ester in a powder form, are mixed with sufficient appro-

1. British Thomson-Houston Co., Ltd., A. Ward and G. Bray, E. P. 320649; abst. C. A. 1930, **24**, 2562; J. S. C. I. 1929, **48**, 1023-B; Brit. Plastics, 1930, **1**, 221.

2. British Celanese, Ltd., E. P. 303898; abst. J. S. C. I. 1930, **49**, 571-B.

3. British Celanese, E. P. 282723; abst. J. S. C. I. 1928, **47**, 853-B.

4. British Celanese, Ltd., E. P. 304596; abst. C. A. 1929, **23**, 4832; J. S. C. I. 1929, **48**, 1012-B; Silk J. 1929, **5**, 66. See C. Dreyfus, E. P. 309377; abst. C. A. 1930, **24**, 735.

5. British Celanese, Ltd., E. P. 305992; abst. C. A. 1929, **23**, 5021; J. S. C. I. 1930, **49**, 656-B; Brit. Plastics, 1930, **2**, 135.

6. British Celanese, Ltd., E. P. 282723; abst. J. S. C. I. 1928, **47**, 853-B.

7. British Celanese, Ltd., E. P. 306397; abst. J. S. C. I. 1930, **49**, 714-B; Brit. Plastics, 1930, **2**, #16, 185.

priate plasticizer to produce the sheet *in situ*, the whole being pressed under 300-500 lb. per sq. in. at 50-80° (preferably 70°) until consolidated. A valuable lacquer and coating composition results[1] by combining cellulose acetate and a furfuraldehyde-acetone resin (produced by alkaline condensation), and which is said to give clear, adherent films. Similarly, coating compositions of cellulose acetate with synthetic resins produced from aniline and furfural[2], or furfural condensed with toluidine, xylidine, naphthylamine or from substituted amine such as nitroaniline are useful. Or synthetic resins produced from phenol and furfural, acetone and furfural[3], or a "natural" or semi-synthetic resin may be combined with cellulose acetate, either with or without the addition of plastifying agents[4].

In the preparation of netting, gauze, fabric or other open work of reticulated material a homogeneous mixture of cellulose acetate and synthetic resin is employed, the latter being of the phenol-aldehyde, ketone-phenol-aldehyde, phenol-furfuraldehyde, aromatic amine-furfuraldehdye or ketone-furfuraldehyde types[5]. In the preparatory treatment of cellulose for esterification purposes[6], cotton linters or wood pulp are said to be rendered more suitable for subsequent use by a treatment with hydrofluoric acid. Or[7], coincidental with this treatment with HF may be submission of the cellulose to hot vapors of acetic or formic acids, so that the vapors condense within the cellulosic material. As a glass substitute, iron or steel wire netting is coated

1. British Celanese, Ltd., E. P. 307289; abst. J. S. C. I. 1930, **49**, 469-B; Brit. Plastics, 1930, **2**, #13, 52 Suppl.; abst. C. A. 1929, **23**, 5338.
2. W. Moss and B. White, E. P. 307290; abst. C. A. 1929, **23**, 5338. See also W. Moss, E. P. 303169; abst. C. A. 1929, **23**, 4582.
3. W. Moss and B. White, E. P. 307291; abst. C. A. 1929, **23**, 5338.
4. W. Moss, E. P. 307292; abst. C. A. 1929, **23**, 5338.
5. W. Moss, E. P. 307462; abst. C. A. 1929, **23**, 5285; J. S. C. I. 1930, **49**, 205-B; Brit. Plastics, 1930, **1**, #10, 446.
6. British Celanese, Ltd., E. P. 308348; abst. J. S. C. I. 1930, **49**, 610-B; Brit. Plastics, 1930, **2**, #15, 135; Silk J. 1929, **6**, #62, 70.
7. H. Dreyfus, E. P. 263938; abst. J. S. C. I. 1927, **46**, 247-B. See H. Dreyfus, E. P. 249173; abst. J. S. C. I. 1926, **45**, 436-B.

with a solution of wholly or partially polymerized vinyl compound resin with cellulose acetate[1], polymerization of the former substance being completed, if desired, after application of the coating material.

It has been found that acetate filaments and yarns may be temporarily colored, continuously with their production, by passing over wick, pad or roller supplied with a tinting fluid consisting of a fugitive coloring matter, a non-drying animal, vegetable or mineral oil, and a sulfonated oil[2].

Compositions useful as plastic masses or in the manufacture of artificial filaments, films and dopes are prepared by incorporating with cellulose esters, an arylsulfonamide or alkyl derivative thereof[3], particularly benzene- or toluene-sulfonanilid or their *N*-methyl derivatives. To raise the safe ironing temperature of acetate rayon material[4], the addition of further quantities of alkali as NaOH is said to be obviated by the use, at the commencement, of a quantity of alkali solution greater than 120 times the weight of the material to be treated, i.e., 130-160 times such weight[5]. Especially valuable plastic compositions are said to be producible from cellulose acetate when a specified viscosity ester is used, and combined with a plastifier also of known viscosity in the amount combined therewith[6]. If the cellulose acetate is to exhibit an improved or complete resistance to the delustering action of hot aqueous media, ethyl alcohol (not methyl) may be used. However, methyl alcohol may be added to a cellulose acetate solution for dry spinning of artificial silk in order to reduce the viscosity of the solution and facilitate drawing out of the filaments (tension spin-

1. British Celanese, Ltd., E. P. 308587, Addn. to E. P. 307462; abst. C. A. 1930, **24**, 239; J. S. C. I. 1930, **49**, 99-B; Brit. Plastics, 1930, **1**, #10, 446.
2. British Celanese, Ltd., E. P. 308733; abst. J. S. C. I. 1930, **49**, 1063-B.
3. G. Schneider, E. P. 308798; abst. C. A. 1930, **24**, 498.
4. C. Dreyfus, E. P. 304596; abst. C. A. 1929, **23**, 4832.
5. C. Dreyfus, E. P. 309377, Addn. to E. P. 304596; abst. C. A. 1930, **24**, 735; Silk J. 1929, **6**, #63, 66.
6. G. Schneider, E. P. 310045; abst. C. A. 1930, **24**, 725; Silk J. 1929, **6**, #63, 68.

ning) during manufacture[1]. In order to obtain a differential delustering effect on fabrics containing cellulose acetate[2], so that after treatment with delustering agents such as wet steam, hot soapy or other aqueous solutions, one fiber or series of fibers may be made of one kind of acetylated cellulose, and the balance of a cellulose acetate exhibiting different physical properties.

In the carbonization of a fabric presenting lace-like, gauze-like or open-work effects[3], fabrics composed of mixtures of cellulose acetate with cotton, linen or reconstituted cellulose may be used[4]. A valuable resinous combination is said to result by the admixture with cellulose acetate of lactic acid, preferably of 90%, when heated under reflux for several hours, and the volatile matter then distilled off[5]. Or, a plastic or celluloid-like molding composition having a base of cellulose acetate[6], may be manufactured by incorporating, at any convenient stage and with or without the use of volatile solvents, one or more esters of aromatic sulfonic acids of the formula $R.SO_2.OR'$, where R is an aryl radical and R′ an aryl or alkyl hydrocarbon group containing at least two carbon atoms. To reduce the inflammability of organic cellulose esters[7] there is incorporated therein one or more aromatic compounds containing bromo-substituted aliphatic side chains, e.g., benzyl bromide, benzylidene bromide, in the proportion of 2-40 parts to 100 parts of the cellulose derivative. If cellulose acetate silk is hydrolyzed with an alkali or base in the presence of ethyl alco-

1. C. Dreyfus and W. Whitehead, E. P. 310046; abst. J. S. C. I. 1930, **49**, 943-B; Silk J. 1929, **6**, #63, 68; C. A. 1930, **24**, 725.
2. C. Dreyfus and W. Whitehead, E. P. 310845; abst. C. A. 1930, **24**, 734; Silk J. 1929, **6**, #63, 68.
3. British Celanese, Ltd., E. P. 274074; abst. J. S. C. I. 1928, **47**, 811-B.
4. C. Dreyfus, H. Platt and R. Dort, E. P. 310936, Addn. to E. P. 274074; abst. C. A. 1930, **24**, 734; J. S. C. I. 1930, **49**, 318-B.
5. British Celanese, Ltd., E. P. 311657; abst. J. S. C. I. 1930, **49**, 1039-B.
6. British Celanese, Ltd., E. P. 312688; abst. J. S. C. I. 1930, **49**, 985-B.
7. British Celanese, Ltd., E. P. 313134; abst. J. S. C. I. 1930, **49**, 1061-B.

hol[1], or particularly glycol or other polyhydric alcohol[2], it has been found possible to hydrolyze 95% of the ester content of the cellulose acetate, using an amount of NaOH theoretically sufficient to hydrolyze but 3% of the ester, alkali ethoxides as sodium methoxide, sodium ethoxide being preferred hydrolyzing agents.

The ironing temperature of cellulose acetate fabrics may be raised and at the same time colored by treatment with a logwood dye and then with an oxidizing solution such as sodium bichromate and acetic acid[3]. An acetate fabric dyed a full black in this manner may be ironed with safety at 240-260°. 1.75% sodium bichromate solution acidified with 1% acetic acid at 60° for 20 minutes is recommended. In order to obtain self-lubricated acetate yarns which are readily scoured and dyed[4], cellulose acetate is dissolved in solvent mixtures consisting of acetone with 1-30% of a glycol or other polyhydric water-soluble alcohol, under such conditions that a substantial portion of the latter is retained in the product.

It has been discovered that when cellulose acetate yarns or fabrics (cellulose acetate, formate, propionate or butyrate) are saponified by means of gaseous or vaporous saponifying agents[5], the materials may possess increased tensile strength and greater power for absorbing moisture in spite of the fact that they have undergone considerable saponification, and may not possess any greater affinity for

1. C. Cross and C. Dreyfus, E. P. 125153; abst. J. S. C. I. 1919, **38**, 427-A.

2. W. Whitehead and C. Dreyfus, E. P. 313404; abst. C. A. 1930, **24**, 1229; J. S. C. I. 1930, **49**, 1107-B; Silk J. 1929, **6**, #65, 80.

3. C. Dreyfus, E. P. 313970; abst. C. A. 1930, **24**, 1227; The Rayon Record, 1930, **4**, #19, 1011. In E. P. 304596, and Addn. E. P. 309377, raising the safe ironing temperature of cellulose acetate textiles may be accomplished by partly saponifying by means of an alkali solution having a hydroxyl-ion concentration insufficient to cause irregular saponification. Or (E. P. 310045) by employing solutions in which the solvent is ethyl alcohol.

4. British Celanese, Ltd., E. P. 313885; abst. J. S. C. I. 1930, **49**, 1146-B.

5. W. Whitehead and C. Dreyfus, E. P. 313971; abst. C. A. 1930, **24**, 1229; Silk J. 1929, **6**, #65, 78.

cotton dyestuffs, but retain their affinity for the dispersed dyestuffs such as the S. R. A. series. Complete saponification may be effected so that they have more or less the dyeing properties of cellulosic materials.

Matte effects are produced on fabrics made of cellulose acetate by applying to them an effect composition containing a water-insoluble thickening agent, an effect material, and a solvent for the thickening agent which is a non-solvent for the cellulose acetate contained in the fabric[1]. Where but a superficial saponification effect is to be produced on cellulose acetate fabrics, this may be modified by using relatively strong solutions (up to 5.2% NaOH)[2] at temperatures below 35°, and white or colored effects may be produced on the materials thus superficially saponified[3]. Pattern effects may be obtained on cellulose acetate by forming thereon an oxidation coloration before or after application of an agent which inhibits the formation of the coloration[4]. Such colorations may be produced by oxidation of amines, e.g. aniline[5], *p*-aminodiphenylamine, and 2:4-diaminodiphenylamine[6], suitable inhibiting agents being sodium and potassium hydroxides and carbonates and sodium phenoxide. To produce discharge effects on cellulose acetate materials[7], other discharging oxidants, e.g., 30% hydrogen peroxide, silver peroxide, nitric acid, acid permanganate, sodium peroxide, but preferably bleaching powder

1. British Celanese, Ltd., E. P. 314396; abst. Silk J. 1929, **6**, #65, 80.

2. British Celanese, E. P. 314447, Addn. to E. P. 304596, 309377; abst. J. S. C. I. 1931, **50**, 292-B; Silk J. 1929, **6**, #66, 68; C. A. 1930, **24**, 1521.

3. C. Dreyfus and H. Platt, E. P. 314446; abst. C. A. 1930, **24**, 1521.

4. British Celanese, Ltd., E. P. 314501; abst. J. S. C. I. 1931, **50**, 390-B; The Silk J. and Rayon World, 1931, **7**, #81, 50.

5. Silver Springs Bleaching & Dyeing Co., Ltd., and A. Hall, E. P. 337746; abst. J. S. C. I. 1931, **50**, 198-B.

6. Silver Springs Bleaching & Dyeing Co., Ltd., and A. Hall, E. P. 259699; abst. J. S. C. I. 1926, **45**, 976. See their E. P. 246879; abst. J. S. C. I. 1926, **45**, 317-B.

7. British Celanese, Ltd., E. P. 315005, Addn. to E. P. 312655; abst. J. S. C. I. 1931, **50**, 292-B.

followed by citric acid, are considered preferable[1] to chlorates previously specified for this purpose.

In the manufacture of cellulose acetate lacquers, the use of solvents which evaporate slowly are recommended[2], such as methylene chloride together with an aliphatic or cyclic alcohol or a polyhydric alcohol. In the production of heat- or sound-insulating jackets, very fine threads of cellulose acetate are advocated[3] on account of the fact that they are non-hygroscopic. It is claimed[4] that the tendency to bleed in the sizing and subsequent de-sizing of cellulose acetate yarns that have been dyed with water-insoluble dyes solubilized by dispersing agents, is reduced by using a size containing glue or gelatin and which is substantially neutral. If it is desired to saponify acetate yarns[5], there is applied to the material a paste composed of an alkali saponifying agent as sodium or potassium hydroxide, carbonate or silicate or trisodium phosphate, the material preferably being quickly dried after application of the paste, and finally steamed.

In the production of protective coatings[6], cellulose acetate is treated with a synthetic resin of the phenol-aldehyde or phenol-ketone type, and subsequently converted into the infusible state[7]. For use in molded articles, films and coatings, the British Celanese[8] recommend compositions comprising cellulose acetate, a synthetic resin condensation product of a toluenesulfonamide and an aldehyde in the presence of a small proportion of urea, and one or more of

1. British Celanese, Ltd., and G. Ellis, E. P. 312605; abst. J. S. C. I. 1929, **48**, 678-B.
2. W. Moss, E. P. 315279; abst. C. A. 1930, **24**, 1740; J. S. C. I. 1931, **50**, 108-B.
3. British Celanese, Ltd., E. P. 315280; abst. J. S. C. I. 1931, **50**, 48-B; British Plastics, 1931, **2**, #21, 432.
4. H.Platt, E.P. 315428; abst. C.A. 1930, **24**, 1750. Can.P. 313857.
5. C. Dreyfus and G. Schneider, E. P. 316521; abst. C. A. 1930, **24**, 1991; Silk J. 1929, **6**, #66, 70.
6. British Celanese, Ltd., E. P. 316984; abst. J. S. C. I. 1931, **50**, 127-B; Brit. Plastics, 1931, **2**, #23, 8.
7. Celanese Corp. of America, E. P. 317026; abst. J. S. C. I. 1929, **48**, 811-B.
8. British Celanese, Ltd., E. P. 317454; abst. J. S. C. I. 1931, **50**, 128-B; Brit. Plastics, 1931, **2**, #23, 529.

the following plasticizers, triacetin, diphenylolpropane, xylylmethylsulfonamide. Another method of producing artificial coatings[1] is combining cellulose acetate with 1-25% of its weight of synthetic resins obtained by the condensation of aldehydic or ketonic substances with phenols, or of sulfonamides with aldehydes. It appears that the luster of acetate silk[2] may be reduced by precipitation therein of a white insoluble substance after pre-treatment with a swelling agent, good results being obtainable by precipitating barium, calcium and strontium carbonates, phosphates or sulfates; formic and acetic acids being suitable swelling agents. Barium thiocyanate acts both as a precipitating and swelling agent.

In the partial saponification of artificial silk from organic cellulose esters (cellulose formate, acetate, propionate, butyrate)[3], the saponifying material together with a thickening agent is applied in limited quantities as by a padding mangle, and afterwards quickly dried. In the manufacture of artificial horsehair, bristles and straw of denier 20-2000[4], from cellulose acetate by the evaporative method, the heavy filaments in the heated metier casing, while still containing solvent, are supported by passing over or around one or more heated feed devices, which rotate each with a linear speed greater than the one preceding. In another method of cellulose acetate artificial filament formation[5], the solutions are extruded through orifices of compact or squat shape, having indentations in the form of re-entrant angles, into a precipitating medium or evaporative atmosphere, or

1. W. Moss and B. White, E. P. 317457; abst. J. S. C. I. 1931, **50**, 128-B; British Plastics, 1931, **2**, #23, 529.

2. British Celanese, Ltd., E. P. 318467; abst. J. S. C. I. 1931, **50**, 347-B.

3. H. Platt and C. Dreyfus, E. P. 318468, Addn. to E. P. 295591; abst. C. A. 1930, **24**, 5497; Silk J. and Rayon World, 1930, **6**, #68, 66.

4. W. Whitehead and C. Dreyfus, E. P. 318630; abst. C. A. 1930, **24**, 2294; J. S. C. I. 1931, **50**, 59-B.

5. W. Whitehead and C. Dreyfus, E. P. 318631; abst. C. A. 1930, **24**, 2293; Silk J. and Rayon World, 1930, **6**, #68, 66; J. S. C. I. 1930, **49**, 985-B.

through a cluster of circular holes, which are so close together that the filaments after extrusion coalesce to form an apparently single thread.

Cellulose acetate yarns may be delustered and rendered opaque without crinkling or distortion by applying tension or stress during the delustering operation[1], as by winding under tension from one reel to another. If heavy filaments as artificial straw, or bristles of 500-200 denier are to be produced[2], dry-spinning solutions containing at least 30% by weight of cellulose acetate are used. It has been found that the presence of the usual size on cellulose acetate yarns used for warp in fabrics does not prevent the satisfactory printing upon them of dyes which have an affinity for this type of artificial silk. Thus for the production of a colored fabric[3], cellulose acetate warp yarn is sized and wound on a beam; it is then suitable printed, dried and woven into fabric, using a weft yarn of any suitable fiber or color.

J. Billing and the British Celanese[4] concentrate acetic acid by two or more solvents so chosen that the preferential extraction of acid rather than water is increasingly marked in successive solvents. For instance, 15-30% acetic acid may be extracted with methylated ether and the resulting 70% acid concentrated to 97-98% by extraction with methylene dichloride or a mixture of ether and light petroleum. Materials consisting of natural silk and cellulose acetate are degummed by heating with an alkaline liquor containing alkali (Na or K) hydroxides, borates, silicates, phosphates, phenolates, cresolates, soap or a sulfonated soap or oil, the *p*H value of which is maintained at 10-10.5

1. British Celanese, Ltd., E. P. 318642; abst. Silk J. and Rayon World, 1930, **6**, #68, 66.
2. W. Whitehead and C. Dreyfus, E. P. 318643; abst. C. A. 1930, **24**, 2294; J. S. C. I. 1931, **50**, 242-B.
3. C. Dreyfus, E. P. 318840; abst. C. A. 1930, **24**, 2617; J. S. C. I. 1931, **50**, 292-B. See H. Platt and C. Dreyfus, E. P. 314501; abst. C. A. 1930, **24**, 1523.
4. E. P. 320606; abst. C. A. 1930, **24**, 2473; J. S. C. I. 1930, **49**, 233-B.

throughout the treatment[1], remembering that if the temperature be raised above 80° the cellulose acetate may be partially or wholly delustered. If the acetate silk[2] is treated with potassium or sodium zincate of such alkalinity as to produce partial hydrolysis, absorption is then assisted by addition of swelling agents. The treated material has affinity for basic acid, mordant or direct dyes, and is particularly suited for production of discharge effects. The acetate silk may also be treated with a tin salt to produce an analogous effect[3].

In the dyeing of cellulose esters[4], photographic or pattern effects are producible on fabrics on films formed from or containing the esters by incorporating one or more diazotizable amines in the material, exposing to the action of light of varying intensity corresponding to the effect desired, and fixing by development. Or[5], if black dyeings are desired, there is oxidized on the materials a mixture of *p*-aminodiphenylamine and aniline uniformly applied with the addition of lactic or acetic acid and a swelling agent such as alcohol with a thickening agent. Catalysts as salts of vanadium, copper or chromium and an after chroming treatment adds to the fastness. In order to color cellulose acetate fabrics uniformly[6], they are locally sprayed with the coloring matter in solution in an organic liquid such as benzene, alcohol, trichlorethylene or carbon tetrachloride. Bright yellow results from 2.4-dinitrodiphenylamine in benzene, heliotrope by diaminoanthraquinone in methylated

1. British Celanese and G. Ellis, E. P. 306067; abst. C. A. 1929, **23**, 5049; J. S. C. I. 1929, **48**, 353-B. See British Celanese and G. Ellis, E. P. 264936; abst. C. A. 1928, **22**, 317.
2. British Celanese, Ltd., and G. Ellis, E. P. 306611, Addn. to E. P. 320775; abst. J. S. C. I. 1929, **48**, 354-B.
3. British Celanese, Ltd., and G. Ellis, E. P. 302775; abst. J. S. C. I. 1929, **48**, 354-B.
4. British Celanese and G. Ellis, E. P. 310773; abst. C. A. 1930, **24**, 733.
5. British Celanese and G. Ellis, E. P. 311435; abst. C. A. 1930, **24**, 973.
6. British Celanese, Ltd., and G. Ellis, E. P. 314208; abst. C. A. 1930, **24**, 1228; J. S. C. I. 1929, **48**, 716-B; Silk J. 1929, **6**, #65, 80. See British Celanese, Ltd., E. P. 282036; abst. J. S. C. I. 1929, **48**, 169.

spirit, orange by *p*-nitrobenzeneneazodiphenylamine, and red by 2-methoxy-4-nitrobenzeneazodiethylaniline.

In order to increase the resistance to ironing and possess an affinity for a great variety of dyestuffs, cellulose formate, acetate, propionate and butyrate and the products obtained by treating alkalized cellulose with such esterifying agents as *p*-toluenesulfonyl chloride, are separately subjected to partial or superficial hydrolysis and to a weighing treatment[1]. In another method of coloring cellulose acetate[2], the following diphenylamines may be used: 4-chloro-2-nitro-3′-methyl-, 4-chloro-2-nitro-4′-ethoxy-, 4-chloro-2-nitro-4-acetamido-, 4-bromo-2-nitro-, 4-bromo-2-nitro-4′-methoxy-, 2-nitro-, 2-nitro-4-methyl-, 2-nitro-4′-ethoxy-4-methyl, 4-chloro-2′-nitro-, 4-bromo-2′-nitro-, and 2-nitro-4′-acetamido-diphenylamines. Or[3] the same compounds may be used in the form of dispersions[4].

Acetate silk may also be dyed with dehydrothiotoluidine either diazotized and coupled in substance, or on the fiber with non-sulfonated coupling components (phenol, *b*-naphthol, 2:3-hydroxynaphthoic acid, dimethylaniline, *b*-naphthylamine, 2:3-aminonaphthoic acid, 1:2-aminonaphthol ethyl ether) or condensed with a chloronitrobenzene, especially 1-chloro-2:4-dinitrobenzene to dye yellow[5]. Or the acetate silk may be dyed with 1.4-naphthoquinone

1. British Celanese, Ltd., and G. Ellis, E. P. 319420; abst. C. A. 1930, **24**, 2600; J. S. C. I. 1930, **49**, 139-B; Silk J. and Rayon World, 1930, **6**, #68, 68. The weighting may be performed according to E. P. 258874, 259899, 260290, 277602, 280094, 281084, 284798, 285941, 309876; abst. J. S. C. I. 1928, **47**, 288; 1927, **46**, 29ᴐ; 1928, **47**, 154, 227, 296, 330, 444, 477; 1929, **48**, 596.

2. British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 305560, Addn. to E. P. 239470; abst. J. S. C. I. 1929, **48**, 281-B; C. A. 1929, **23**, 4831.

3. British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 305566, Addn. to E. P. 237943; abst. J. S. C. I. 1929, **48**, 281-B; C. A. 1929, **23**, 4831. See British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 298699; abst. C. A. 1929, **23**, 3110. British Celanese, Ltd., G. Ellis, H. Olpin and E. Kirk, E. P. 298933; abst. C. A. 1929, **23**, 3110.

4. British Celanese, Ltd., and G. Ellis, E. P. 219349; abst. J. S. C. I. 1924, **43**, 906. British Cellulose & Chemical Mfg. Co., Ltd., and G. Ellis, E. P. 224925; abst. J. S. C. I. 1925, **44**, 39.

5. British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 306981; abst. J. S. C. I. 1929, **48**, 358-B. Belg. P. 353232.

derivatives obtained by subjecting[1] 2.5-di- substituted-*B*-benzoylpropionic acids, or their derivatives with a free 6-position, to ring closure with dehydrating agents and simultaneous oxidation, preferably by treatment with sulfuric acid or with a mixture of boric acid and sulfuric acid. The *B*-benzoylpropionic acid derivatives may be made by condensing succinic anhydride or its derivatives such as the mono- or di-chloro- or bromo-derivatives, with *p*-substituted benzene derivatives having 2 positions ortho to each other free, such as hydroquinone, hydrotoluquinone, 1.2-dimethyl-3.6-dihydroxybenzene, *p*-aminophenol, *p*-chlorophenol and 3.4-dichlorophenol (suitably with use of aluminum chloride).

In another method[2] acetate silk is dyed directly with benzo- or naphthaquinone mono- and di-arylimides or with arylamino-derivatives of the quinones. Examples are: 2:5-dianilino-*p*-benzo-quinone (reddish-grey), 2:5-di-(*p*-aminoanilino)-*p*-benzo-quinone (brown), 2:5-*bis*-(*p*-dimethylaminoaniline) *p*-benzoquinone (purple-brown), 3:6-dichloro-2:5-dianilino-*p*-benzoquinone (yellow), 2-*p*-anisidino-*a*-naphtha-quinone (heliotrope), 1-amino-4-*p*-tolylimino-*b*-naphthol (orange), 1-imino-4-*p*-aminoanilino-*b*-naphthol (puce).

Or[3], acetate silk may be dyed with azo dyes containing the anthraquinone nucleus such as dyes obtained by coupling diazotized primary aminoanthraquinones or their derivatives with components such as *p*-xylidine, cresidines, anisidines, *m*-toluidine, *m*-phenylenediamine, nitro-*m*-phenylenediamine, phenol, *m*-aminophenol, monoacetyl-*m*-aminophenol, dimethyl-*m*-aminophenol, 1 (or 2)-naphthylamine, *w*-hydroxyethyl-1-naphthylamine, *y*-chloro-*b*-hydro-

1. British Celanese, Ltd., G. Ellis, H. Olpin and E. Kirk, E. P. 315331; abst. C. A. 1931, **24**, 1650.

2. British Celanese, Ltd., G. Ellis, H. Olpin and E. Kirk, E. P. 322463; abst. J. S. C. I. 1930, **49**, 320-B. See their E. P. 321401; abst. J. S. C. I. 1930, **49**, 54.

3. British Celanese, Ltd., G. Ellis, H. Olpin and D. Mosby, E. P. 310827; abst. C. A. 1930, **24**, 733; J. S. C. I. 1929, **48**, 678-B. Belg. P. 353564.

xypropyl-1-naphthylamine or 1-amino-2-methoxynaphthalene.

In still another process[1], acetate silk is treated with an aqueous dispersion of a 2:3-hydroxynaphthoic arylamide (particuarly the *m*-nitro-anilide or the *p*-anisidide), rinsed, and passed through a diazo solution (e.g., diazotized *p*-nitroaniline or 5-nitro-*o*-anisidine).

The inflammability of cellulose esters may be diminished[2] by addition of a bromine derivative of an acidylated aromatic amine such as acetyl-4-bromomethylanilide, acetyl-2, 4- or 3, 4-dibromoanilide, acetyl-2, 4, 6- or 2, 4, 5-tribromoanilide, acetyl-2, 4, 6-tribromomethylanilide, diacetyl-3, 5-dibromo-2-toluidide, diacetyl-1, 3, 6-tribromo-2-naphthalide or benzoyl-2, 4, 6-tribromoanilide.

In the manufacture of acetate filaments by the dry or evaporated method[3], the solution is extruded and spun into a chamber in which they traverse a path of 3-5 yards, the threads so obtained being unusually regular in their physical characteristics, and less of solvent outside the chamber prevented[4], or[5], the filaments may be drawn at varying linear speeds by such means as passing them round a roller, the peripheral speed of which is varied, whereby a more or less frequent regular and systematic variation in denier is imparted. For dyeing, printing or stenciling on cellulose acetate fabrics[6], there is used unsulfonated compounds containing one urea or thiourea group substituted by a nitroaryl group, or of unsulfonated azo dyes obtainable by

1. British Celanese, Ltd., G. Ellis, H. Olpin and E. Walker, E. P. 310779; abst. J. S. C. I. 1929, **48**, 678-B.
2. British Celanese, Ltd., and A. Daly, E. P. 319073; abst. C. A. 1930, **24**, 2599.
3. British Celanese, Ltd., and H. Dreyfus, E. P. 315729, Addn. to E. P. 165519; abst. J. S. C. I. 1929, **48**, 810-B.
4. For manufacture of twisted yarns or threads and apparatus therefor, see British Celanese, Ltd., W. Dickie, T. Platts and L. Latham, E. P. 304806; abst. J. S. C. I. 1929, **48**, 243-B.
5. British Celanese, Ltd., H. Dreyfus, W. Dickie and W. Taylor, E. P. 321762; abst. J. S. C. I. 1930, **49**, 98-B.
6. British Celanese, Ltd., H. Dreyfus, G. Ellis, T. Ockman and H. Olpin, E. P. 316526; abst. C. A. 1930, **24**, 1991.

coupling diazotized amino-substituted symmetrical diarylureas or diarylthioureas with coupling compounds.

Anhydrides as acetic anhydride[1] are produced by heating the vapors of the corresponding acid which may be dilute, and are condensed while carrying away the water by the vapor of an "entraining liquid" such as carbon tetrachloride, benzene and admixtures of ethyl ether and petroleum ether, but avoiding liquids which are solvents for the anhydride and have a boiling point higher than that of water. Or[2], the acid may be mixed as a spray or vapor with an inert gas such as steam, nitrogen or hydrogen, which may be preferably heated to 600-1200°, the acid being preferably preheated to 150-300°. Or the acetic acid vapor may be passed at 550-650° over a carbon catalyst prepared by charring a solution of cane sugar with or without the addition of tungstic or phosphoric acids, tungstates other than alkali tungstates, or sodium phosphate[3]. In a modification of the foregoing[4] the vapors from the thermal anhydrisation of acetic acid are met by a liquid stream in the presence or absence of catalysts, of solvent at 0-20°, the solvent being a mixture of ether and light petroleum. The solution of acetic anhydride is separated from the aqueous layer and concentrated by distillation.

Cellulose acetate may be spun vertically downwards into heated cells or chambers each of which, containing any desired number of spinning nozzles, is either open at the end remote from the nozzles, or is partially closed to ensure even distribution of the air. The chambers are provided

1. British Celanese, Ltd., H. Dreyfus and C. Haney, E. P. 303772, Addn. to E. P. 256663; abst. C. A. 1929, **23**, 4484; J. S. C. I. 1929, **48**, 235-B.

2. British Celanese, Ltd., H. Dreyfus and C. Haney, E. P. 304156; abst. C. A. 1929, **23**, 4712; J. S. C. I. 1929, **48**, 275-B.

3. British Celanese, Ltd., and S. Green, E. P. 312587; abst. J. S. C. I. 1929, **48**, 671-B; C. A. 1930, **24**, 864.

4. British Celanese, Ltd., S. Green and R. Widdowson, E. P. 310863; abst. J. S. C. I. 1929, **48**, 636-B.

with a collector device so that substantially all of the air is drawn through the vicinity of the spinning nozzles[1].

Azo dyes for coloring cellulose acetate have been described[2]. Where phosphoric acid is added as a catalytic promoter in cellulose acetate manufacture[3], copper or copper phosphate may be added thereto with improved results[4]. In the production of safety glass[5], sheets of cellulose acetate which have been treated with a mixture of a non-solvent, e.g. methylated spirit and a plasticizer as triacetin, are applied while wet to one or more sheets of glass and subjected to heat and pressure, the edges being sealed by means of a solution containing acaroid resin.

In a spinning cell for making filaments from cellulose acetate[6], a fluid stream is applied 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 their denier is reduced by stretching. In the preparation of acetic anhydride[7], the vapor of acetic acid is passed over tungstic acid, or magnesium, calcium, strontium or barium tungstates, which may be carried by pumice, kieselguhr or carborundum, and used in an apparatus made of or lined with silica, copper, gold, graphite or nickel-chromium steels such as "staybrite."

In the production of sheet material for airplane panels[8], perforated sheet metal plates are placed between sheets of

1. British Celanese, Ltd., H. Dreyfus, E. Kinsella, J. Bower and W. Taylor, E. P. 304674; abst. J. S. C. I. 1929, **48**, 353-B.
2. British Celanese, Ltd., D. Mosby, H. Olpin an.' G. Ellis, E. P. 319308; abst. J. S. C. I. 1930, **49**, 137-B; C. A. 1930, **24**, 2609. See their E. P. 319390; abst. J. S. C. I. 1930, **49**, 139-B.
3. British Celanese, Ltd., H. Dreyfus and W. Bader, E. P. 283989; abst. J. S. C. I. 1928, **47**, 223-B.
4. British Celanese, Ltd., and H. Oxley, E. P. 317867; abst. J. S. C. I. 1929, **48**, 887-B.
5. British Celanese, Ltd., and J. Rooney, E. P. 320374; abst. J. S. C. I. 1929, **48**, 1011-B; Brit. Plastics, 1930, **1**, 330.
6. British Celanese, Ltd., and W. Taylor, E. P. 322557; abst. C. A. 1930, **24**, 2883; Silk J. and Rayon World, 1930, **6**, #70, 62. Compare E. P. 165519, 198023.
7. British Celanese, Ltd., R. Widdowson and S. Green, E. P. 314555; abst. J. S. C. I. 1929, **48**, 708-B; C. A. 1930, **24**, 1393.
8. British Celanese, Ltd., and W. Wirz, E. P. 305694; abst. C. A. 1929, **23**, 5019.

cellulose acetate which may be subjected to heat and pressure to permeate the metal perforations. It is claimed that compositions suitable for removing water-soluble stains from acetate silk previous to the treatment of the material with a usual dry cleaning liquid, comprises soap, water and a substance such as cyclohexanol, cyclohexanone or their homologues, which is readily soluble in the dry cleaning liquid, and also somewhat soluble in or miscible with water[1].

C. Brown[2] has discussed in detail methods of safeguarding the storage of photographic picture and X-ray films, both nitrate and acetate, and directions given for the proper construction of storage vaults. J. Bulir in pointing out objections raised against the Stiastny method for refractometric determination of formic acid in the presence of acetic acid[3] alleges fairly accurate results are obtainable (0.2 gm. formic acid per 100 cc.) provided no other substances and water are present in the solution. In the J. Bulmer patent for cellulose acetylation[4] the cellulose is mixed with acetic acid sufficiently concentrated to crystallize by cooling, and then allowed to stand until uniform absorption takes place, when the mass is cooled until solidified by crystallization. Acetic anhydride and a condensing agent are then added, and the process allowed to take the normal course. For mixing components in cellulose acetylation[5], P. Bungartz has devised a special apparatus.

According to H. Burns and J. Wood[6], the dyeing of cellulose acetate silk by means of aqueous suspensions of

1. L. Hubbard, E. P. 307508; abst. C. A. 1929, **23**, 5332.
2. Safety Engineering, 1929, August, 65.
3. Chem. Listy, 1929, **23**, 25; abst. C. A. 1929, **23**, 4647. See also Chem. Listy, 1920, **14**, 6, 45; abst. C. A. 1921, **15**, 353.
4. F. P. 666084; abst. Cellulose, 1930, **1**, 127. F. P. 666630; abst. C. A. 1930, **24**, 1508; Cellulose, 1930, **1**, 127. Can. P. 291654. E. P. 298819; abst. C. A. 1929, **23**, 3098. Ital. P. 275387. Swiss P. 138026. Belg. P. 356418, 357061. Australian P. 17711.
5. F. P. 668904; abst. C. A. 1930, **24**, 1551.
6. J. Soc. Dyers Colourists, 1929, **45**, 12; abst. C. A. 1929, **23**, 2829; J. S. C. I. 1929, **48**, 168-B. Cf. V. Kartaschov, Helv. Chim. Acta, 1925, **8**, 928; abst. J. S. C. I. 1926, **45**, 49-B. Helv. Chim. Acta, 1926, **9**, 152; abst. J. S. C. I. 1926, **45**, 188-B. V. Kartaschov and G. Farine, Helv. Chim. Acta, 1928, **11**, 813; abst. J. S. C. I. 1928, **47**, 812-B.

bases such as the amino derivatives of anthraquinone is an adsorption phenomenon. It is claimed[1] especially concordant results in the catalytic production of acetic anhydride from acetic acid are obtainable, if the reaction is carried out under pressure of carbon dioxide to avoid the formation of acetone. The Canadian Celanese Co.[2] mordant cellulose acetate by subjecting the ester to the simultaneous action of a chromium salt (as acetate), furfural and acetic acid. A paint for celluloid is prepared[3] by grinding zinc oxide in a mixture of shellac dissolved in methyl alcohol and cellulose acetate in solution, to which are added dissolved non-inflammable celluloid cuttings in a mixture of acetone, alcohol and benzene.

T. Carswell[4] has examined the effect of incorporating various arylsulfonamides as plasticizers with cellulose acetates for lacquer formation, and finds no apparent relationship between the chemical constitution of these compounds and their "relativity" (weight of plasticizer x 100 weight of cellulose acetate) in cellulose acetate, but *p*-toluenemethylenesulfonamide has a significantly high value. Replacement of NMe by NEt 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 diminution of tensile strength. *p*-Toluenemethylenesulfonamide derivatives produce films of greater fastness to light than the corresponding benzene or xylene compounds. Derivatives with an NEt group are faster to light than corresponding methyl compounds, but an N-phenyl group markedly decreases fastness. The best

1. J. Campardou and J. Folie-Desjardins, F. P. 683815; abst. C. A. 1930, **24**, 5045.
2. Can. P. 295343.
3. R. Carruthers, E. P. 319978; abst. C. A. 1930, **24**, 2621; J. S. C. I. 1929, **48**, 989-B.
4. J. Ind. Eng. Chem. 1929, **21**, 1176; abst. J. S. C. I. 1930, **49**, 857-B; C. A. 1930, **24**, 738; Brit. Plastics, 1930, **2**, 100; Rayon Record, 1930, **4**, 283.

results in this connection were obtained with *p*-toluenemethylenesulfonamide. Relationships between chemical constitution of the plasticizer and resistance of films to outdoor exposure were indefinite, except that the sulfonmethyleneamide is superior to simple alkyl derivatives.

J. Caudri[1] has devised a method of titrating acetic anhydride in mixtures of methyl or ethyl alcohol and water, in which a portion of the anhydride is converted into ethyl acetate when titrated with alkali, the amount of anhydride present being determined by taking the sum of the "acid number" and the "ester number," or the mixture may be titrated potentiometrically with standardized ammonia. The Celluloid Corp[2] prepare cellulose acetate films by the extrusion of solutions at a temperature somewhat below the boiling point of the solvent employed, into an atmosphere maintained at a raised pressure, the quantity of solvent being such that the solution does not readily flow at the ordinary temperature. Or[3], as an especially appropriate solvent for film formation is advocated mixtures containing a lower alkyl acetate in preponderant proportions, and preferred composition being (parts by weight) ethyl acetate 82.5, ethyl alcohol 8.5, water 9.

P. Chaumeton and V. Yarsley[4] have given a comprehensive historical account of the development and manufacture of cellulose acetates, with data on the characteristics of suitable cotton. In three patents issued to Chemische Fabrik vorm. Sandoz, cellulose mono- and di-acetate fibers[5] obtained by direct acetylation of cellulose without structural alteration, may be dyed or printed either while

1. Rec. trav. chim. 1929, **48**, 778; abst. J. S. C. I. 1929, **48**, 1039-A.
2. E. P. 310540; abst. J. S. C. I. 1930, **49**, 943-B; Brit. Plastics, 1930, **2**, 278.
3. Celluloid Corp., E. P. 314087; abst. J. S. C. I. 1930, **49**, 1120-B; C. A. 1930, **24**, 1235.
4. Brit. Plastics, 1929, **1**, 275.
5. E. P. 323011; abst. C. A. 1930, **24**, 2897; J. S. C. I. 1930, **49**, 370-B; Silk J. and Rayon World, 1930, **6**, #70, 64; Rayon Record, 1930, **4**, 338. E. P. 306877; abst. J. S. C. I. 1929, **48**, 354-B; C. A. 1929, **23**, 5330. F. P. 663053; abst. C. A. 1930, **24**, 509.

still in a swollen state from the acetylation or due to after treatment of the dried fibers with aqueous solutions of formic, acetic or butyric acids. To alter the properties of these threads[1] without changing the physical structure, steaming under pressure to increase resistance to direct cotton dyes may be resorted to. It is advised[2] during the acylation process to keep the cellulose fibers in movement, the esterification being carried out with mixtures containing insufficient acetic anhydride to form the triacetate and at a high temperature. The cellulose is first placed in contact with one or two components of the acetylating bath, and the other constituents afterwards added.

H. Clarke and C. Malm[3] prepare cellulose aceto esters containing higher acyl groups by adding 5 (parts by weight) of hydrolyzed, acetone-soluble cellulose acetate containing about 36.6% of acetyl to an esterifying mixture containing 15 of stearic acid, 20 chloracetic anhydride and 0.05 magnesium perchlorate, the mixture being maintained at 60-65° for 4 hrs., the ester being then precipitated with agitation into warm methyl alcohol. After washing with the latter, the precipitate may be dissolved in acetone, from which transparent, flexible films result. The precipitate contains 45.7% stearyl. In place of stearic acid may be substituted other acids, resulting in the formation of aceto- and acetochlor-propionate, *n*-butyrate, *iso*-butyrate, *n*-valerate, *iso*-valerate, *n*-caproate, *n*-heptylate, caprylate, pelargonate, caprate, laurate, myristate, palmitate, crotonate, cyclohexanecarboxylate, benzoate, *o*-methoxybenzoate, *o*-chlorbenzoate, acetylsalicylate, phenylacetate, hydrocinna-

1. Chemische Fabrik vorm. Sandoz, E. P. 318366; abst. C. A. 1930, **24**, 2310; J. S. C. I. 1929, **48**, 976-B.

2. Chemische Fabrik vorm. Sandoz, F. P. Addn. 36592 to F. P. 635304; abst. C. A. 1930, **24**, 6035. E. P. 314913, Addn. to E. P. 280493; abst. J. S. C. I. 1929, **48**, 811-B; C. A. 1930, **24**, 1523. D. R. P. 530395.

3. U. S. P. 1698048; abst. Plastics, 1929, **5**, 573; C. A. 1929, **23**, 1268; J. S. C. I. 1929, **48**, 594-B. E. P. 304278; abst. C. A. 1929, **23**, 4818; U. S. P. 1690620. E. P. 290570, E. P. 290571; abst. C. A. 1929, **23**, 980. F. P. 653742; abst. C. A. 1929, **23**, 3807. E. P. 287880; abst. C. A. 1929, **23**, 512.

mate, acetostearate, cinnamate, aceto-*o*-methoxybenzoate and aceto-di and -tetrachlor-, and aceto-di- and -tetrabrom- stearates of cellulose. Cellulose aceto- and acetochlor-bromstearate are also described. In a complementary patent[1] cellulose aceto-*a*-bromstearate containing 11% bromide and soluble in acetone, chloroform and benzene is detailed. Or[2] mixed esters may be formed soluble in acetone and benzene and suitable for film and filament formation when for every 24 C. atoms of the cellulose molecule, less than 4 (but more than one-third of one acyl group) from the higher aliphatic acids such as lauric, myristic and stearic having more than 8C. atoms, the remaining acyls being acetyl groups. Thus[3] monochloracetic anhydride and *o*-chlorbenzoic acid gives cellulose aceto-*ortho*-chlorbenzoate, soluble in chloroform and insoluble in acetone. By varying the reactants, an acetone soluble cellulose ester is obtainable. They prepare organic cellulose esters[4] by mercerizing cellulose, dehydrating with a substantially anhydrous neutral organic liquid, and then esterify in the usual manner. Following this method[5] cellulose acetostearate, acetopalmitate, chloracetate and chlorstearate may be prepared. Cellulose acetate is preparable[6] by treating cellulose or a cellulose conversion product with acetic acid in the presence of a substituted organic acid anhydride. The anhydride is said to induce esterification of the cellulose by the acetic acid present, the effect being more noticeable in the case of substituted anhydrides not capable of esterifying. It is claimed that aqueous for-

1. U. S. P. 1698049; abst. Plastics, 1929, **5**, 512; C. A. 1929, **23**, 1267; J. S. C. I. 1929, **48**, 594-B. E. P. 304279; abst. J. S .C. I. 1930, **49**, 655-B; Brit. Plastics, 1930, **2**, 135.
2. H. Clarke and C. Malm, U. S. P. 1704282; abst. C. A. 1929, **23**, 2033; Plastics, 1930, **6**, 91.
3. H. Clarke and C. Malm, U. S. P. 1704283; abst. C. A. 1929, **23**, 2033; Plastics, 1929, **5**, 515.
4. H. Clarke and C. Malm, U. S. P. 1716422; abst. Plastics, 1930, **6**, 26; C. A. 1929, **23**, 3807.
5. H. Clarke and C. Malm, U. S. P. 1735159; abst. Plastics, 1930, **6**, 336; C. A. 1930, **24**, 723.
6. H. Clarke, C. Malm and R. Stinchfield, E. P. 313408; abst. C. A. 1930, **24**. 1217.

mic acid may be concentrated by the addition thereto of propyl alcohol forming *n*-propyl formate, the mixture being heated below the boiling point of water so that an azeotropic mixture of water and *n*-propyl formate distills, the dehydrated formic acid being then separated from the remaining propyl ester by fractionation[1].

In the manufacture of ketene[2], vapors such as those of acetone which are decomposed by heat into substances including ketene are passed through a chamber containing a network of metal such as copper (free from iron or nickel) having high thermal conductivity, and a melting point above the reaction temperature, which may be about 650-670°. R. Clavel[3] produces woolly effects on acetylcellulose filaments by treating with a solution of lower aliphatic acid as 8% acetic acid with 0.5% Turkey red oil at about the boiling point of the solution. He[4] prepares white or colored discharges on artificial silks as acetate silk, weighted with tin or zinc salts as previously described, and dyed with direct dyes, which are readily discharged by means of pastes containing sodium hydrosulfite such that clear, white or colored effects result[5].

He prepares a leather substitute[6] by treating cellulose acetate material in hank or fabric form with a phenolic compound such as a tannin, the material being further subjected to washing and treatment with a salt of bismuth, zinc, silver, or iron, then dyed and treated with a finishing solution such as paraffin or an oil.

1. H. Clarke and D. Othmer, E. P. 318633; abst. J. S. C. I. 1930, **49**, 895-B; C. A. 1930, **24**, 2143.

2. H. Clarke and C. Waring, U. S. P. 1723724; abst. C. A. 1929, **23**, 4485. E. P. 309577; abst. J. S. C. I. 1930, **49**, 452-B; C. A. 1930, **24**, 630.

3. U. S. P. 1716423; abst. C. A 1929, **23**, 3819; J. S. C. I. 1929, **48**, 640-B. See E. P. 206818; abst. J. S. C. I. 1924, **43**, 743-B.

4. R. Clavel, E. P. 308757; abst. J. S. C. I. 1930, **49**, 238-B.

5. R. Clavel, E. P. 277602; abst. J. S. C. I. 1928, **47**, 154-B. E. P. 280094; abst. J. S. C. I. 1928, **47**, 296-B. E. P. 300894; abst. J. S. C. I. 1929, **48**, 811-B. E. P. 303129; abst. J. S. C. I. 1929, **48**, 774-B.

6. R. Clavel, U. S. P. 1727862; abst. C. A. 1929, **23**, 5349. E. P. 252661; abst. C. A. 1927, **21**, 2397. Can. P. 275369; abst. C. A. 1928, **22**, 1249. See also Can. P. 292887.

According to L. Clement[1] excellent nitrocellulose and acetylcellulose solvents result by mixing ethyl alcohol and acetone in the proportion by volume of 4 to 2, or 1 to 1[2], the alcohol being anhydrous. In making multicolor screens for color photography[3] having a regular straight line pattern a film of cellulose acetate is coated with a solution of cellulose nitrate before applying the dyes. For dyeing acetate silk partially alkylated products of *p*, *p*-diaminoanthrarufin are used[4], the products being produced by blocking one amido group, by an acyl or other groups of *p*, *p*-diaminoanthrarufin and submitting to the moderating action of alkylating agents, then eliminating the blocking group[5]. This firm has also patented an apparatus for cellulose acetylation[6].

The Compagnie Scientifil[7] have evolved a machine for the dry spinning of acetone solutions of cellulose acetate, comprising a winding mechanism, a driving roller extending longitudinally with 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. In this manner one bobbin may be shifted below the corresponding nozzle to remove the full bobbin and start the winding on the first mentioned bobbin frictional driving engagement with the roller.

The Consortium f. Elektrochemische Industrie[8] prepare acetaldehyde by heating vinyl esters with water in the presence of catalysts capable of transforming paralde-

1. U. S. P. 1713512; abst. J. S. C. I. 1929, **48**, 594-B; Brit. Plastics, 1929, **1**, 113.
2. U. S. P. 1713997; abst. J. S. C. I. 1929, **48**, 594-B; Brit. Plastics, 1929, **1**, 113; C. A. 1929, **23**, 3573.
3. Compagnie d'Exploitation des Procedes de Photographie en Couleurs L. Dufay (known as Versicolor Dufay), E. P. 322432; abst. C. A. 1930, **24**, 2681.
4. Compagnie Nationale de Matiéres Colorantes et Manufactures de Produits Chimiques du Nord, Réunies établissements Kuhlmann, F. P. 700004; abst. C. A. 1931, **25**, 3490.
5. *Ibid.* F. P. 695981; abst. C. A. 1931, **25**, 2859.
6. *Ibid.* E. P. 304227; abst. C. A. 1929, **23**, 4819.
7. Can. P. 291033.
8. Can. P. 289633. F. P. 652078; abst. C. A. 1929, **23**, 3479.

hyde to acetaldehyde, then adding substances of dispersive action. The process may be modified by heating the vinyl ester with a carboxylic acid[1], or a volatile inorganic acid may be added to the superheated vapors, the mixed vapors being then passed through a heated reaction vessel[2]. To concentrate acetic acid[3], they extract the diluted acid with a chlorinated hydrocarbon at lower than minus 20°. B. Corson, J. Thomas and D. Waugh have described solvents[4], being the methyl, ethyl, propyl, butyl, amyl and *iso*-amyl esters of dimethylethylacetic acid, with their physical constants.

It has been found[5] that the tendency of cellulose acetate to melt during laundering may be obviated or reduced by incorporating with the cellulose ester during manufacture, methyl, ethyl or butyl silicates, which may be added to the solutions from which the artificial threads are made. W. Crooks and C. Walton[6] have given details and various examples for the incorporation of cellulose derivatives with rubber and resins, the solids preferably being pretreated with the vapor of the solvent subsequently incorporated, to produce the solution or plastic mass.

In discussing the application of acetate silk to linings of men's wear[7], R. Curtis renders cellulose acetate resistant to hot iron pressing, a simple method for "iron-proofing" it being to run the fabric through an American padder (11° Tw. NaOH at 140° F.) at 100 yds. per minute, picking up liquor 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. Since the method involves the partial regeneration of the

1. Consortium fur Elektrochemische Industrie, Can. P. 289634.
2. *Ibid.* Can. P. 289992. F. P. 671283; abst. C. A. 1930, **24**, 2143. Ital. P. 269387.
3. *Ibid.* Can. P. 293561. E. P. 308210; abst. J. S. C. I. 1930, **49**, 135-B; C. A. 1930, **24**, 129. Ital. P. 260174.
4. J. Am. Chem. Soc. 1929, **51**, 1950; abst. C. A. 1929, **23**, 3438.
5. Courtaulds, Ltd., and C. Diamond, E. P. 317936; abst. C. A. 1930, **24**, 2290; J. S. C. I. 1929, **48**, 893-B.
6. E. P. 303152; abst. C. A. 1929, **23**, 4542.
7. Textile World, 1929, **76**, 760; abst. C. A. 1930, **24**, 1743.

cellulose, it cannot be applied when cross-dyeing effects are required.

M. Cusin and P. Chevalet prepare partially esterified hydrocellulose by treatment with crystallizable acetic acid and sulfuric acid at low temperatures in determined proportions, the mass gelatinizing when forming a transparent paste[1]. This product after precipitation in water or dilute ethyl alcohol forms the finished product. Or the reactivity of the cellulosic material may be enhanced by a preliminary treatment with formic and acetic acids. The product is a cellulose acetoformate, or formylacetate. Products utilizable as vat dyes or pigments for coloring cellulose acetate[2] are made by reacting with ammonia or with a primary monoamine of the benzene or naphthalene series on phthalic anhydride, phthalimide or the mono- or di-amide of phthalic acid in the presence of iron, copper or nickel or their corresponding chloride, sulfate or sulfide.

A. Davis[3] prepares a "Poucis" sheet for mimeography by impregnating Japanese yoshino paper with a lacquer comprising cellulose acetate 225, acetone 4000, zinc oxide 300, monobenzoylbutyl tartrate 1125, diamyl phthalate 375, chlornaphthalene 225, castor oil 60. M. Deschiens[4] has contributed two papers, one on the properties, analysis and practical testing of cellulose acetate, and the other[5] on standardized solubility determinations for various cellulose acetates. R. Dort[6] has given receipts for dyeing celanese drapery cloths with SRA colors.

In the C. Dreyfus process of controlling the temperature of reaction masses[7], the liquefied gas is introduced

1. U. S. P. 1722202; abst. C. A. 1929, **23**, 4571; Plastics, 1930, **6**, 90.
2. H. Drescher, J. Thomas and Scottish Dyes, Ltd., E. P. 322169; abst. C. A. 1930, **24**, 2890.
3. Brit. Plastics, 1929, **1**, 164.
4. Chim. et Ind. 1929, **21**, 1131; abst. Brit. Plastics, 1929, **1**, 152; C. A. 1929, **23**, 4569; J. S. C. I. 1929, **48**, 675-B.
5. Chim. et Ind. Special No. 1929, **21**, 564; abst. C. A. 1929, **23**, 4062.
6. The Melliand, 1929, **1**, 102; abst. C. A. 1929, **23**, 3347.
7. C. Dreyfus, Can. P. 295859.

into the liquid cooling medium, the gas being preferably nitrogen, distributing the liquefied gas through the cooling medium and allowing the gas to evaporate, thereby lowering the temperature. As applied to concentrating aqueous solutions of the lower fatty acids[1], a mixture of 80% methylene chloride, 20% ether may be used in connection with artificial refrigeration. In the preparation of cellulose acetate, the cellulose is treated with a solution of nitric acid before or after conversion, in conjunction with acetic acid[2]. The amount of nitric acid used is preferably 1-2% of the weight of the cellulose[3].

Threads and films of cellulose acetate resistant to warm, aqueous agents and which have a lesser tendency to become opaque or wrinkle with such agents[4] are made by the use of acetone containing ethyl alcohol in amounts either less than 5%, or 10%-40%. If the solvent comprises acetone with 2%-5% or more of methyl alcohol[5], and the cellulose acetate has preferably an acetic acid value of about 54.5% with less than 1% water, especially valuable films are said to be producible. In the formation of coatings which are substantially light fast[6], C. Dreyfus advocates combining a normally light sensitive synthetic resin of the phenol-aldehyde type, to which resin a dark color has been imparted, with dissolved cellulose acetate. A ketone-phenol-aldehyde resin[7] may also be used. If the plasticity of the cellulose acetate or other organic cellulose derivative is made suitable, and the viscosity preferably kept above 600, especially valuable plastics are said to result[8].

In the preparation of printed fabrics containing plastic

1. C. Dreyfus, Can. P. 295629.
2. *Ibid.* F. P. 682060; abst. C. A. 1930, **24**, 4390. See F. P. 677927; abst. C. A. 1930, **24**, 3368.
3. *Ibid.* F. P. 686332; abst. C. A. 1931, **25**, 591.
4. *Ibid.* F. P. 673544; abst. C. A. 1930, **24**, 2601. Can. P. 293458.
5. *Ibid.* F. P. 673483; abst. C. A. 1930, **24**, 2601.
6. *Ibid.* Can. P. 295242.
7. *Ibid.* Can. P. 293641.
8. *Ibid.* F. P. 673029; abst. C. A. 1930, **24**, 2292.

cellulose derivatives[1], the fabric is first wetted and a transfer sheet then placed thereon coated with dye dissolved therein. The design is then impressed into the cellulose plastic surface. Or[2], the fabric may be simultaneously embossed and printed by transferring a dyestuff from a transfer agent to a cellulose acetate fabric, and simultaneously subjecting the fabric to an embossing operation. In still another method[3], the whole surface of the fabric may be printed with a dye, and then locally discharged. In another method of printing cellulose acetate fabrics[4], a dyestuff and ethylene dichloride is used. In order to simulate warp print effects on fabrics composed of or containing cellulose formate, acetate, propionate or butyrate[5], the cellulose ester material which is to constitute the warp or weft is subjected to a treatment to enhance the affinity for dyes different from that of the untreated material, and then using a dye having a selective affinity for one of the component materials. Textiles or other products composed of cellulose acetate[6] having a m. pt. above 250° are obtained by saponifying cellulose acetate having an acetyl content of 53-55%, to a proportion of 3-11% of its weight, and afterwards fabricating the textile of this compound.

Cloth may be given the appearance of lace, gauze or other perforated effects[7] by submitting the cloth containing cellulose acetate threads and vegetable fibers, to a carbonization treatment. In the C. Dreyfus process for acetate silk production[8], spinning solutions and a coagulating bath are used, the latter being kept at a temperature above atmospheric, and the coagulating bath kept above the temperature of the spinning solution. Mineral oils are prefer-

1. C. Dreyfus, Can. P. 290861.
2. *Ibid.* Can. P. 288363.
3. *Ibid.* Can. P. 289906.
4. *Ibid.* Can. P. 290464.
5. *Ibid.* E. P. 317455; abst. C. A. 1930, **24**, 2309. See also E. P. 306534; abst. C. A. 1929, **23**, 5048.
6. *Ibid.* F. P. 666398; abst. C. A. 1930, **24**, 1523.
7. *Ibid.* F. P. 636608; abst. C. A. 1929, **23**, 719. F. P. Addn. 36860 to F. P. 636608; abst. C. A. 1931, **25**, 1103.
8. *Ibid.* F. P. 684144; abst. C. A. 1930, **24**, 5496.

ably used to coagulate the solution, and the filaments bobbined at such a speed that small cross-section threads are obtained.

To reduce the tendency to laddering of knitted fabrics containing cellulose acetate[1], the material is treated with acetone so that the fibers or threads are caused to slightly adhere together without substantial alteration in texture or appearance.

C. Dreyfus advocates acetylating cellulose with acetic acid in the presence of phosphoric acid[2], or introducing the cellulose into an airtight container which is then evacuated[3], introducing glacial acetic acid heated to around its boiling point (the added acid being insufficient to completely satisfy the vacuum), acting for one hour upon the cellulose with the acid[4]. Ultra-violet light transparent glass is said to result by inserting a sheet of cellulose acetate between two sheets of glass of high quartz content[5]. In the impregnation of paper[6], hydrous cellulose acetate is mixed with paper stock in a pulp beater, the resulting product being sheeted, dried, and the sheets then passed through heated rollers to cause the cellulose acetate to coalesce to a laminated product.

In the treatment of solids with normally liquid substances in the preparation of plastic masses, the latter is treated with a liquid having an affinity for the cellulose acetate, the liquid being applied in attenuated form as in the vapor phase, or in admixture with an inert gas[7]. To prepare acetate yarn for textile operations[8], it is suggested to swell the acetate fiber by a preliminary wetting out operation, then proceed in the usual manner. If the fabric of cellulose acetate is to be printed[9], a paste is locally applied

1. C. Dreyfus, U. S. P. 1719173; abst. C. A. 1929, **23**, 4084.
2. *Ibid.* Can. P. 287095.
3. *Ibid.* F. P. 679429; abst. C. A. 1930, **24**, 3911. Compare C. Dreyfus and G. Schneider, E. P. 316521; abst. C. A. 1930, **24**, 1991.
4. *Ibid.* Can. P. 287774.
5. *Ibid.* Can. P. 293732.
6. *Ibid.* Can. P. 294371.
7. *Ibid.* Can. P. 295243.
8. *Ibid.* Can. P. 295666.
9. *Ibid.* Can. P. 295667.

containing a dyestuff that tends to deluster the fabric and an agent which counteracts the delustering tendency, then ageing and scouring the fabric. Or different colored fabrics may be produced by using a material other than cellulose acetate and having a design of cellulose material imprinted thereon[1]. In order to produce a moire effect on acetate textiles[2], the individual fibers are cellulose acetate, but some of the fibers are intentionally permanently deformed to produce the effect desired. In coating a metallic screen[3], a composition comprising a partially polymerized vinyl compound in insufficient quantity to close the meshes is first applied, followed by a sufficient application of cellulose acetate so that the meshes are all closed.

Fabrics containing both vegetable fibers and cellulose acetate or propionate are subjected to a carbonization action with aluminum chloride or hydrochloric acid to remove the vegetable fiber (as cotton), then sodium sulfate or other delustering preventative is applied[4]. Cellulose acetate may also be delustered by the addition of a thiocyanate as of ammonium or calcium[5], or the sulfates or phosphates of barium, calcium or strontium[6]. If it is desired to weight[7], the cellulose acetate silk is first immersed in a 30% tannin solution at about 55°, followed by 4% tartar emetic at 35°, or a treatment with 5% stannic chloride in the cold for 24 hours, or a 30% solution at 45-55°. Discharge effects are said to be producible on fabrics or yarns of cellulose acetate[8] made from or containing superficially saponified ester by discharge dyes, but applying the discharge locally. The

1. C. Dreyfus, Can. P. 295825.
2. *Ibid.* Can. P. 295858.
3. *Ibid.* Can. P. 295668.
4. C. Dreyfus, R. Dort and H. Platt, U. S. P. 1725857; abst. C. A. 1929, **23**, 5049.
5. C. Dreyfus and H. Platt, U. S. P. 1740889; abst. C. A. 1930, **24**, 1230; J. S. C. I. 1930, **49**, 186-B. See E. P. 282722; abst. J. S. C. I. 1929, **48**, 353-B.
6. C. Dreyfus, F. P. 681060; abst. C. A. 1930, **24**, 4390.
7. C. Dreyfus and H. Platt, U. S. P. 1731298; abst. Cellulose, 1930, **1**, 66; C. A. 1930, **24**, 238; J. S. C. I. 1929, **48**, 976-B. Cf. E. P. 260290; abst. J. S. C. I. 1928, **47**, 477-B.
8. *Ibid.* E. P. 314446; abst. C. A. 1930, **24**, 1521.

process of superficial saponification has also been patented, and several modifications of the same, including saponification with 5-20% NaOH solutions below 35°. A surface coating having a low moisture vapor tension[1] is said to result when a surface is first coated with a nitrocellulose lacquer, and then applying a coat of a lacquer of an organic cellulose derivative. This should be of especial interest to the food packing industry, especially in the cold packing of fish where cellophane or similar sheets are used almost exclusively, but not with entire satisfaction due to brittleness at low temperature.

In producing colored films of cellulose derivatives[2] there is added to the cellulose solution a relatively water-insoluble coloring compound rendered soluble, which has an affinity for the cellulose derivative, and adding thereto a dyestuff of oily or fatty characteristics. A moulding powder has been brought forward as capable of extensive application[3], in which 100 lbs. cellulose acetate finely ground is heated with 30 lbs. triacetin in 100 lbs. benzol until most of the water has been driven off, when the mass is cooled and may be worked up in any suitable manner.

The inventive ramifications of H. Dreyfus in the cellulose ester field in 1929 have been unusually prolific and noteworthy. In the production of aliphatic anhydrides, especially anhydride for cellulose esterification purposes, acetic acid in spray or vapor is mixed with steam, nitrogen or hydrogen heated to 600-1200°, the acid being preferably preheated to 150-300°[4]. The anhydride may then be separated by fractional condensation, or passed through a solvent as chlorbenzenes, benzyl ether, tetrachlorethane, acetins, anisole, *p*-cresyl acetate, phenetol or paraffin, by means of an entraining liquid or water-binding substance. Or the

1. C. Dreyfus and W. Moss, Can. P. 292644.
2. C. Dreyfus and G. Ellis, Can. P. 293375.
3. C. Dreyfus and G. Schneider, U. S. P. 1732330; abst. Plastics, 1930, **6**, 336; Brit. Plastics, 1930, **1**, 447; C. A. 1930, **24**, 239; J. S. C. I. 1930, **49**, 138-B.
4. H. Dreyfus, F. P. 657423; abst. C. A. 1929, **23**, 4231.

vapor of the acid may be heated with sulfur dioxide at 200-900° in the presence of contact material as carborundum, pumice, or kieselguhr[1], and the formed anhydride recovered. Or the acid vapors are heated[2] and the water removed by vapor of carbon tetrachloride, benzene, gasoline, petroleum ether or mixtures of these, which do not dissolve the anhydride and boil below 100°. Or[3], the water may be separated from the anhydride by passing the vapors under the surface of a cooled extraction liquid as chloroform, alone or admixed with ether.

The acid vapor may be impregnated with carbon dioxide (1-10 times as much CO_2 as acid)[4] in the presence of catalysts, fire clay or a fused silica tube being used for the apparatus[5]. As a suitable catalyst for use in a heated condition, have been patented tungstic acid, and Ca., Mg., Sr., and Ba. tungstates (but not alkali metal tungstates). The temperature is preferably 550-650°[6]. Instead of CO_2, a mixture of CO and CO_2 may be used[7], or[8] the catalyst may be a non-crystalline carbon such as produced by the carbonization of sugar. Phosphoric acid[9] or sodium metaphosphate are recommended catalysts. Or the anhydride formed from the reaction chambers may be separated by condensation while carrying along the steam by the vapors of one or more liquids[10], the boiling points of which are

1. H. Dreyfus, E. P. 313418; abst. C.A. 1930, **24**, 1124; J.S.C.I. 1929, **48**, 670-B. Compare F. P. 668219; abst. C. A. 1930, **24**, 1393.
2. *Ibid.* F. P. 656901; abst. C. A. 1929, **23**, 4230.
3. *Ibid.* F. P. 656902; abst. C. A. 1929, **23**, 4230. Cf. F. P. 647227; abst. C. A. 1929, **23**, 2447.
4. *Ibid.* E. P. 312585; abst. C. A. 1930, **24**, 864; J. S. C. I. 1929, **48**, 671-B. F. P. 667498; abst. C. A. 1930, **24**, 1124.
5. *Ibid.* E. P. 257968; abst. C. A. 1927, **21**, 3057. E. P. 280972; abst. C. A. 1928, **22**, 3417. See E. P. 310863; U .S. P. 1735956, 1735957, 1735958, 1735959, 1735962; abst. C. A. 1930, **24**, 629.
6. *Ibid.* F. P. 667553; abst. C. A. 1930, **24**, 1124.
7. *Ibid.* F. P. 667498, 667499; abst. C. A. 1930, **24**, 1124. E. P. 256663, 256664; abst. J. S. C. I. 1926, **45**, 897-B. E. P. 312586; abst. C. A. 1930, **24**, 864.
8. *Ibid.* F. P. 667500; abst. C. A. 1930, **24**, 1124.
9. *Ibid.* F. P. 657604; abst. C. A. 1929, **23**, 4484.
10. *Ibid.* F. P. Addn. 36747 to 656901; abst. C. A. 1931, **25**, 971.

between those of the anhydride and water, e.g., toluene or a xylene.

Acetic anhydride may also be prepared by causing the reaction zone vapors to strike a current of liquid which is a solvent for the anhydride but practically insoluble in water, as mixtures of ether or chloroform with one or more hydrocarbons as gasoline or petroleum ether[1]. Or the aliphatic anhydride may be heated in the presence of non-metallic inorganic or organic bases as ammonia, primary, secondary and tertiary alkylamines, tetralkylammonium bases, pyridine, picoline, quinoline, piperidine, aniline, alkylanilines, cyclohexylyamine, toluidines, or their hydrochlorides, sulfates or phosphates[2]. Acetic acid vapor may be passed with hydrogen at 500-700° through a copper tube[3] which has previously been heated to the required temperature in hydrogen. Nickel, cobalt, iron, or alloys of these or other metals, which in the form of acetates are reduced to the metallic state by hydrogen at the reaction temperature, may be used instead of copper.

Instead of heating in the presence of phosphoric acid[4], which may be deposited upon or admixed with porous materials, and which is applicable for the production of other anhydrides as propionic anhydride, may be used carbon, charcoal, and carborundum with phosphoric acid. The apparatus may be lined with gold or platinum (if not too expensive)[5]. In producing acetic anhydride by the H.

1. H. Dreyfus, F. P. 667208; abst. C. A. 1930, **24**, 1124. Contrast F. P. 657604, 658111; E. P. 303772; abst. C. A. 1929, **23**, 4484.

2. *Ibid.* E. P. 317907; abst. C. A. 1930, **24**, 2144; J. S. C. I. 1929, **48**, 888-B. F. P. 674988; abst. C. A. 1930, **24**, 2759.

3. *Ibid.* E. P. 305147; abst. J. S. C. I. 1929, **48**, 275-B; C. A. 1929, **23**, 4712. Cf. E. P. 289972; abst. C. A. 1929, **23**, 850; F. P. 658111; abst. C. A. 1929, **23**, 4484; see F. P. 656901; abst. C. A. 1929, **23**, 4230.

4. *Ibid.* E. P. 280972; abst. C. A. 1928, **22**, 3417; J. S. C. I. 1928, **47**, 82-B. U. S. P. 1735959, 1735962; abst. J. S. C. I. 1930, **49**, 51-B. E. P. 279916; abst. J. S. C. I. 1928, **47**, 45-B. F. P. Addn. 36811 to 634167; abst. C. A. 1931, **25**, 971.

5. *Ibid.* E. P. 312733; abst. C. A. 1930, **24**, 864.

Dreyfus process[1], acetic acid is heated in admixture with at least 2% of HCl, HBr or HI at 90-100°, or[2] in the presence of aliphatic acids substituted in the alkyl rest by a halogen or sulfonic group, or in the hydroxyl group by residues of phosphoric acids, such as mono- or poly-, chloro- or bromo- acetic or propionic acids, e.g., a mixture of vapors of acetic acid containing 5-7% of chloracetic acid is passed through an earthenware tube containing pumice or kieselguhr at 450-600°. The acetic acid may likewise be heated in the presence of a phenol or an aliphatic acetyl derivative of a phenol, cresol, xylenol or their acetyl derivatives[3], or glycerol or acetated glycerol (acetin)[4]. In a modification[5], the temperature is maintained between 400-600°.

Higher homologues of acetic anhydride (propionic and butyric anhydrides)[6], are made by the thermal decomposition of the vapors of the corresponding acids in the presence of phosphoric acid at 400-500°, or by passing the vapor[7] of the acid, in the presence of one or more substituted aliphatic acids which are alkacyl derivatives of inorganic acids, such as mono- or poly-chloracetic acids, bromacetic acids, chlor (or brom) propionic acids, sulfacetic acids, or phosphoacetic acids. The mixture contains 1-10% of the substituted acid. Similarly[8] a phenol or alkacyl derivative, or polyhydroxy alcohol or alkacyl derivative may be employed[9].

In the production of acetic acid, H. Dreyfus recommends isomerizing methyl formate by heating it in the

1. H. Dreyfus, E. P. 314132; abst. C. A. 1930, **24**, 1124; J. S. C. I. 1929, **48**, 708-B. F. P. 671859; abst. C. A. 1930, **24**, 2144. Cf. F. P. 668219; abst. C. A. 1930, **24**, 1392.
2. *Ibid.* E. P. 318662; abst. C. A. 1930, **24**, 2144; J. S. C. I. 1930, **49**, 8-B.
3. *Ibid.* E. P. 318663; abst. C. A. 1930, **24**, 2144; J. S. C. I. 1930, **49**, 8-B.
4. *Ibid.* E. P. 318664; abst. C. A. 1930, **24**, 2144; J. S. C. I. 1930, **49**, 8-B. See also E. P. 313418; abst. C. A. 1930, **24**, 1124.
5. *Ibid.* F. P. 667292; abst. C. A. 1930, **24**, 1124.
6. *Ibid.* F. P. Addn. 37089 to 634167; abst. C. A. 1931, **25**, 971.
7. *Ibid.* F. P. 675817; abst. C. A. 1930, **24**, 2759.
8. *Ibid.* F. P. 675818; abst. C. A. 1930, **24**, 2759.
9. *Ibid.* F. P. 675819; abst. C. A. 1930, **24**, 2759.

vapor phase under pressure[1] with a catalyst comprising zinc acetate, or metal oxides or methylates which are capable of forming such acetates, at not exceeding 450°, or[2] by passing methane and CO_2 under pressure in contact with heated catalyst of Ni, or Fe. carbonates, between 120° and 300°. Or[3], methyl alcohol and CO may be heated with an oxide of Zn., Cu., Sn., Pb., or zinc acetate, or the methylates of Zn., Al. or Sn., with or without K. of Na. acetates. Acetone is simultaneously formed.

In the treatment of waste acids used in the manufacture of cellulose acetate[4] for the production of acetaldehyde, keten or acetic anhydride, the dilute acid is subjected to a reduction process whereby the acetic acid content is converted into acetaldehyde, which is separated from the resulting mixture by fractional condensation. Or[5], the acetic acid may be extracted from aqueous solutions by solvents in two or more stages, the solvents being so chosen that in each stage the ratio of acid to water in the extract is greater than in the stage preceding. With acetic acid the first stage may be effected with ether or ethyl acetate, or ether with petroleum ether or halogenated hydrocarbons.

Keten, acetic acid or acetic anhydride[6] may be prepared by converting acetaldehyde into keten or products comprising keten by subjecting in vapor form at relatively high temperatures to Ni., Cu., Zn., or other hydrogen-splitting catalyst. Acetic acid or methyl acetate is obtained by reaction of dimethyl ether and CO[7] in presence of alkali

1. U. S. P. 1697109; abst. C. A. 1929, **23**, 1141; J. S. C. I. 1929, **48**, 200-B. E. P. 259641; abst. J. S. C. I. 1926, **45**, 1013-B. Can. P. 289157.
2. H. Dreyfus, U. S. P. 1704965; abst. C. A. 1929, **23**, 1909; J. S. C. I. 1929, **48**, 388-B. Compare E. P. 226248; abst. J. S. C. I. 1925, **44**, 148-B. Also U. S. P. 1697109; abst. C. A. 1929, **23**, 1141.
3. *Ibid.* Can. P. 289159, 289160, 289163.
4. *Ibid.* Can. P. 289161.
5. *Ibid.* F. P. 677882; abst. C. A. 1930, **24**, 3250.
6. *Ibid.* Can. P. 289162.
7. *Ibid.* E. P. 319030; abst. C. A. 1930, **24**, 2473; J. S. C. I. 1930, **49**, 95-B. F. P. Addn. 36739; abst. C. A. 1931, **25**, 970. U. S. P. 1743659; abst. C. A. 1930, **24**, 1392.

alcoholates or alkali formates as catalysts, the production depending upon the proportion of water present in the reaction mixture.

Cellulose may be esterified by fatty acid anhydrides in the presence of HCl, HBr, or HI, or their Fe., Mn., Co., Ni. salts, the acid or halide being each present in amounts at least equal to 2% by weight of the cellulose. The cellulose may be pretreated with formic or acetic acids before esterification to increase their reactivity[1]. Or[2] zinc chloride, bromide or iodide may be used in conjunction with HCl, HBr, or HI.

The cellulose prior to esterification may be treated with a mixture of hot acetic acid with sodium acetate[3], or the anhydride in liquid or vapor form may be diluted with an inert diluent[4], the treatment being followed by submission to the usual acetylating mixture. Cellulose acetate and esters of higher homologues of acetic acid (propionate and butyrates) or mixed cellulose esters (aceto-propionate, aceto-butyrate, propio-butyrate) may be prepared by subjecting the cellulose to a preliminary treatment with formic or acetic acids, then esterifying with the appropriate anhydride and acid in the presence of one or more chlorides, bromides or iodides of P., As., or Sb.[5]. The cellulose may be treated with acetic acid in the form of vapor[6], or by formic

1. H. Dreyfus, F. P. 660623; abst. C. A. 1930, **24**, 238. F. P. Addn. 36175 to 660623; abst. C. A. 1930, **24**, 4156. F. P. 664674; abst. C. A. 1930, **24**, 961. F. P. 666896; abst. Cellulose, 1930, **1**, 126; C. A. 1930, **24**, 1217. E. P. 309201; abst. J. S. C. I. 1929, **48**, 593-B; Silk Journal, 1929, **6**, #63, 66; C. A. 1930, **24**, 499. E. P. 312098; abst. J. S. C. I. 1929, **48**, 750-B; Brit. Plastics, 1929, **1**, 152.

2. *Ibid.* E. P. 308323; abst. Silk Journal, 1929, **6**, #62, 70, J. S. C. I. 1929, **48**, 593-B.

3. *Ibid.* U. S. P. 1731299; abst. Cellulose, 1930, **1**, 34; C. A. 1930, **24**, 238; J. S. C. I. 1929, **48**, 976-B. E. P. 207562; abst. J. S. C. I. 1924, **43**, 129-B. F. P. Addn. 36935 to 675354; abst. C. A. 1931, **25**, 1081.

4. *Ibid.* F. P. 675354; abst. C. A. 1930, **24**, 2880.

5. *Ibid.* E. P. 311790; abst. Silk Journal, 1929, **6**, #64, 64; C. A. 1930, **24**, 961; J. S. C. I. 1929, **48**, 594-B. Can. P. 303094. Belg. P. 372409. Ital. P. 274795. Swiss P. 143347. See F. P. 601297, 615906, 615907, 617655.

6. *Ibid.* U. S. P. 1711111; abst. C. A. 1929, **23**, 3098; J. S. C. I. 1929, **48**, 514-B. E. P. 263939; abst. J. S. C. I. 1927, **46**, 247-B.

acid[1], or in the presence of stannic chloride, bromide or iodide as catalyst[2], or ferric chloride or bromide[3].

Products capable of resisting the delustering action of boiling water, or wet steam, are obtained by dry spinning acetone solutions of cellulose acetate containing less than 2.5% water, or more than 12-28%, under such conditions that precipitation of the cellulose acetate does not take place during the spinning process, the process being equally applicable to cellulose formate, propionate or butyrate[4]. For the production of effects of patterns on woven or knitted cellulose acetate fabrics, there is locally applied to the fabric formic, acetic, propionic, butyric, chlor-acetic, amino-acetic, glycollic, lactic, citric or succinic acids, preferably thickened with starches or gums[5]. If the acetate silk is treated with a swelling agent and then stretched beyond its elastic limit[6], it is said to be more resistant to deterioration by hot aqueous media. H. Dreyfus has also described a spinning chember[7], tension-controlled device for pirns for use in loom shuttles[8], and the construction of a pressure pump[9], all designed for cellulose acetate filament production.

In treating textiles containing natural silk with alkaline liquors[10], the silk is protected against the action of the

1. H. Dreyfus and C. Haney, U. S. P. 1697907; abst. Plastics, 1929, **5**, 573; J. S. C. I. 1929, **48**, 242-B; C. A. 1929 ,**23**, 1267. E. P. 288657; abst. J. S. C. I. 1928, **47**, 444. H. Dreyfus, E. P. 308322; abst. Silk Journal, 1929, **6**, #62, 70; C. A. 1930, **24**, 239; J. S. C. I. 1929, **48**, 593-B.

2. H. Dreyfus, E. P. 312096; abst. C. A. 1930, **24**, ›62; J. S. C. I. 1929, **48**, 750-B; Brit. Plastics, 1929, **1**, 152. Ital. P. 274657.

3. *Ibid.* E. P. 312095; abst. C. A. 1930, **24**, 962; J. S. C. I. 1929, **48**, 750-B; Brit. Plastics, 1929, **1**, 152. F. P. 685277. Belg. P. 372407, 372408. Ital. P. 273653.

4. H. Dreyfus and Celanese Corp. of America, E. P. 320363; abst. C. A. 1930, **24**, 2600; J. S. C. I. 1929, **48**, 1011-B; Silk J. and Rayon World, 1930, **6**, #68, 70. F. P. 672306; abst. C. A. 1930, **24**, 2293. See also F. P. 657764; abst. C. A. 1929, **23**, 4572.

5. H. Dreyfus, Can. P. 287773, 293051, 293053.

6. *Ibid.* Can. P. 293057.

7. *Ibid.* F. P. 661810; abst. C. A. 1930, **24**, 500.

8. *Ibid.* Can. P. 293065.

9. *Ibid.* F. P. 677462; abst. C. A. 1930, **24**, 3113.

10. *Ibid.* F. P. 677262; abst. C. A. 1930, **24**, 3118. Cf. F. P. 669247; abst. C. A. 1930, **24**, 1750; F. P. 661936; abst. C. A. 1930, **23**, 510.

reagent by a coating of cellulose acetate. Cellulose acetate silk[1] may be hydrolyzed by NaOH, KOH, sodium aluminate or sodium silicate. Best results are alleged to result[2] when the filaments are made from solutions of cellulose acetate by spinning or molding followed by a partial alkali saponification.

In dry spinning of cellulose acetate solutions[3] containing volatile solvents, one or more non-solvents of the ester, possessing a boiling point higher than the volatile solvent, is used, a representative formula being cellulose acetate 27, acetone 65.8, xylene 3.6, and diacetone alcohol 3.6 parts. An apparatus for carrying out such a process[4] involves an evaporating agent directed towards the region in which the filaments leave the spinning nozzles. It is advocated[5] to keep the volatile solvents at a predetermined heat during passage of the solution of cellulose acetate to the spinning nozzles. Staple fibers may be produced in this manner[6].

In the production of hollow filaments by dry spinning cellulose acetate solutions[7], there is added to the spinning solution containing a volatile solvent, high boilers in such proportions that the latter are incompletely evaporated during the spinning operation. Solvents with a boiling range of about 35° difference are suggested[8], such as acetone and acetaldehyde, alcohol and methyl formate, methyl formate and cyclobutanone or acetone and water. Drawing out fine filaments is thus facilitated. Acetone and acetic

1. H. Dreyfus, F. P. 676127; abst. C. A. 1930, **24**, 2899. See also E. P. 258874, 260290; abst. J. S. C. I. 1928, **47**, 228-B, 477-B. E. P. 284798; abst. C. A. 1928, **22**, 4836. E. P. 309876; abst. C. A. 1930, **24**, 735. Belg. P. 342075, 344890.
2. *Ibid.* F. P. 687471; abst. C. A. 1931, **25**, 815.
3. *Ibid.* F. P. 666897; abst. C. A. 1930, **24**, 1218.
4. *Ibid.* F. P. 679618; abst. C. A. 1930, **24**, 3902.
5. *Ibid.* F. P. 677461; abst. C. A. 1930, **24**, 3113. Can. P. 292894.
6. *Ibid.* E. P. 322417; abst. J. S. C. I. 1930, **49**, 100-B.
7. *Ibid.* E. P. 317097; abst. C. A. 1930, **24**, 1979; J. S. C. I. 1929, **48**, 937-B. Can. P. 292895, 292896. F. P. 666898; abst. C. A. 1930, **24**, 1218.
8. *Ibid.* E. P. 317098; abst. C. A. 1930, **24**, 1979; J. S. C. I. 1929, **48**, 937-B.

acid, acetone-acetic, acid-ethyl alcohol, ethyl alcohol-hydrocarbon, methyl acetate-cyclobutanone are combinations also recommended[1].

For diminishing the luster of acetate filaments, H. Dreyfus has been granted protection for the operation of steaming[2], the use of thiocyanate, zinc chloride or ammoniacal copper, all in aqueous solution[3], or alkali metal zincates[4]. Acetate filaments free from luster are prepared by dry spinning solutions in volatile solvents containing water, under such conditions that the water exercises a precipitating action on the filaments in the nascent state[5], or organic precipitating agents as ethyl alcohol, cyclohexanol, benzene, xylene, gasoline, petroleum ether or esters may be used instead of water in amount of 1-40, preferably 5-30% of the solution[6].

In the dyeing of cellulose acetate according to the H. Dreyfus methods, where dyes are used insoluble or practically insoluble in water[7], the colors may be solubilized by treating them with a sulfoaromatic acid as sulfobenzene ricinoleic acid, sulfophenol ricinoleic acid or sulfonaphthalene ricinoleic acid or their Na., K. or ammonium salts. Unsulfonated azo derivatives of dehydrothio-*p*-toluidine[8], or the use of azo dyestuffs containing an anthraquinone nucleus, by the coupling of a diazotized anthraquinone derivative have received patent protection[9].

A compound containing at least one urethane residue, e.g., 4.4-dinitrodiphenylurethane (dyeing yellow)[10], or one amino group substituted by an aliphatic grouping containing not less than 2 OH groups, e.g., an azo dye from picra-

1. H. Dreyfus, F. P. 667209; abst. C. A. 1930, **24**, 1217. Compare F. P. 664064, 664065; abst. C. A. 1930, **24**, 963.
2. *Ibid.* F. P. 686644; abst. C. A. 1931, **25**, 605.
3. *Ibid.* F. P. 678399; abst. C. A. 1930, **24**, 3646.
4. *Ibid.* Can. P. 293067.
5. *Ibid.* F. P. 664064; abst. C. A. 1930, **24**, 963.
6. *Ibid.* F. P. 664065; abst. C. A. 1930, **24**, 963.
7. *Ibid.* Can. P. 293050.
8. *Ibid.* Can. P. 293066.
9. *Ibid.* Can. P. 293064.
10. *Ibid.* U. S. P. 1735960; abst. C. A. 1930, **24**, 972.

mic acid and dihydroxypropylaniline[1], or a coloring compound containing at least one thiourethane residue, e.g., the product obtained by heating 1-acetylaminoanthraquinone 4-isothiocyanate with ethyl alcohol or alcoholic potash[2] have also been put forward.

The relative affinity for basic dyes of textiles containing cellulose acetate and cotton may be regulated by treatment with a mordant or tannin under such conditions that no swelling of the cellulose derivative takes place[3]. Cellulose acetate may be colored by applying thereto a free arylide of a hydroxynaphthoic acid with an amine and afterwards diazotizing[4], or[5] by treatment with monazo, disazo or polyazo dyes obtained by diazotizing and coupling aminonitro compounds containing two or more aryl groups with one or several molecules of the same or different coupling constituents. Thus an orange-gold shade is produced on cellulose acetate by the dye, 2.4-dinitro-4′-aminodiphenylamine plus phenol. The cellulose acetate may also be colored by applying an aqueous dispersion of one or more dyes or organic compounds which are relatively insoluble[6], the dye being entirely in the colloid state.

Basic derivatives of anthraquinone are prepared by treating leucohydroxyanthraquinones or anthranols with ammonia or alkylamines at ordinary or increased pressure in the presence of NaOH and oxidizing. Thus, 1.2.5.8-tetrahydroxyanthraquinone is reduced and refluxed with methylamine, and the resulting leuco compound oxidized with sodium perborate. Cellulose acetate is dyed a greenish blue[7]. Cellulose acetate film may be uniformly dyed and there is transferred to it a design with a mixture containing

1. H. Dreyfus, U. S. P. 1735961; abst. C. A. 1930, **24**, 972.
2. *Ibid.* U. S. P. 1735963; abst. C. A. 1930, **24**, 972.
3. *Ibid.* F. P. 675466; abst. C. A. 1930, **24**, 2896. Can. P. 292893. Cf. F. P. 658415; abst. C. A. 1929, **23**, 5329.
4. *Ibid.* F. P. 667167; abst. C. A. 1930, **24**, 1227.
5. *Ibid.* F. P. 682202; abst. C. A. 1930, **24**, 4405.
6. *Ibid.* F. P. 668864; abst. C. A. 1930, **24**, 1749. Compare F. P. 667167; abst. C. A. 1930, **24**, 1227.
7. *Ibid.* F. P. 667415; abst. C. A. 1930, **24**, 1226.

starch, a gum, chlorates and potassium ferricyanide, the mixture having a tendency to bleach and discharge the dye[1]. If there is applied substituted amino derivatives of benzo- or naphtho-quinones in the unreduced state, of mono- or di-amides of benzo- or naphtho-quinones or substituted derivatives, cellulose acetate is colored a yellow-brown[2].

Textiles of cellulose acetate are treated with alkaline solutions of tin, zinc, K. or Na. stannates or zincates being particularly advantageous[3], because the textile absorbs a considerable amount of the metallic radical and becomes more resistant to heat treatments and shows an affinity to direct cotton dyes, mordant dyes and indigoid and anthraquinone vat dyes. Absorption of the alkaline solutions is favored by adding swelling agents such as thiocyanates. The H. Dreyfus diazotyle process comprises the incorporation of a diazotizable substance in a cellulose acetate base[4]. The surface is then exposed to light and developed in the usual manner.

In order to produce cellulose acetates of unusually high viscosity[5], the cellulose is esterified with a strong condensing agent such as acetic anhydride and sulfuric acid in the presence of a quantity of acetic acid at least six times the weight of the cellulose[6]. For the manufacture of methyl alcohol[7] water gas containing about 1 molecule hydrogen to 1 molecule CO is subjected to the action of heat and pressure in presence of catalysts, which unite in themselves the dual capacity of initiating the combination of H. and CO (probably to form formaldehyde), and having at the

1. H. Dreyfus, F. P. 667211; abst. C. A. 1930, **24**, 1227.
2. *Ibid.* F. P. 679489; abst. C. A. 1930, **24**, 3910. See also F. P. 668864; abst. C. A. 1930, **24**, 1749.
3. *Ibid.* F. P. 661936; abst. C. A. 1930, **24**, 510.
4. *Ibid.* F. P. 667210; abst. C. A. 1930, **24**, 1228.
5. *Ibid.* U. S. P. 1708787; abst. J. S. C. I. 1929, **48**, 470-B; Plastics, 1929, **5**, 699; C. A. 1929, **23**, 2569. See also E. P. 207562; abst. J. S. C. I. 1924, **43**, 129-B.
6. See U. S. P. 1217722, 1278885, 1280974, 1280975, Re- 14338. E. P. 20977, 1911; 20852, 1912; 6463, 1915; 14101, 1915; 100009, 101555.
7. H. Dreyfus, Can. P. 289156.

same time a sufficiently basic character to transform the initial products directly into methyl alcohol. Keten[1] may be prepared by combining 3 molecules CO with 1 molecule H. under heat and pressure and in presence of such catalysts as zinc or copper oxides, zinc or copper chromate, zinc aluminate, potassium zincate, or mixtures of zinc oxide-potassium carbonate, and especially chromates or vanadates. Ripening of cellulose esters may be effected in an organic medium in which the ester is initially insoluble and in which the ripening agents (water, alcohols, glycerol, lactic acid) are insufficiently soluble to enable the ripening to be effected, e.g., mixtures of ether with benzene or toluene[2]. The ripening may be carried out in the presence of acids or acid salts, or salts of aromatic amines.

E. I. du Pont de Nemours[3] manufacture cellulose acetate continuously by causing the reacting material to pass, during the reaction process, through apparatus of small diameter compared to the length, by rotating the same about an inclined axis; the material, during its progress through the apparatus, being subjected to the action of internal devices affecting the manner of mixing, and speed of rotation. This firm produces lacquers and plastics suitable for artificial leather manufacture by using carboxylic esters of a phenoxyethyl alcohol, e.g., *b*-phenoxyethyl phthalate or laurate with cellulose acetate[4].

According to Durand & Huguenin A. G., acetyl silk may be dyed or printed with a solution of an ester of a vat dye, dried, vaporized, and afterwards developed by prolonged oxidation at high temperature[5]. W. Dyes[6] has

1. H. Dreyfus, Can. P. 289158.
2. *Ibid.* F. P. 679284; abst. C. A. 1930, **24**, 3901.
3. E. du Pont de Nemours & Co., Soc. Chim. des Usines du Rhone Florentin Biduad, Can. P. 291000.
4. E. du Pont de Nemours & Co., E. P. 306911; abst. Brit. Plastics, 1930, **2**, #17, 100; J. S. C. I. 1930, **49**, 900-B; C. A. 1929, **23**, 5338.
5. F. Addn. 33853 to 571264; abst. C. A. 1929, **23**, 3817. Cf. E. P. 274094; abst. C. A. 1928, **22**, 2066.
6. Jentgen's Artificial Silk Review, 1929, **1**, 68.

given an unusually comprehensive review of Celanese, Rhodiaseta, Aceta and other cellulose acetate products with copious bibliographic references.

Eastman Kodak Co.[1] remove water from aqueous acetic acid by mixing with ethylene dichloride and distilling. C. Ebert and T. Becker[2] prepare cellulose acetate by acetylation in the presence of thionyl chloride, zinc or cuprous chlorides, hydrolyzation being conducted so as to obtain an ester soluble in acetone and ethyl acetate. They acetylate cotton 25, with acetic anhydride 75, and glacial acetic acid 100, at 65°, after the addition of 0.25 $ZnCl_2$ or Cu_2Cl_2 and 1.4 thionyl chloride.

G. H. Ellis has disclosed five processes for the dyeing of cellulose acetate, in one of which[3] is used basic dyes for the anthracene series such as aminoanthraquinones in the form of soluble modifications obtained by pretreating them with a sulfonated ricinoleic acid compound. Or there may be employed[4] an aqueous dispersion of a relatively water-insoluble dye prepared by treating the coloring material with a solubilizing agent of sodium sulforicinoleate in xylene. The fastness to light of cellulose derivatives colored with azo colors[5] is increased by treatment with diethylaniline chloride or other simple organic amino compound. Dyeing may also be effected[6] by the use of relatively insoluble unreduced indophenol dyes, which are employed in the form of solubilized modifications obtained by pretreating them with sodium sulforicinoleate, or[7], the coloring materials may be of the indigoid series.

1. Can. P. 291770.
2. U. S. P. 1701229; abst. Plastics, 1929, **5**, 337; C. A. 1929, **23**, 1504; J. S. C. I. 1929, **48**, 280-B. E. P. 289973; abst. J. S. C. I. 1928, **47**, 920-B.
3. U. S. P. 1719324; abst. C. A. 1929, **23**, 4083; J. S. C. I. 1929, **48**, 717-B. E. P. 219349; abst. J. S. C. I. 1924, **43**, 906-B.
4. U. S. P. 1723271; abst. C. A. 1929, **23**, 4580; J. S. C. I. 1930, **49**, 238-B. E. P. 284376; abst. J. S. C. I. 1928, **47**, 229-B.
5. U. S. P. 1723230; abst. C. A. 1929, **23**, 4580.
6. U. S. P. 1740890; abst. C. A. 1930, **24**, 1227.
7. U. S. P. 1740891; abst. C. A. 1930, **24**, 1227.

A. Eichengruen[1] produces fine filaments of less than 3-4 denier by the extrusion through normal apertures of cellulose acetate dissolved in either (1) acetone or a latent solvent, (2) methylene chloride together with a higher boiling coagulant, (3) alcohol, benzene or water, the dimensions of the extruded filaments being regulated by adjusting the relative amounts of the constituents, keeping the cellulose acetate in solution, and varying the winding speeds, which should be greater than 75 meters per minute. J. Elgersma[2] prepares highly esterified acetylnitrocellulose. After acetylating partly nitrated cellulose with acetic acid and anhydride in the presence of sulfuric acid as catalyst, excess of anhydride is removed, and the whole kept at 30-50° until the cellulose sulfate present has been transformed into acetate.

The I. G. Farbenindustrie[3] form acetaldehyde and acetic acid by passing a mixture of methane, H. and O., or substances yielding O, over tin, silver or mercury vanadates as catalysts. Or[4], mercury phosphate, vanadate or sulfate; or the vanadates of Ag. or Sn., or oxides of Zn., Fe., Mn., Ce., Ag. or Sn., or the oxides of W. or V. Acetaldehyde may be formed by hydration of acetylene in the presence of a solution of mercuric and ammonium salts, such as formed with ammonium sulfate 500, mercuric oxide 10 and sulfuric acid 183 parts for each 1000 parts water[5]. In the

1. E. P. 317408; abst. J. S. C. I. 1929, **48**, 848-B; Silk Journal, 1929, **6**, #67, 70. F. P. 669309; abst. Cellulose, 1930, **1**, 150; C. A. 1930, **24**, 1740.

2. E. P. 317854, 317855; abst. Brit. Plastics, 1931, **2**, #21, 159; J. S. C. I. 1931, **50**, 16-B; C. A. 1930, **24**, 2291; Silk Journal, 1929, **6**, #67, 72. F. P. 680385; abst. C. A. 1930, **24**, 3900. Holl. P. 20725; abst. C. A. 1930, **24**, 4633. F. P. 658324; abst. C. A. 1929, **23**, 5317.

3. E. P. 304855; abst. C. A. 1929, **23**, 4712; J. S. C. I. 1929, **48**, 315-B. F. P. 645967; abst. C. A. 1929, **23**, 1910. F. P. 671285; abst. C. A. 1930, **24**, 2145. See also E. P. 313864; abst. C. A. 1930, **24**, 1125.

4. I. G. Farbenindustrie, E. P. 321241; abst. C. A. 1930, **24**, 2474; Chem. Zentr. 1930, I, 1367. F. P. Addn. 36583; abst. C. A. 1930, **24**, 5768.

5. *Ibid.* E. P. 319542; abst. C. A. 1930, **24**, 2474; J. S. C. I. 1930, **49**, 94-B. F. P. 657027; abst. C. A. 1929, **23**, 4231.

separation of formic and acetic acids by rectification[1], carbon tetrachloride, benzene, benzine or trichlorethane are added to lower the boiling point of the acetic acid. Or[2], the separation may be effected by adding an entraining liquid soluble in acetic, but not in formic, acid to the mixture of acids, when, upon distilling the azeotropic mixture of formic acid and added liquid (together with any water present) is first collected, glacial acetic acid remaining in the distilling vessel.

In the manufacture of glacial acetic from the dilute acid, the I. G. Farbenindustrie[3] cool the dilute acid with vigorous agitation to —26° (eutectic point of acetic acid-water), the ice crystals are removed, and the 60% acid obtained treated with a substance which forms a double compound from which acetic acid may be regenerated, e.g., carbamide or potassium acetate. The double compound is frozen out and glacial acetic acid vacuum distilled from the separated product. Other means of concentration may be used[4]. To produce aldehyde[5], acetylene is passed into concentrated solution of salts showing acid reaction (zinc, chromic or ferric chlorides) at 110-140°, with or without the addition of mercury or uranium compounds. The acetic acid may be concentrated to about 60%, then a substance added which forms an addition compound with acetic acid[6] (as urea, other amide, *p*-toluidine or potassium acetate),

1. I. G. Farbenindustrie, A.-G., F. P. 668629; abst. C. A. 1930, **24**, 1651. Can. P. 295135.
2. *Ibid.* E. P. 305594; abst. J. S. C. I. 1930, **49**, 409-B; C. A. 1929, **23**, 4711.
3. *Ibid.* E. P. 312173; abst. J. S. C. I. 1930, **49**, 1015-B.
4. *Ibid.* E. P. 315397 Addn. to 312173; abst. J. S. C. I. 1930, **49**, 1142-B; C. A. 1930, **24**, 1651. Cf. E. P. 312173; abst. C. A. 1930, **24**, 863; J. S. C. I. 1930, **49**, 1015-B. F. P. 675288; abst. C. A. 1930, **24**, 2756. F. P. 652820; abst. C. A. 1929, **23**, 3716. In F. P. 665412; abst. C. A. 1930, **24**, 863, concentration is carried out with solvents to which have been added a liquid having the property of eliminating water from the solvent, such as ethyl acetate-benzene, benzyl alcohol-benzene or methylcyclohexanone-benzene. Cf. E. P. 294636; abst. C. A. 1929, **23**, 1909. F. P. 647682; abst. C. A. 1929, **23**, 2449.
5. *Ibid.* E. P. 313864; abst. J. S. C. I. 1929, **48**, 708-B.
6. *Ibid.* E. P. 312137; abst. C. A. 1930, **24**, 863.

the additional remaining water being removed by distillation or crystallization.

To produce halogenated cellulose acetates, the triacetate is dissolved or suspended in an indifferent medium as tetrachlorethane, and treated with a chlorinating agent as phosphorous pentachloride to replace all of the hydrogen atoms of the acid radical of the cellulose carboxylate with Cl. The products show increased stability towards hydrolytic agents and increased solubility[1]. Phosphorous trichloride, while exposing the mixture to light, is also recommended[2]. Cellulose esters of the higher fatty acids may be formed by acting upon cellulose with the chloride of a higher fatty acid in presence of an organic base, raising the temperature from 100° to 200° during the course of the process[3], then heating the insoluble ester thus formed to a temperature above 100°[4]. In the manufacture of cellulose acetonitrates (nitroacetates)[5], cellulose is treated with acetic acid and anhydride at 50-100° and ammonium nitrate or urea nitrate in the presence of 0.3-1% sulfuric acid, or by adding nitric acid at an advanced state of acetylation[6].

Cotton acetylation baths may be formed with the addition of naphthalenesulfonic acid substituted with phenyl, butyl or higher alkyl radicals, solvent assisting substances such as the reaction product of oleic acid and sulfuric acid being added[7]. Acetone soluble cellulose acetates may be obtained by treating a cellulose triacetate isolated as such, with a mixture of dilute mineral acids, as a mixture of

1. I. G. Farbenindustrie, A.-G., E. P. 306132; abst. C. A. 1929, **23**, 5040; J. S. C. I. 1930, **49**, 504-B.
2. *Ibid.* Can. P. 294946. F. P. 669178; abst. Cellulose, 1930, **1**, 150.
3. *Ibid.* Can. P. 294305. 4. *Ibid.* Can. P. 294306.
5. *Ibid.* E. P. 319285; abst. J. S. C. I. 1931, **50**, 343-B; C. A. 1930, **24**, 2600. W. Walter and L. Lock, U. S. P. 1819397.
6. *Ibid.* F. P. 681143; abst. C. A. 1930, **24**, 4390. Cf. D. R. P. 483999, F. P. 664214, 664459; abst. C. A. 1930, **24**, 961.
7. *Ibid.* E. P. 309203; abst. C. A. 1930, **24**, 499; Silk Journal, 1929, **6**, #63, 66; J. S. C. I. 1929, **48**, 469-B. Swiss P. 134626.

dilute nitric and sulfuric acids[1]. The cellulose may be acetylated below 50° with less than 2% (on the weight of the cellulose) of sulfuric acid, part of the fatty acid normally present being replaced by monochloracetic acid[2].

Acetate silk may be prepared by spinning the material into a solution containing ammonium nitrate[3], to which is added an inorganic salt (ammonium thiocyanate, zinc chloride) having a swelling or solvent action, together with sugar and a small amount of acetone. Or the coagulated thread after emergence from the spinning bath[4] is treated with dilute formic or acetic acids while still under tension, and the stretched thread afterwards passed through a hardening or setting bath during the winding operation[5].

In dressing artificial silk yarn, a cellulose di- or polyfatty acid of an alkali metal salt of such an acid, obtained by treating alkalicellulose with at least twice the proportion of a salt of a halogenated fatty acid necessary for the formation of the mono-substituted compound, is useful for dressing artificial silk yarn[6]. In producing patterns on fabrics[7], by stamping prepared sheets laid on the surface, the prepared sheets comprise two layers of pliable material, the lower layer softens when heated and the upper layer does not become sticky when warmed. The lower layer may be of rubber, higher aliphatic cellulose esters, and the other layer resinous substances of higher melting point.

1. I. G. Farbenindustrie, A.-G., E. P. 312232; abst. Silk Journal, 1929, **6**, #64, 66; C. A. 1930, **24**, 962. E. Specifications 1930, 1905; 24067, 1906, are referred to. F. P. 674478; abst. C. A. 1930, **24**, 2600; F. P. 664214; abst. C. A. 1930, **24**, 961. Ital. P. 270389, 273936. Belg. P. 366321, 368313, 370088.

2. *Ibid.* E. P. 305674; abst. Brit. Plastics, 1930, **2**, #17, 230; J. S. C. I. 1930, **49**, 814-B; Silk Journal, 1929, **5**, #60, 68; C. A. 1929, **23**, 4818.

3. *Ibid.* E. P. 312671 Addn. to 233342; abst. Silk Journal, 1929, **6**, #64, 68; J. S. C. I. 1930, **49**, 1022-B; C. A. 1930, **24**, 963. F. P. 674761; abst. Chem. Zentr. 1930, II, 843. Ital. P. 278314.

4. *Ibid.* E. P. 318646; abst. J. S. C. I. 1931, **50**, 242-B; Silk Journal, 1929, **6**, #67, 72; C. A. 1930, **24**, 2293.

5. *Ibid.* E. P. 309558; abst. J. S. C. I. 1930, **49**, 986-B; C. A. 1930, **24**, 734. F. P. 682084; abst. C. A. 1930, **24**, 4391.

6. *Ibid.* E. P. 317117; abst. C. A. 1930, **24**, 1992.

7. *Ibid.* E. P. 311741; abst. C. A. 1930, **24**, 975.

A sheet of cellulose acetate is used as a carrier and subsequently removed.

To increase the luster of acetate silk[1], it may be treated with a dilute organic acid as acetic, formic or propionic, stretched, and finally washed while maintaining or increasing the luster. To prevent accidental uncoiling of films[2], two of the turns of the film at the end are stuck together with a readily disrupted adhesive, a 15% solution of cellulose acetate in benzene having been patented for this purpose. Cellulose laurate 15%, in benzene[3] has also been patented for this purpose.

In order to render cellulose acetate solutions capable of stretch spinning in salt baths, the ester dissolved in acetone is spun into a calcium chloride setting bath to which is added either ethyl acetate, aniline, pyridine, chlorethyl hydroxide, benzene, ethyl alcohol or chlorbenzene. If the ester is to be spun from an acetic acid solution into a sodium acetate setting bath, here may be added tetrachlorethane[4]. If it is desired to stabilize the acetate silk against boiling and make resistant to the action of alkalis, the ester is prepared from acetic acid with about 0.2 molecules or more of a higher fatty acid as propionic or butyric to one molecule of cellulose ester[5]. In the production of acetate silk by the wet process[6], the setting bath is composed of concentrated liquid oily solutions of high viscosity, using sugar, glycerol, glycol or urea, with or without the additions of such salts as ammonium nitrate or sulfocyanide, or zinc chloride.

1. I. G. Farbenindustrie, A.-G., E. P. 309558; abst. C. A. 1930, **24**, 734; Silk Journal, 1929, **6**, #63, 66; J. S. C. I. 1930, **49**, 986-B.

2. *Ibid.* E. P. 307499; abst. C. A. 1929, **23**, 5123.

3. *Ibid.* E. P. 307399.

4. *Ibid.* D. R. P. 479003; abst. C. A. 1929, **23**, 4819. Compare D. R. P. 477066; abst. C. A. 1929, **23**, 4070.

5. *Ibid.* F. P. 686922; abst. C. A. 1931, **25**, 814. Or (F. P. 662353; abst. C. A. 1930, **24**, 498; see C. A. 1930, **24**, 238) stabilization of cellulose acetate may be effected by a final treatment with an hydrolytic agent, as 0.025% sulfuric acid below 100°.

6. *Ibid.* F. P. 682912; abst. C. A. 1930, **24**, 4632.

The I. G. Farbenindustrie claim[1] that acetate silk having a high degree of resistance to boiling may be obtained by using acetone-soluble cellulose acetates prepared by known methods, preferably in the stabilized form, and insoluble or nearly so in 70% alcohol. The filaments made with the hydrolysis products formed at a certain stage of this treatment differ by their high resistance to boiling, from the rayons obtained from the hydrolysis of products formed in a later stage of the process, which are nearly or completely soluble in dilute alcohol. Such a result appears surprising in view of the small difference in the acetic acid contents of the products of the different stages of hydration, which is 54-56% for the products comprehended in the patent, and 53% for the products of the other stages of hydrolysis. In another process[2], acetylcellulose silk is treated with swelling agents after leaving the precipitating bath and then drawn, during winding the filament being treated with a hardening agent. Thiocyanates or zinc chloride may be added to the precipitating bath[3].

Resistance when dry or wet in acetate silk may be increased and the denier made finer[4] by drawing it out to more than 50% while charged with formic or acetic acids, then carefully and gradually eliminating the acid while maintaining or increasing the traction. A long spinning nozzle[5], as glass or metal spinning nozzles with long opening of small diameter are advocated[6], the thread being drawn after leaving the nozzle. Bobbins for winding textile threads may be improved by coating them with cellulose

1. I. G. Farbenindustrie, A.-G., F. P. 681696; abst. Cellulose, 1930, **1**, #9, 246; C. A. 1930, **24**, 4391. E. P. 319014; abst. C. A. 1930, **24**, 2602; Silk Journal and Rayon World, 1930, **6**, #68, 66.
2. *Ibid.* F. P. 681301; abst. C. A. 1930, **24**, 4391. E. P. 318646; abst. C. A. 1930, **24**, 2293.
3. *Ibid.* F. P. 674761; abst. C. A. 1930, **24**, 2883.
4. *Ibid.* F. P. 672301; abst. C. A. 1930, **24**, 2293.
5. *Ibid.* F. P. 674268; abst. C. A. 1930, **24**, 2601.
6. *Ibid.* F. P. 674269; abst. C. A. 1930, **24**, 2601.

derivatives of higher fatty acids[1], a layer of resin being applied over the composition.

Production of plastics which are resistant to water and difficultly flammable[2] are made from mixed esters of cellulose as cellulose aceto-propionate or aceto-butyrate[3]. Or threads and films may be made of chlorinated organic cellulose esters[4], or mixtures of such derivatives with cellulose acetate, may be dyed with basic dyes. The chlorinated esters dye more readily[5]. In dyeing combinations of cellulose and esterified cellulose[6] for the production of especial effects, staining of the esterified cellulose is prevented by adding to the dyebath a phenol condensation product with sulfuric acid and formaldehyde, or a sulfurized derivative of a phenol or amorphous sulfonic acid which precipitates glue in acid solution, and dyes are used (enumerated in the patent) which have little or no affinity for the esterized cellulose[7].

Pure white or colored effects are said to be produced on acetate silk by dyeing the cloth with dischargeable diazotizable products[8], diazotizing, developing and afterwards toning with dischargeable dyes applied to the filaments, finally locally treating with suitable discharge paste. In producing black dyes with white or colored effects on acetate silk[9], the reserves of mechanical action[10] may be replaced by reserves of chemical action, and the black developed by vaporization.

1. I. G. Farbenindustrie, A.-G., F. P. 673996; abst. C. A. 1930, **24**, 2618. E. P. 311287; abst. C. A. 1930, **24**, 976; Brit. Plastics, 1930, **2**, #17, 229. Can. P. 290805.
2. *Ibid.* F. P. 680860; abst. C. A. 1930, **24**, 4128. Compare F. P. 659116; E. P. 295940; abst. C. A. 1929, **23**, 5283.
3. *Ibid.* F. P. 664459; abst. C. A. 1930, **24**, 961. See also D. R. P. 139669 and F. P. 662624. F. P. Addn. 37820 to 664459.
4. *Ibid.* E. P. 306132; abst. J. S. C. I. 1930, **49**, 504-B; C. A. 1929, **23**, 5040.
5. *Ibid.* E. P. 308780; abst. J. S. C. I. 1930, **49**, 762-B.
6. *Ibid.* E. P. 306876; abst. C. A. 1929, **23**, 5330.
7. E. P. 195619; abst. C. A. 1923, **27**, 3613. D. R. P. 346883.
8. I. G. Farbenindustrie, F. P. 678901; abst. C. A. 1930, **24**, 3656.
9. *Ibid.* F. P. 666507; abst. C. A. 1930, **24**, 1522.
10. *Ibid.* F. Addn. 36398 to 666507; abst. C. A. 1930, **24**, 4171.

Cellulose derivatives of naphthenic acid (cellulose naphthenates)[1] or of saturated or unsaturated higher fatty acids, containing more than eight carbon atoms, are rolled or calendered at a raised temperature before being shaped. This treatment increases the elasticity of the material, and permits of shaping or bending without loss of pliancy. Esters such as cellulose naphthenate-oleate or starch naphthenate-oleate-stearate[2] are formed by esterification processes of the usual type, and possess properties resembling those of rubber, gutta-percha and balata when worked with sulfur as a vulcanizing agent. They are resistant to acids, alkalis and atmospheric oxygen, and suitable for films, filaments, insulation and impregnation. Useful masses result when acetylcellulose alone or with nitrocellulose[3] is combined with a soluble resinous condensate made from dibasic acids and multivalent alcohols. For coating cigarette tips[4], use is made of an under layer of resinous polymerized vinyl derivatives and an over-layer of cellulose acetate, triphenyl phosphate and acetone. An under layer of bronze powder and vinyl resin is recommended, but the question arises as to the suitability of using finely divided bronze from a hygienic viewpoint.

In the production of acids and esters from alcohols and CO[5] a catalyst is used which does not sinter or melt at the reaction temperature of 380° at 200 atmospheres, and which contains a difficultly reducible metallic oxide and less than two equivalents of an inorganic acid[6]. Examples are chromium metaphosphate with 5% free acid, cerium metaphosphate with 8-10% free acid, and a 9:1 mixture of cerium and aluminum metaphosphates with 0.5-1% free acid.

1. I. G. Farbenindustrie, A.-G., E. P. 315275; abst. British Plastics, 1930, **2**, #17, 230; Cellulose, 1930, **1**, 150; Chem. Abst. 1930, **24**, 1739.
2. *Ibid.* E. P. 318967; abst. C. A. 1930, **24**, 2469; J. S. C. I. 1930, **49**, 1040-B. E. P. 315667; abst. J. S .C. I. 1930, **49**, 820-B.
3. *Ibid.* F. P. 669278; abst. C. A. 1930, **24**, 1753.
4. *Ibid.* D. R. P. 516716; abst. C. A. 1931, **25**, 3139.
5. *Ibid.* E. P. 283989; abst. J. S. C. I. 1928, **47**, 223-B.
6. *Ibid.* E. P. 320457; abst. J. S. C. I. 1930, **49**, 233-B.

In the manufacture of safety glass[1], the middle layer is composed of a fatty acid cellulose ester containing more than 3 C atoms, e.g., laurate, aceto-butyrate, butyro-laurate or butyrate naphthenate, these esters being fast to light and water. Adhesion may be increased by addition of resin such as polymerized vinyl acetate, or resorcinol monoacetate. If it is desired to use a high resistance to acids cellulose ester[2], the latter may be chlorinated when in the suspended or dissolved condition. Examples are given of chlorination of cellulose triacetate and trilaurate with phosphorous pentachloride, and cellulose triacetate with phosphorous trichloride.

Esters of carbohydrates soluble in organic agents, with higher fatty acids or cyclic carboxylic acids, may be made by swelling the carbohydrate in aqueous alkaline solutions, and esterifying the compound with the appropriate acid halide[3], without suppressing the heat of reaction. In this manner have been prepared starch laurate-benzoate, cellulose laurate, cocoanut fatty acid ester of agar, cellulose naphthenate-laurate and starch phenylacetate. The solubility of cellulose esters of higher fatty acids may be increased by heating them at a temperature below 200° in a liquid medium with phosphorous oxychloride[4]. In order to produce a wide range of mixed esters of higher fatty and aromatic acids such as cellulose laurate[5], (1) by employing mixtures of different halides of higher fatty acids, (2) adding the esterifying agent in stages, different acid halides being used at the different stages, (3) substituting for the halide of the higher fatty acid, either wholly or in part, a

1. I. G. Farbenindustrie, A.-G., E. P. 315667; abst. Brit. Plastics, 1930, **2**, #17, 229; J. S. C. I. 1930, **49**, 820-B; C. A. 1930, **24**, 1716. F. P. 678320; abst. C. A. 1930, **24**, 3620.

2. *Ibid.* F. P. 669048; abst. C. A. 1930, **24**, 1739.

3. *Ibid.* F. P. 668686; abst. C. A. 1930, **24**, 1650. Compare E. P. 293316, 293757; abst. C. A. 1929, **23**, 1750. Can. P. 294945.

4. *Ibid.* F. P. 664770; abst. C. A. 1930, **24**, 862. Can. P. 294939.

5. *Ibid.* E. P. 305947; abst. J. S. C. I. 1930, **49**, 814-B. Addn. to E. P. 283181; abst. J. S. C. I. 1928, **47**, 637-B, and E. P. 297766; abst. J. S. C. I. 1929, **48**, 51-B.

halide of a cyclic substituted fatty acid or of an aliphatic carboxylic acid. Or[1], the esterification may be consummated in a single operation by permitting the reaction between the halide of the acid and the carbohydrate to take place with rise of temperature, and heating if necessary. These higher cellulose esters may be recovered from their solutions by steam or vapor precipitation[2]. Thus, a solution of cellulose laurate in monochlorbenzene, pyridine or pyridine chloride is steam treated at 120° when the laurate separates as a fine powder and may be purified by filtration or centrifugalization. In molding cellulose trilaurate[3] the material is subjected to a preliminary rolling treatment for 30 minutes at 60-70° during which time fillers, pigments and dyes may be incorporated. An anti-rust paint has been brought forward[4], comprising cellulose laurate and a heavy metal salt of a high molecular acid such as lead oleate, stearate or palmitate.

Wood or metal surfaces may be prelimininarily coated with cellulose dilaurate or cellulose monoacetate-distearate or similar cellulose esters of aliphatic acids containing more than 10 C atoms in the molecule[5], in solution with resin, rubber or gutta-percha. Or[6], the mastic may contain cellulose laurate or cellulose aceto-laurate and resins. An excellent metal coating solution is said to comprise cellulose trilaurate in a mixture of benzene and xylene to which may be added fatty, resinic or naphthenic acids[7].

White or colored discharge effects are obtainable[8] on

1. I. G. Farbenindustrie, A.-G., E. P. 305601; abst. C. A. 1929, **23**, 4818. Belg. P. 375210. Holl. P. 21860.
2. *Ibid.* D. R. P. 516882; abst. C. A. 1931, **25**, 3167.
3. *Ibid.* F. P. 678254; abst. C. A. 1930, **24**, 3646. E. P. 315275; abst. C. A. 1930, **24**, 1739.
4. *Ibid.* Can. P. 293807.
5. *Ibid.* E. P. 317987; abst. C. A. 1930, **24**, 2291. F. P. 659163; abst. C. A. 1929, **23**, 5338.
6. *Ibid.* F. P. 671053; abst. C. A. 1930, **24**, 1947. Cf. F. P. Addn. 34615 to 621616; abst. C. A. 1930, **24**, 1476. F. P. Addn. 34853 to 619555; abst. C. A. 1930, **24**, 1190.
7. *Ibid.* F. P. 667205; abst. C. A. 1930, **24**, 1235.
8. *Ibid.* F. P. 666463; abst. C. A. 1930, **24**, 1522. F. P. 666507; abst. C. A. 1930, **24**, 1522. See E. P. 311467; abst. C. A. 1930, **24**, 973. E. P. 317333; abst. C. A. 1930, **24**, 2309.

acetate silk by producing a dischargeable azo dye on the fiber, topping this with a dischargeable substantive dye, and locally applying a discharge paste. In the manufacture of organic cellulose esters or combinations of organic and inorganic acid radicals in combination with cellulose[1], the latter may be esterized in a single operation with acetic acid, acetic anhydride in the presence of salts of nitric acid and feeble bases as ammonium sulfate or urea nitrate in the presence of a small quantity of sulfuric acid, or[2], the cellulose may be first treated with nitric acid vapor under conditions such that the fibrous structure of the cellulose is unimpaired, then further nitrated or acetylated. Cellulose nitrates and aceto-nitrates result, the vapor treatment with nitric acid introducing 1.7-3% HNO_3.

H. Feeny[3] in an article on the recent uses for chlorine, details its employment in cellulose acetate manufacture, while C. Field and D. Haslett[4] have pointed out that artificial filaments comprising a mixture of cellulose xanthate and cellulose acetate in epichlorhydrin, mono- or di-chlorhydrin, glycerol or an acetin may be introduced into an ammonium chloride-hydrochloric acid coagulating bath. The xanthate is prepared and ripened in the usual way, but is preferably allowed to spontaneously coagulate, and should contain a minimum amount of water. A suitable spinning solution is made by mixing equal parts of a 5-7% solution of cellulose acetate in epichlorhydrin and an 8-12% solution of cellulose xanthate in glycerol and dichlorhydrin (1:1).

In a criticism of K. Werner and H. Engleman's work on the properties of acetone-soluble cellulose acetate[5], H. Fierz-David has pointed out[6] that the similar earlier work of V. Yarsley was overlooked. E. Fischer and C. Mueller[7]

1. I. G. Farbenindustrie, A.-G., E. P. 303006; abst. C. A. 1929, **23**, 4570. F. P. 681754; abst. C. A. 1930, **24**, 4390.
2. *Ibid.* F. P. 660804; abst. C. A. 1930, **24**, 238.
3. J. Soc. Dyers Colourists, 1929, **45**, 283.
4. E. P. 319294; abst. J. S. C. I. 1930, **49**, 98-B; Silk J. and Rayon World, 1930, **6**, #68, 66.
5. Z. angew. Chem. 1929, **42**, 438; abst. C. A. 1929, **23**, 4569.
6. Z. angew. Chem. 1929, **42**, 826; abst. C. A. 1929, **23**, 5572.
7. U. S. P. 1706484; abst. C. A. 1929, **23**, 2301.

have patented the use of a monoazo dye for dyeing cellulose esters intense yellow shades, formed by coupling diazotized *p*-aminoacetanilid with *p*-cresol. F. Fischer and B. Gotthart[1] have described a process for the stiffening of collars, cuffs and shirt fronts by cellulose acetate impregnation.

In order to obtain primary acetate silk directly from the mother liquor[2], sufficient water (1% excess) is added to the primary acetylating bath to convert acetic anhydride to acetic acid and allow the sulfuric acid to be extracted from the fibers (3 hrs. at 35° being suitable). Before spinning, sodium acetate is added to the solution to neutralize the effect of the sulfuric acid.

In a comprehensive research upon the acetylation of lignin and the preparation of degradation products therefrom soluble in water, H. Friese[3] found that treatment of spruce wood with a mixture of acetic acid, acetic anhydride, and zinc chloride leaves a residue (yield about 150%) retaining the original structure and containing 54.67% of acetic acid and 3.88% methoxyl. Extraction of the residue with acetone removes about 8% of the material, which does not differ appreciably in constitution from the remainder, which is insoluble in all media. The precipitate obtained by pouring the acid liquor into water contains considerable amounts of lignin; a separation of the components is not effected by fractionation. If zinc chloride is replaced by sulfuric acid, about half the wood can be brought into solution, but the residue still contains carbohydrates even after the treatment has been repeated until nothing further is dissolved. Treatment of spruce and pine meal with sulfuric acid and acetic anhydride in differing concentrations at a relatively very low temperature leads to the isolation of a methoxyl-free fraction (A), soluble in chloroform but insoluble in water, and an unsaccharifiable component (B) rich in methoxyl and soluble in water. The portion B, pro-

1. E. P. 311417; abst. C. A. 1930, **24**, 977.
2. N. V. "Fluida," Maatschappij tot Exploitatie van Kunstzijdefabrieken, Holl.P. 20680; abst.C.A.1930, **24**, 4633. Swiss P. 145940.
3. Berichte, 1929, **62-B**, 2538; abst. J. S. C. I. 1929, **48**, 1428-A.

visionally regarded as lignin acetates (about 17% of the wood), is not homogeneous and is divided by hydrolysis into a portion very freely soluble in methyl alcohol and water and a part soluble in water only. The methoxyl content for different preparations varies between wide limits. A slight reducing power towards Fehling's solution is probably due to the presence of traces of sugars. The preparations are soluble in ammonia, alkali hydroxide, and sodium carbonate. Concentrated hydrochloric acid causes resinification. With pyridine and acetic anhydride an acetic acid content of 26-36% is reached, according to the richness in methoxyl. The portion insoluble in methyl alcohol is a brown powder which does not absorb moisture from the air, whereas the soluble portion is extraordinarily hygroscopic (also as acetate). The molecular weights in freezing water are about 600 and 172, respectively. The first-named product has 51% and the last-named only 38%. Products containing 62%, as usually assumed for lignin, have not been isolated. Since oxidation during the course of the reaction is improbable, it is likely that the original lignin is in ether- or ester-like union with a portion of the polysaccharides of the wood. The union is easily disrupted by hydrolysis, but, if drastic conditions are employed, condensation and elimination of water occur simultaneously, thereby explaining the high carbon content of lignin.

In the production of formic, acetic, hydrofluoric and nitric acids from their salts[1], H. Frischer reacts with sulfuric acid, and recovers the acids in a pure state and in a single operation without requiring distillation by forcing the vapors over through hot acid of the kind being produced. The hot vapors may be freed from associated acids such as HCl or H_2SO_4 by adding to the hot acid, through which the vapors are passed, a salt of the acid to be recovered, such as sodium formate or acetate for formic or acetic acids.

1. H. Frischer, U. S. P. 1733152; abst. C. A. 1930, **24**, 381.

W. Fuchs and O. Horn have found[1] that treatment of Willstaetter lignin with acetic anhydride containing sulfuric acid yields almost quantitatively an acetyllignin with 19.2% of acetyl. Elementary analysis, coupled with determinations of methoxyl and acetyl, indicate in a compound, $C_{50}H_{52}O_{20}$, the presence of four methoxyl, four acetoxy-, and very probably an ethylene oxide group in a mixed aromatic-hetero-cyclic system. Lignin in wood can be so acetylated that the product appears to contain three acetyl groups in excess of those present in acetylated Willstaetter lignin. It appears, therefore, that the mixed aromatic-heterocyclic nucleus which must be considered present in wood and isolated lignin is so altered by hydrochloric acid that its activity towards acetylation is diminished. The action of bromine on acetyl-lignin is so greatly influenced by small amounts of water that little information is afforded by a study of the products of the change. Ozone converts acetyl-lignin suspended in acetic acid into about 10% of products resembling those derived from other complex natural materials. Hydrogen peroxide in pyridine does not greatly affect lignin in 48 hours at the ordinary temperature, but, under more drastic conditions the acetyl groups are largely removed; after reacetylation a product with a very slightly increased oxygen content is obtained. Treatment of lignin, acetyl-lignin, and oxidized acetyl-lignin with hydrochloric acid gives very varying amounts of formaldehyde. It is considered doubtful if formaldehyde is a product of the fission of lignin, and the assumed presence of a piperonyl component in lignin is regarded as unjustified[2]. The possibility of characterising lignin in its various forms by quantitative study of its swelling in pyridine is indicated.

1. Ber. 1929, **62**-B, 2647; abst. J. S. C. I. 1929, **48**, 1428-A; C. A. 1930, **24**, 1091. Compare K. Freudenberg, H. Zocher and W. Dürr, Berichte, 1929, **62**-B, 1814; abst. J. S. C. I. 1929, **48**, 1046-A. W. Fuchs and O. Horn, Berichte, 1929, **62**-B, 1691; abst. J. S. C. I. 1929, **48**, 1046-A. W. Fuchs, Ber. 1929, **62**-B, 2125; abst. J. S. C. I. 1929, **48**, 1282-A.

2. K. Freudenberg and M. Harder, Berichte, 1927, **60**-B, 581; abst. J. S. C. I. 1927, **46**, 342-A.

I. Fukushima and Y. Takamatsu[1] find that alkali starch prepared by kneading 1 part starch with 5 parts NaOH solution of various concentrations, may be esterified with 5 parts of *p*-toluenechlorsulfonic acid and 30 parts benzene. The ratio of combined sulfonic acid to starch was calculated from the sulfur content of the product by the method of Carius. Esterification is complete within 24 hours at 40%, and is independent of the amount of *p*-toluenechlorsulfonic acid used. Soluble starch and dextrin produce similar esters, their acid ratio being 1.5 and 1 molecule respectively to 1 molecule $C_6H_{10}O_5$. H. Gardner, C. Knauss and A. van Heuckroth[2] have described a light colored resin formed by condensing phthalic anhydride and triethylene glycol which is compatible with nitrocellulose or cellulose acetate, depending upon the method of preparation.

According to A. Giebmanns[3] triphenyl phosphate makes an excellent gelatinizant for cellulose acetate intended for film formation. In the A. Giebmanns and E. Roth method[4], cellulose is acetylated and ripened by forcing the reaction mixture through one or more pipes under pressure, the mixture having been given a preliminary acetation to make it sufficiently liquid to be pumped. The refining is carried out by introducing the ripening acids into the reaction mass during its passage through the pipe. A particular type of apparatus is described for mixing liquids with solids for carrying out the process[5]. S. Girnunskii[6] has given a resume of new processes for nitrocellulose and acetylcellulose manufacture.

In the production of cellulose acetate, the acetic acid may be recovered in a concentrated form by removal by distillation or extraction before the partial hydration of

1. J. Soc. Chem. Ind. Japan, 1929, **32**, 130; Suppl. Binding, 1929, **32**, 42-B; abst. C. A. 1929, **23**, 5058.
2. Ind. Eng. Chem. 1929, **21**, 57; abst. J. S. C. I. 1929, **48**, 255-B.
3. F. P. 670194.
4. F. P. 670620; abst. C. A. 1930, **24**, 1979.
5. F. P. 670621; abst. C. A. 1930, **24**, 1979.
6. Kunstoffe, 1929, **19**, 82; abst. C. A. 1930, **24**, 4149.

the ester[1], which is then ripened in suspension in a dilute aqueous solution of acids or activators in acetic acid solution. Laminated disk phonograph records may be prepared[2] by covering a paper core with superposed layers, one of cellulose acetate, the other of cellulose nitrate. "Surface noise" is said to be reduced in the record by the use of different compositions. H. Gray claims to produce cellulose esters of organic acids[3], and specifically cellulose acetate[4], by placing the cellulose to be esterified under vacuum, thoroughly mixing under vacuum with an inert volatile organic liquid having dissolved therein the amount of acetylating agent for the reaction and also carrying a catalyst, evaporating off the vehicle from the acetylating bath by vacuum, thereby leaving the components intimately associated. The vacuum is then broken and the esterification concluded in the usual manner.

The de-esterification action of aniline on cellulose acetate has been investigated[5], and when the acetate is saponified with aniline at the boiling point of the latter, the decrease in acetyl content is apparent in as short a time as 2 hrs. After 25 hrs. heating, the product becomes insoluble in chloroform-ethyl alcohol or acetone. After 100 hrs. acetyl content has been reduced from 43.9 to 2.3%. The cellulose equivalent agrees approximately with the theoretical value. The decrease in acetyl content at 148-151° gives a curve of the same form as that obtained at the higher temperature. The specific rotation does not appear to indicate the possibility of a stereoisomeric change comparable with the mutarotation of the sugars, as suggested

1. H. Gisdakis, F. P. 686055; abst. C. A. 1930, **24**, 6013.
2. Gramophone Co., Ltd., and S. Whyte, E. P. 320492; abst. C. A. 1930, **24**, 2563.
3. U. S. P. 1711941; abst. Plastics, 1930, **6**, 25; C. A. 1929, **23**, 3343; Brit. Plastics, 1929, **1**, #7, 284; J. S. C. I. 1929, **48**, 892-B.
4. U. S. P. 1711940; abst. Plastics, 1930, **6**, 25; C. A. 1929, **23**, 3343; Brit. Plastics, 1929, **1**, #7, 284; J. S. C. I. 1929, **48**, 892-B.
5. H. Gray, T. Murray, Jr., and C. Staud, J. Am. Chem. Soc. 1929, **51**, 1810; abst. C. A. 1929, **23**, 3572; J. S. C. I. 1929, **48**, 915-A.

by Knoevenagel. De-esterifying action of aniline at room temperature is exceedingly low.

E. Greenhalgh has discussed the use of Dispersol colors in the dyeing of cellulose acetate[1]. After examination of authentic samples of practically all the leading types of artificial filaments on the market, W. Grier[2] concludes their microscopical characteristics are sufficiently constant to afford a reasonably certain means of identification. The various characteristics of cellulose acetate and rayons are discussed and illustrative photomicrographs given. F. Grove-Palmer[3] gives a resume of methods of cellulose acetate manufacture and methods of dyeing. He advises the use in the laundry of a green olive oil soap used at 77°, and for scrooping, a bath of 1-8% formic or tartaric acids. He also[4] discusses the production of acetate plushes and velvets; their finishing and maintenance; substantive and acid dyes and cross dyeing. W. Gruber has assigned to A. Wacker Ges.[5] a process for the production of acetone-soluble acetylcellulose, in which cellulosic material is treated with an acetylizing agent in the presence of zinc chloride at 55-60° until the cellulose has lost its structure, then continuing the reaction at about 40°. For preparing high-viscosity, acetone-soluble ester[6], he dissolves cellulose acetate 100 in glacial acetic acid 500, and allows to stand in contact with 80 parts $ZnCl_2$. $HCl.2H_2O$ at 20°, complete acetone solubility resulting in about 10-15 hours.

1. Dyer, Calico Printer, 1929, **62**, 599; abst. C. A. 1930, **24**, 1984.

2. Ind. Eng. Chem. 1929, **21**, 168; abst. C. A. 1929, **23**, 2038.

3. Silk Journal, 1929, **6**, #67, 61; #68, 47; abst. C. A. 1930, **24**, 2607.

4. Textile Colourist, 1929, **51**, 834; 1930, **52**, 29, 34, 54; abst. C. A. 1930, **24**, 3906.

5. U. S. P. 1711314 and F. P. 649623; abst. C. A. 1929, **23**, 3098; Plastics, 1930, **6**, #1, 24.

6. U. S. P. 1723614; Plastics, 1930, **6**, #2, 90; J. S. C. I. 1929, **48**, 810-B; Brit. Plastics, 1929, **1**, #6, 233; C. A. 1929, **23**, 4571. Cf. E. P. 291001; abst. C. A. 1929, **23**, 1267.

H. Guinot[1], E. Ricard[2], and E. Ricard and H. Guinot[3] have described a process for the extraction and concentration of acetic acid from dilute solutions, which is a modification of the Suida process for extraction with cresol. W. Gump[4] has disclosed cellulose acetate plastic compositions, utilizing 4-hydroxy-1-tertiary-butylbenzene or its nucleus halogenated derivatives (3-brom-4-oxy-, 3.5-dibrom-4-oxy-, 1-tertiary-butylbenzenes, melting at 50° and 78° respectively). Ethyl-*p*-toluolsulfamid or diethyldiphenyl urea may also be added.

A. Hall[5] renders acetate silk more resistant to deterioration by hot aqueous liquids by stretching it in the set condition beyond the elastic limit. He[6] dyes cellulose acetate black by the following methods: (1) dye with an amine, diazotize and couple with a suitable naphthol; (2) use a direct dyeing black; (3) or an oxidation black; (4) dye with a direct dyeing blue, yellow and red mixture; (5) hydrolyze the acetate filaments and dye with direct colors used for viscose rayons. Coupling with amines is unsatisfactory because of the affinity of cellulose acetate which reduces the amount supplied for coupling and gives an unstable shade. The temperature of coupling should be raised and time increased above normal for a complete reaction[7]. Blacks produced with 2.4-diaminodiphenylamine with oxidizing agents are recommended[8].

1. Chimie et Industrie, 1929, **21**, 243; abst. C. A. 1929, **23**, 2935; J. S. C. I. 1929, **48**, 314-B.
2. U. S. P. 1668380; abst. C. A. 1928, **22**, 2170.
3. Can. P. 279167; abst. C. A. 1928, **22**, 2754.
4. U. S. P. 1740854; abst. C. A. 1930, **24**, 1217; J. S. C. I. 1930, **49**, 780-B; Brit. Plastics, 1930, **2**, #16, 183; Plastics, 1930, **6**, 383.
5. U. S. P. 1709470; abst. C. A. 1929, **23**, 2838; J. S. C. I. 1929, **48**, 470-B. See E. P. 277089; abst. J. S. C. I. 1927, **46**, 964-B.
6. Am. Dyestuff Reptr. 1929, **18**, 671; abst. C. A. 1930, **24**, 1221. Am. Dyestuff Reptr. 1929, **18**, 545; abst. C. A. 1929, **23**, 5323. Refers to E. P. 295488.
7. Silver Springs Bleaching & Dyeing Co., Ltd., and A. Hall, E. P. 258699; abst. C. A. 1927, **21**, 3134. A. Hall, U. S. P. 1657255; abst. C. A. 1928, **22**, 1050.
8. British Celanese, Ltd., and G. Ellis, E. P. 311435; abst. C. A. 1930, **24**, 973.

H. Hamm and R. Stevens[1] in measuring the stress-strain relation of wet rayons find that cellulose acetate filaments lose strength with rise of temperature and elongation due to wetting and stretch at break increase.

Acetylene at 25 lb. pressure per sq. inch[2] is led into 25-30% sulfuric acid at 68°, mercurous sulfate added, the entrained water and acid removed from the exit gas, and the acetaldehyde formed separated from excess acetylene. H. Hands and Spicers, Ltd.,[3] have patented a plastic and monophenyldicresyl phosphate. In strengthening glass according to the P. Head method[4], ethyl lactate is used, either alone or in conjunction with other solvents. Edges are sealed by bevelling in V-shape and either cauterizing or filling with oleaginous material. Triacetin or methylcyclohexanone may be added. It is said that cellulose fibers are rendered immune to substantive dyes by partly acetylating them in the presence of formaldehyde, or a derivative or condensation product of formaldehyde, which tends to retard the weakening or solution of the threads without hindering the acetylation[5]. Cellulose may be treated with 85% formic acid in order to obtain an intermediate product suitable for acetylation, the assumption being that the final product is cellulose acetoformate (cellulose formylacetate)[6].

H. Heimann and A. Bayerl[7] claim that treating cellulose with lactic acid gives rise to new cellulose compounds

1. U. S. Bureau Standard J. Res., 1929, **3**, 927; abst. J. S. C. I. 1930, **49**, 367-B.
2. C. Hand, T. Bartram and A. Maude, U. S. P. 1738649; abst. J. S. C. I. 1930, **49**, 754-B.
3. Can. P. 289854.
4. E. P. 321977; abst. J. S. C. I. 1930, **49**, 103-B; Brit. Plastics, 1930, **1**, #10, 448.
5. Heberlein & Co., E. P. 312280; abst. J. S. C. I. 1930, **49**, 858-B; C. A. 1930, **24**, 962; Silk Journal, 1929, **6**, #64, 66. E. P. 280493 is referred to. F. P. 660794; abst. C. A. 1930, **24**, 238. Ital. P. 272590.
6. H. Heimann and A. Bayerl, U. S. P. 1722914; abst. C. A. 1929, **23**, 4570; E. P. 263128; 268289; Can. P. 273515.
7. U. S. P. 1728206; abst. Cellulose, 1930, **1**, 35; J. S. C. I. 1929, **48**, 894-B; C. A. 1929, **23**, 5316. Compare E. P. 268289; abst. J. S. C. I. 1928, **47**, 444-B.

as valuable intermediate products in the manufacture of cellulose esters. Cotton 1, is introduced with stirring into 20 parts 80% lactic acid for 3 hrs. at 80°, excess acid being then removed by pressing. B. Helferich and S. Bottger[1] have found that the interaction of hydrofluoric acid on cellulose gave cellan, which upon boiling with acetic acid-pyridine mixture yielded an acetylcellan readily hydrolyzable with methyl alcoholic sodium methoxide to methyl-glycoside. Helle-Staux[2] has given general data on cellulose acetate manufacture.

Acetic acid vapors, it is claimed[3], may be dissociated into acetic anhydride and water by diffusion through porous material[4]. K. Herstein has expounded a solid solution theory of dyeing cellulose acetate silk[5]. R. Herzog and B. Lange[6] have shed considerable light on the characterization of colloidal solutions by the state of polarization of their Tyndall light, the change in polarization angle on standing being given for various cellulose acetate solutions. In investigating the reversible and irreversible lattice changes of cellulose triacetate, K. Hess and C. Trogus[7] find that when fibrous cellulose triacetate is allowed to swell in cyclohexanone, methyl alcohol, benzene, pyridine or chloroform-methyl alcohol, an expansion of the lattice at right angles to the fiber is observed, and the original dimensions are regained when the solvent is removed. If the material is completely dispersed in chloroform the lattice is destroyed, and on reprecipitation with methyl alcohol a different lattice is formed. K. Hickman and D. Hyndman[8] have given

1. Annalen, 1929, **476**, 150; abst. J. S. C. I. 1930, **49**, 72-A.
2. Russa, 1929, **4**, 513; abst. C. A. 1929, **23**, 3572.
3. F. Henglein and F. Schleicher, U. S. P. 1735453; abst. C. A. 1930, **24**, 630; J. S. C. I. 1930, **49**, 9-B. Patent cites E. P. 301562; abst. J. S. C. I. 1929, **48**, 122-B.
4. W. Herrmann and H. Deutsch, U. S. P. 1714783 and F. P. 651728; abst. C. A. 1929, **23**, 3479; J. S. C. I. 1930, **49**, 652-B. E. P. 288213; abst. C. A. 1929, **23**, 609; J. S. C. I. 1930, **49**, 275-B.
5. Rayon, 1929, **8**, #4, 7, 10, 34; abst. C. A. 1930, **24**, 242.
6. Berichte, 1929, **62-B**, 491; abst. C. A. 1929, **23**, 4610.
7. Z. physikal. Chem. 1929, B, **5**, 161; abst. J. S. C. I. 1929, **48**, 1222-A.
8. J. Franklin Inst. 1929, **207**, 231; abst. C. A. 1929, **23**, 2607.

directions with 24 cuts, for constructing apparatus from pyroxylin and cellulose acetate sheeting.

H. Hoffman and E. Reid[1] have traced the development of cellulose acetate lacquers and described modern methods for their manufacture. It is stressed that a "richer" solvent mixture is needed than in the case of pyroxylin lacquers. Methyl ether of ethyleneglycol phthalate (methyl cellosolve phthalate) and ethyl pentaethylene glycol are valuable plasticizers, while among the limited range of resins suitable for use, the glycol phthalate type looks most promising. General notes on acetate lacquers, viscosity, blush-resistance and speed of evaporation are given and typical formula quoted, with data on the following unusual solvents: dimethyl cellosolve, 1.4-dioxan, cellosolve, methylcellosolve acetate, cellosolve acetate, ethyl *a*-hydroxy*iso*butyrate, dichlordiethyl ether, glycol monoacetate and diacetate, carbitol, carbitol acetate, mesityl oxide, propyleneglycol ethyl ether acetate, ethyl oxybutyrate, glycol dimethyl ether, glycol methylethyl ether, glycol diethyl ether and propyleneglycol methylether.

The Holzverkohlungs Industrie[2] produce concentrated acetic acid by mixing 50% acetic acid with sodium and potassium acetates and distil at 170°. Butyric acid may be extracted from its solution in acetone oil by concentrated aqueous potassium and zinc butyrates. S. Horii[3] prepares a stencil sheet for mimeograph work with synthetic resin, cellulose acetate or mannan acetate with a tempering agent of methylene-, ethylene- or propylene-glycol ricinoleate or oleate. An excellent electric resistance material is said to be made by mixing a finely subdivided conductor of nickel or iron reduced from the oxide without fusion with a cellulose acetate binder, the mixture while viscous, being spread

1. Ind. Eng. Chem. 1929, **21**, 955; abst. J. S. C. I. 1929, **48**, 924-B; Brit. Plastics, 1929, **1**, #7, 284; C. A. 1930, **24**, 251.

2. E. P. 306105; abst. J. S. C. I. 1930, **49**, 50-B; C. A. 1929, **23**, 4950. E. P. 302268; abst. C. A. 1929, **23**, 4230.

3. U. S. P. 1698705; abst. C. A. 1929, **23**, 1229. E. P. 310181; abst. C. A. 1930, **24**, 699. E. P. 289511; abst. C. A. 1929, **23**, 680. Can. P. 315803.

on glass plates. To remove stains from Celanese, L. Hubbard[1] and R. Huerlick[2] have detailed various methods and possibilities of acetate silk dyeing with two patterns attached. As an insulating composition suitable for use on wires, S. Hull[3] recommends cellulose acetate 30, phenolic condensation product 10, and furfural 300 parts. At 800° or higher[4], acetic acid undergoes a reaction of hydration into keten as well as a reaction of demethanation into CO_2.

A variable resistance material appears to result by mixing a finely divided conductor other than carbon[5] with a binder as cellulose acetate or other organic cellulose derivative, the mixture being spread on glass while still in the viscous state.

Readily reversible reactions involving splitting off of water as producing acetic anhydride from acetic acid[6] are effected in presence of CO_2 and a catalyst promoting action between CO and steam, e.g., a mixture of acetic acid vapor and CO is passed at 500-600° over sodium metaphosphate, and then at 350° over a catalyst prepared by heating manganese carbonate in a current of CO at 300-500°, iron being excluded. Acetaldehyde may be dissolved in acetic acid in the liquid phase and oxidized by means of air or oxygen at 30-40°[7] in the presence of cobalt acetate as catalyst. If manganese acetate is used, it requires a little cobalt acetate as a "starter." Acetic acid may be produced by a continuous process[8] when the acid, containing a suitable catalyst,

1. Silk Journal, 1929, **5**, #60, 53; abst. C. A. 1929, **23**, 5322.
2. Jentgen's Rayon Review, 1929, **1**, 204.
3. U. S. P. 1698870; abst. C. A. 1929, **23**, 1191.
4. C. Hurd and K. Martin, J. Am. Chem. Soc., 1929, **51**, 3614; abst. C. A. 1930, **24**, 339.
5. Howards & Sons, Ltd., and M. Bandli, E. P. 314306; abst. C. A. 1930, **24**, 1305.
6. T. Ewan, H. Roberts and Imperial Chemical Industries, Ltd., E. P. 316898; abst. C. A. 1930, **24**, 1869. For the continuous manufacture of aliphatic esters, see Australia P. 15337.
7. H. Golding, F. Leicester, H. Hirst, S. Rowell and Imperial Chemical Industries, Ltd., E. P. 308937; abst. J. S. C. I. 1929, **48**, 426-B; C. A. 1930, **24**, 381.
8. Imperial Chemical Industries, Ltd., S. Rowell and H. Hirst, E. P. 304350; abst. C. A. 1929, **23**, 4711. U. S. P. 1778511; abst. C. A. 1930, **24**, 5768; J. S. C. I. 1930, **49**, 1103-B.

is fed down a tower and acetaldehyde vapor and oxygen supplied at the bottom of the tower, different zones in the tower being maintained. Gases nearly saturated with acetic acid vapor may be recovered and substantially freed from water vapor by treating with a thin countercurrent stream of water, not more than sufficient to just saturate the mixture with water vapor. Acetone and methyl alcohol may be similarly recovered[1]. In another continuous process for acetic acid production from acetaldehyde[2], a 10-25% solution of acetaldehyde is oxidized to acetic acid by oxygen in extremely divided form, such as obtainable by passing the gas through a porous plate system.

A coating composition has been brought forward[3] comprising cellulose acetate, resinous polybasic ester of a monoalkyl glycerol, softener and solvent. In preparing pigmented celluloids[4], the color is incorporated with the ester while the product is in the wetted condition, the water being afterwards removed by rolling between heated rolls. Tricresyl phosphate may be added to the above[5].

E. Jodrey[6] manufactures electrical condensers by continuously coating paper with an adhesive, a conducting layer of copper or other metal foil being coated with cellulose acetate, and the latter combined with the former. E. Johns induces non-flammability to cellulose articles[7] by treatment of the celluloid with cellulose acetate over which is superposed shellac in solution to impart a gloss. A. Johnson has evolved a series of tests[8] for distinguishing artificial

1. R. Riley and Imperial Chemical Industries, Ltd., E. P. 310141; abst. C. A. 1930, **24**, 670.
2. S. Rowell and Imperial Chemical Industries, Ltd., E. P. 319433; abst. C. A. 1930, **24**, 2473; J. S. C. I. 1930, **49**, 94-B. F. P. 662384; abst. C. A. 1930, **24**, 380.
3. Imperial Chemical Industries, Ltd., and F. Hahn, E. P. 316323.
4. W. Jenkins and Imperial Chemical Industries, Ltd., E. P. 309964; abst. C. A. 1930, **24**, 724. Australia P. 15658.
5. W. Jenkins and Imperial Chemical Industries, Ltd., E. P. 309840; abst. C. A. 1930, **24**, 723.
6. E. P. 305515; abst. J. S. C. I. 1929, **48**, 290-B.
7. British Plastics, 1929, **1**, #7, 271.
8. Textile World, 1929, **76**, 1787; abst. C. A. 1930, **24**, 1517.

filaments made by the viscose, cuprammonium, nitro and acetate processes, while R. Jones[1] has contributed details on cellulose acetate molding plastics, including fillers used, temperature and molds required, and the details of hand and auto pressing.

In the manufacture of stable, highly acetylated cellulose by the J. Jurling process[2], the sulfuric acid which combines with the cellulose during the esterizing process may be replaced by its equivalent of acetyl, giving a product corresponding in acetyl content to the triacetate, and characterized by increased stability to heat, if, on completion of the acetylation process, a slight excess of water (or an alcohol) is added to combine with the excess of acetic anhydride. Samples taken before and after stabilization show, respectively, acetyl (as acetic acid) 57.87% and 61.75%, sulfuric acid 3.71% and 0.05%, and have charring point 130° and 210°.

Kalle & Co. claim[3] that shrinking at low temperatures of capsules made from cellulose acetate is prevented by using as a dispersion medium an aqueous solution of sodium chloride or acetate, magnesium sulfate or calcium chloride. Or[4], shrinkage may be avoided during storage by immersing the capsule in a water-miscible, non-volatile liquid, which does not possess a greater swelling action upon the cellulose ester than water, such as glycerol 28 Be., polyglycol, sorbite, glycerol mono-lactate or their mixtures. Y. Kami[5] finds the ash content of acetate silks of commerce to vary between 0.05-2.07%, and the fat and oil content 0.09-0.84%.

In preparing hollow filaments of viscose, nitrocellulose or cellulose acetate according to the H. Karplus method[6],

1. British Plastics, 1929, **1**, #4, 141.
2. E. P. 313198; abst. J. S. C. I. 1929, **48**, 677-B; Silk Journal, 1929, **6**, #64, 68; C. A. 1930, **24**, 962; British Plastics, 1929, **1**, #4, 152.
3. E. P. 317728; abst. C. A. 1930, **24**, 2290. D. R. P. 531433.
4. E. P. 319736; abst. C. A. 1930, **24**, 2600.
5. J. Cellulose Inst. Tokyo, 1929, **5**, 233; abst. British Plastics, 1930, **1**, #8, 329; J. S. C. I. 1929, **48**, 975-B.
6. U. S. P. 1707164; abst. C. A. 1929, **23**, 2294.

the solutions before being spun, are incorporated with liquid or solid non-crystalline substances such as bone oil, liquid paraffin (paraffin oil) or sodium oleate, which during the following spinning and finishing operations do not evolve gases or vapors. These substances are afterwards removed from the filament by suitable solvents. R. Keenan[1] has investigated the formation of thin films of organic colloids on mercury surfaces and finds that cellulose acetate and gelatin produce very irregular and rigid films, whereas those of rubber are elastic. With cellulose nitrates the limit film thickness varied in an inverse relation with the viscosity of the solution[2]. M. Kerth and E. Pfeffer[3] have given recipes for the printing of indigosols on cellulose acetate, and K. Kishida has patented a method for ornamenting bottles with patterns on films of cellulose acetate[4].

M. Klein[5] acetylates cellulose in a bath composed of glacial acetic acid, and sulfur trioxide at —10° to avoid sulfonation of the acetic acid. In order to obtain acetone-soluble cellulose acetates, he also[6] saponifies, while conserving the desired physical characteristics, by incorporating the salt of a bivalent metal as the chloride, nitrate or sulfate of magnesium, zinc, iron or lead, before adding the auxiliary catalyst necessary for the saponification. In preparing dyes for cellulose acetate containing neither carboxyl or sulfuric acid groups[7], diazotized glycol 2-amino-4-nitrophenyl ether or other suitable diazo compound having at least 1 H atom of its aromatic nucleus substituted by a radical of glycol is coupled with an azo component as *m*-toluidine; the dye may be developed with *b*-naphthol. Or the

1. J. Phys. Chem. 1929, **33**, 371; abst. C. A. 1929, **23**, 2630.
2. See Kolloid-Z. 1929, **47**, 289.
3. Rayon, 1929, **8**, #6, 10.
4. E. P. 313350; abst. C. A. 1930, **24**, 937.
5. F. P. 686012; abst. C. A. 1930, **24**, 6013.
6. F. P. 686019; abst. C. A. 1930, **24**, 6014.
7. O. Knecht, U. S. P. 1711390; abst. C. A. 1929, **23**, 3106; J. S. C. I. 1929, **48**, 512-B.

glycol may be substituted by a glycerol radical[1], such as glycerol-2-amino-4-nitrophenyl ether.

Kodak-Pathe[2] prepare cellulose aceto-esters containing higher acyl groups by treating partially deacetylated cellulose acetate with an organic anhydride higher than acetic anhydride. Thus cellulose heated with chloracetic anhydride and chloracetic acid in presence of magnesium perchlorate with addition of *a*-bromstearic acid in acetic acid, gives cellulose aceto-*a*-bromstearate. The aceto-*a*-chlorstearate may similarly be prepared[3]. This firm prepares cellulose acetate compositions of low inflammability for use in the manufacture of films and varnishes[4] by mixing phosphoric acid with acetone-soluble cellulose acetate, the acid being added to the acetate dissolved in acetone. Acetylcellulose may be hydrolyzed or deacetylated[5] by treatment with a solution of phosphoric and sulfuric acids, the amount of phosphoric being greater than the sulfuric, and the sum of the two being less than 1% of the total solution. The reacting mixture temperature is kept below 40°. Or the cellulose may be acetylated by treatment with a solution of a lower fatty acid saturated with nitrogen tetroxide until the solubility of the product in potash reaches at least 15%, then acetylating in a bath containing acetic anhydride, phosphoric and sulfuric acids[6].

In making cellulose esters[7], the diluting reaction acid may be replaced wholly or in part by a solvent for primary esters of cellulose, particularly methylene chloride, a reflux apparatus being used. Halogenated mixed cellulose esters

1. O. Knecht, U. S. P. 1711391; abst. C. A. 1929, **23**, 3106; J. S. C. I. 1929, **48**, 512-B. See E. P. 245758; abst. J. S. C. I. 1927, **46**, 469-B.
2. F. P. 667556, 667557; abst. Cellulose, 1930, **1**, #4, 126; C. A. 1930, **24**, 1217.
3. Kodak-Pathe, F. P. 681437; abst. C. A. 1930, **24**, 4306. E. P. 318633; abst. C. A. 1930, **24**, 2143. H. Clarke and D. Othmer, U. S. P. 1826302.
4. F. P. 685913; abst. C. A. 1930, **24**, 6014.
5. *Ibid.* F. P. 686401; abst. C. A. 1931, **25**, 592. E. P. 350417.
6. Kodak-Pathe, F. P. 687084; abst. C. A. 1931, **25**, 812. F. P. 685913; abst. C. A. 1930, **24**, 6014.
7. Kodak-Pathe, F. P. 698689; abst. C. A. 1931, **25**, 3167.

are formable by treating nitrocellulose in an esterifying bath containing an acyl group having an ethylenic chain until a mixed ester containing NO_2 groups and the acyl group is produced, then halogenating the acyl group[1]. According to another process[2], hydrated or partially hydrated cellulose is esterified by a monocarboxylic acid containing an ethylenic side chain by heating them together to a temperature below that at which a harmful degradation of the cellulose takes place. Esterification with crotonic, cinnamic and undecylenic acids (monochlorbenzene, being added to lower the boiling point) results in the formation of cellulose crotonate, cinnamate and undecylenate (see p. 833, n. 7).

O. von Kohorn and H. Schupp[3], in the manufacture of hollow filaments by the dry spinning of cellulose acetate, add to the spinning solution a substance which forms on the extruded filaments a firm skin which is stretched during the escape from the still fluid core of the enclosed solvent. The characteristics of the product depend upon the size of the internal cavities of the filaments. These may be varied by adjusting the proportion of added substance, and by variation of the spinning conditions. With large cavities, the product is said to be dull and lusterless, while luster increases with decrease in cavity size. It is possible to obtain a product having a half-matt luster and the appearance and feel of wool. So-called "alveolar silk."

D. Krueger has contributed on the determination of the acetic acid content of cellulose acetate with 31 references[4]; a discussion of the saponification constants of cellulose acetates[5]; and experiments on the solubility and

1. Kodak-Pathe, F. P. Addn. 35292 to 655803; abst. C. A. 1930, **24**, 2290.
2. Kodak-Pathe, F. P. 655803; abst. C. A. 1929, **23**, 4071.
3. E. P. 314543; abst. Silk Journal, 1929, **6**, #66, 68; J. S. C. I. 1931, **50**, 153-B; C. A. 1930, **24**, 1509. F. P. 677204; abst. C. A. 1930, **24**, 3113; Cellulose, 1930, **1**, #8, 228. Belg. P. 361480.
4. Farben-Ztg. 1930, **35**, 2032; abst. C. A. 1930, **24**, 4387.
5. Melliand's Textilber. 1929, **10**, 208; abst. C. A. 1929, **23**, 4570.

particle size of this ester[1]. Diffusivity experiments failed to show a sufficient difference in particle size between a laboratory preparation of an acetone-insoluble cellulose acetate and a sample of Cellit to account for the difference in solubility. By using Eulers' formulas, the particle size in a 1% solution of triacetate in acetone was calculated to be from 19 to 31x10 mm., whereas Einstein's formula gave values approximately double these. The molecular weight was indicated to lie between the extremes of 600 and 1100, depending somewhat upon the method of calculation.

In the production of shaped bodies for tools of material difficult to work[2], a mixture of carbides and nickel or cobalt powder is mixed with cellulose acetate as a binding material and the mixture pressed into shape and allowed to harden. After grinding and polishing to obtain the more complicated shapes, they are heated to remove the binding material and sintered. In the G. Lacroix[3] method of acetic acid concentration, a mixture of acid and water is vaporized and passed over neutral potassium acetate dissolved in an aliphatic acid in which acetic acid is insoluble, and with which it combines to form a compound from which it can subsequently be liberated.

A. Landucci[4] produces films and filaments by dissolving cellulose acetate or nitrate in a suitable solvent and forming into the desired shape, coagulation being effected in an aqueous bath to obtain a more or less opaque product which is then rendered transparent by hot drying. According to L. Laska and F. Weber[5], dyes suitable for coloring cellulose acetate strong yellow and red to blue-violet shades, contain as one constituent a naphthylaminecarboxylic acid (suitably, 2, 3-naphthylaminecarboxylic acid) together with another component such as resorcinol, *b*-naphthylamine,

1. The Melliand, 1929, **1**, 1406; Melliand's Textilber. 1929, **10**, 966; abst. C. A. 1930, **24**, 1501.
2. F. Krupp, E. P. 313619; abst. J. S. C. I. 1930, **49**, 616-B.
3. Belg. P. 358248; abst. C. A. 1930, **24**, 863.
4. U. S. P. 1713289; abst. C. A. 1929, **23**, 3344; Plastics, 1930, **6**, #2, 90. Compare U. S. P. 1658725; abst. C. A. 1928, **22**, 1237.
5. U. S. P. 1702832; abst. C. A. 1929, **23**, 1757.

ethyl-*b*-naphthylamine, *b*-naphthol, 2,3-aminonaphthoic acid, dimethyl-*m*-toluidine,phenylmethylpyrazolone, *m*-phenylenediamine,*m*-toluylenediamine, 1,5-naphthylenediamine, *a*-naphthylamine, dimethylaniline, *o*-anisidine, *p*-aminoacetanilide, *p*-phenylenediamine, *p*-nitroaniline, *p*-nitro-*o*-anisidine, *p*-cresidine, 2,4-dinitroaniline, aminohydroquinone-dimethyl ether, aniline *o*-toluidine, *o*-chloroaniline, 2,5-dichloroaniline, *m*-chloroaniline or *p*-nitroaniline.

In an article contributed by L. Lawrie[1] for dyeing cellulose acetate filaments, dyestuffs which are in a dispersed state are used, the "Duranol," "Dispersol" and "Celliton" colors being of this type. Acetate rayon may be mordanted either by the use of ferric chloride[2], or swelling agents as formic or acetic acids, furfuraldehyde, phenol or pyridine[3]. H. La Trayas[4] has reviewed the work of M. Nopitsch[5], and W. Weltzien[6] on the use of ultra-violet rays for distinguishing between different rayons. In the production of "Self lighting" tips for cigarets, P. and A. Lifchuz[7] apply two coatings of cellulose acetate or nitrate containing potassium chlorate, which in the first coating is much finer than in the second. Friction materials may also be added.

It is claimed that cellulose acetate is rendered more susceptible to dyes[8] by applying gelatin either over the whole fabric or filament, or over selected areas, then drying at 100° or higher for an hour. Oxidizing agents such as hypochlorites destroy this increased susceptibility to dyes, but it is not destroyed by ordinary washing, soaping

1. Artificial Silk World, 1929, **2**, 187; abst. C. A. 1929, **23**, 3577.
2. Brit. Celanese, Ltd., G. Rivat and E. Cadgene, E. P. 273692; abst. J. S. C. I. 1928, **47**, 744-B.
3. Brit. Celanese, Ltd., G. Rivat and E. Cadgene, E. P. 273693; abst. J. S. C. I. 1928, **47**, 891-B.
4. Russa, 1929, **4**, 171; abst. C. A. 1929, **23**, 2830.
5. Melliand's Textilber. 1928, **9**, 136, 241, 330; abst. C. A. 1928, **22**, 3049.
6. Die Seide, 1928, **33**, 306.
7. E. P. 314145; abst. C. A. 1930, **24**, 1221.
8. H. Livsey, G. Holden and J. and J. M. Worrall, Ltd., E. P. 313980; abst. C. A. 1930, **24**, 1227.

or vatting. Vat dyes may be discharged without destroying the enhanced affinity of the treated fabric for dyes. According to L. Lloyd and E. Priestley[1], in the analysis of union materials composed of various artificial silks, cellulose acetate silk may be determined by acetone extraction. B. Lougovoy[2] reduces the viscosity of cellulose esters by preparing a solution of the ester in a solvent of high dispersive power which is diluted with a mixture of the latter with a miscible non-solvent, whereby an ester of lower viscosity is precipitated.

A shoe stiffening composition[3] results by the use of a gelatinizable stiffening substance in fibrous form as cellulose acetate, in making stiffener blanks, which may afterwards be softened by heat (see p. 525, n. 4).

In the production of differential dyeing effects on fabrics containing cellulose acetate[4], the fabric is saponified according to any desired pattern by applying an alkaline paste, by printing, brushing or spraying methods, then drying, steaming and washing; the saponified parts being then dyed with cotton dyes. The paste contains sodium or potassium hydroxides or carbonates, together with a swelling agent as pyridine, acetone and alkali thiocyanate. India rubber may be bonded to cellulose derivatives[5] by treating the surface of the rubber with a mutual solvent for rubber and cellulose acetate, as cyclohexanol. A cellulose acetate or nitrate lacquer containing a mutual solvent is then applied to the softened surface, resulting in an increased strength of adhesion.

C. Malm and H. Clarke[6] claim that when cellulose is

1. J. Soc. Dyers and Col. 1929, **45**, 201; abst. J. S. C. I. 1929, **48**, 712-B.
2. U. S. P. 1726357; abst. J. S. C. I. 1929, **48**, 892-B.
3. W. Lund and L. Mellerio, U. S. P. 1720243; abst. C. A. 1929, **23**, 4310. S. Lovell, U. S. P. 1711956; abst. C. A. 1929, **23**, 3316.
4. Lyons Piece Dye Works, E. P. 310844; abst. J. S. C. I. 1930, **49**, 1024-B.
5. C. Macintosh & Co., Ltd., S. Brazier and G. Thompson, E. P. 305745; abst. J. S. C. I. 1929, **48**, 295-B.
6. J. Am. Chem. Soc. 1929, **51**, 274; abst. C. A. 1929, **23**, 971; J. S. C. I. 1929, **48**, 299-A.

esterified on heating with acetic acid, the reaction coming to an end when the resulting product contains 6-7% acetyl (110 hrs. boiling under atm. pressure) this corresponds to the compound, $C_{24}H_{39}O_{20}$ Ac. Analogous effect is produced with acetic or propionic acid, and butyric acid. Hydrated cellulose, prepared by regeneration of cellulose from its nitrate, from viscose, from its solution, in Schweitzer's reagent or from dissolved cellulose acetate, on heating with acetic acid, yields esters having a limiting composition expressed by the formula, $C_6H_9O_5C_2H_3O_2$. Mercerized cellulose behaves in the same way as hydrated cellulose, while cellulose regenerated from cellulose acetate, which has preserved its original fibrous structure deports itself, in this reaction, more like normal cellulose. In view of the definite limit of esterifiability of native cellulose by acids alone, it is concluded that the constitution of cellulose must be expressed as a multiple, of the unit, $C_{24}H_{40}O_{20}$.

E. Mardles has determined[1] that the viscosity of a cellulose acetate solution in cyclohexane, acetone or benzyl alcohol increases with concentration of cellulose. Fractional precipitation by addition of a substance in which the acetate is insoluble shows the ash content decreases with acetate concentration decrease. The number of cc. of precipitant necessary to add to 1 cc. of a solution of cellulose acetate or nitrate in order not to produce the slightest turbidity is given as a relative measure of solubility. Acetone and petroleum ether were used as precipitants while many solvents of both acetate and nitrate were studied. These were benzene, toluene, xylene, pentane, petroleum ether, amylene, heptylene, ethyl alcohol, and water for acetone. For petroleum ether as precipitant they were acetone, methyl acetate, amyl acetate, tolyl acetate, ethyl formate, acetic acid and methyl alcohol. The reversible change sol to gel was studied with respect to temperature and concentration of the cellulose derivative. Dispersity of the cellulose de-

1. Kolloid-Z. 1929, **49**, 4; abst. C. A. 1930, **24**, 236; J. S. C. I. 1929, **48**, 975-B.

rivatives is closely related to solubility. The solubilities of various cellulose derivatives were studied in different liquid mixtures. Nitrocellulose, cellulose acetate and zanzibar copal were observed at several concentrations of benzyl alcohol and anisole and for different times of solution. In all cases maximum solubility was observed with cellulose acetate and kauri copal in the same solvents. Swelling and solution are closely related as seen with cellulose acetate dissolved in mixtures of alcohol-water and nitrobenzene-alcohol. Diagrams are shown for solubility of cellulose acetate in the ternary mixtures, methylethyl ketone-butyl-formate-alcohol and acetone-benzene-alcohol. The former is given with respect to the temperature of precipitation and the latter in terms of solubility. Breaks in the curves for viscosity and the surface tension as functions of concentration of component mixtures of cyclohexane and benzyl alcohol in which cellulose acetate is dissolved are the same.

A. Maude[1] concentrates acetic acid containing about 10% water in a single phase distillation with about 20% of its volume of benzene[2]. In the method of cellulose acetate production as laid down by G. Morden[3], cellulose is treated with sulfuryl chloride, glacial acetic acid and acetic anhydride, acetylation being subsequently finished in a second stage by treatment with acetic anhydride, glacial acetic acid and sulfuric acid. The laminated sheets of J. McIntosh[4] are produced by passing fibrous sheets of paper, asbestos or textile fabrics through a cellulose acetate solution, the solvent being evaporated and the dried sheets superposed to form a layer of the desired thickness, and then heated under pressure. The product is said to be suitable for gears and radio panels.

1. U. S. P. 1722532; abst. C. A. 1929, **23**, 4484; J. S. C. I. 1929, **48**, 806-B.
2. H. Matheson, U. S. P. Re-17377; abst. C. A. 1929, **23**, 4230; J. S. C. I. 1929, **48**, 772-B. See original pat. No. 1410207; abst. C. A. 1922, **16**, 1781; J. S. C. I. 1922, **41**, 347-A. See also E. P. 132558; abst. J. S. C. I. 1919, **38**, 846-A.
3. F. P. 663268; abst. C. A. 1930, **24**, 723. E. P. 294415; abst. C. A. 1929, **23**, 2033. Can. P. 292490.
4. U. S. P. 1697077; abst. C. A. 1929, **23**, 1229.

In an illuminating article on the fractional precipitation of cellulose acetate[1], J. McNally and A. Godbout precipitated a 10% solution of cellulose acetate (acetyl value 44.5) in acetone with a mixture of acetone and water (1:3). The amount of acetate precipitate was found to depend on the length of time the solution is allowed to stand after adding the precipitant, e.g., after standing 2, 4 and 16 hours the respective amounts precipitated were 50, 65 and 85 per cent. After repeated precipitation, drying and re-solution, the acetate changed but little, although the viscosity suffered an increase of about 13% after nine precipitations. The acetyl numbers and specific rotations of various fractions were sensibly constant, but the variations in melting point, viscosity and solubility show that the original acetate contained a series of micellae differing either in the number of anhydroglucose units, or in the manner in which these units are joined together in the micelle.

The fractions precipitated first are more insoluble in solvents in general, than the later fractions.

Solubility determinations were made using the following solvents: methyl, ethyl, *n*-propyl formates; methyl, ethyl, *n*-propyl, *iso*propyl, *n*-butyl, *n*-heptyl, phenyl, benzyl, resorcinol acetates; methyl, ethyl, butyl phthalates; mono- and tri-acetin, methyl, ethyl, benzyl alcohols; cyclohexanol, dimethyl, methylethyl, diethyl ketones; cyclohexanone, methylcyclohexanone, chloroform, bromoform, trichlorethane, tetrachlorethane, pentachlorethane, dichlorethylene, trichlorethylene, tetrachlorethylene.

M. Melamid claims nitro- or acetyl-cellulose and lacquers made therefrom may be colored by using tinted con-

1. J. Amer. Chem. Soc. 1929, **51**, 3095; abst. Rayon Record, 1930, **4**, #6, 338; J. S. C. I. 1929, **48**, 1427-A; C. A. 1929, **23**, 5571. Compare the following, G. Whitby, J. McNally and W. Gallay, Trans. Roy. Soc. Canada, 1928, **22**, 27. H. Staudinger, Berichte, 1926, **59**, 3019. G. Whitby and J. Katz, J. A. C. S. 1928, **50**, 1160. Knoevenagel, Z. angew. Chem. 1924, **27**, 507. H. de Mosenthal, J. S. C. I. 1911, **30**, 782. J. McBain, C. Harvey and L. Smith, J. Phys. Chem. 1926, **30**, 347. S. Sheppard, Nature, 1921, **73**, 17.

densation products, e.g., synthetic resins in a finely divided state as color carriers, mordant dyeing with aluminum oxide being preferably used at the same time[1]. He also prepares a plastic[2] by treating phenols, cresols and naphthols in acid or alkaline solution with quantities of aldehyde lower than the ratio 1:1, and adding cellulose acetate. R. Metzger[3] recommends dyeing acetate silk with suitable insoluble dyes as 1.4.5.8-tetraminoanthraquinone, which is difficultly soluble in water, with a sulfonated mineral oil. Acetylcellulose films may be prepared by adding water to the dissolved ester[4], the water being afterwards extracted by such hygroscopic alcohols as glycerol or glycol. E. Mossgraber[5] has described a device for supplying acetylcellulose to the spinning heads for filament formation. A. Mueller[6] has prepared a series of dihydroxyanthraquinone diglucosides and given their physical characteristics.

Ethylenethiodiglycol[7], which fixes at ordinary temperatures, is introduced into a dyestuff solution comprising setocyanine, acetic acid and a tannin with a thickener, and the solution used to dye cellulose acetate without steaming. C. Mullin has detailed facts concerning the various plants around the world manufacturing cellulose acetate[8]; also[9], recent developments in producing calendered effects on celanese, and the general properties of acetate silks[10]. He also has contributed a discussion and review on recent tendencies in producing special effects on acetate silk, tin-weighted

1. M. Melamid, F. P. 677853; abst. C. A. 1930, **24**, 3383.
2. F. P. 677854; abst. C. A. 1930, **24**, 3332.
3. U. S. P. 1738660; abst. J. S. C. I. 1930, **49**, 944-B; C. A. 1930, **24**, 973.
4. J. Michael A.-G. für Chemische und Metallurgische Industrie, F. P. 668369; abst. Cellulose, 1930, **1**, #4, 126; C. A. 1930, **24**, 1509.
5. D. R. P. 517932; abst. C. A. 1931, **25**, 2849.
6. Berichte, 1929, **62-B**, 2793; abst. J. S. C. I. 1930, **49**, 71-A.
7. H. Muller, U. S. P. 1717242; abst. C. A. 1929, **23**, 3817.
8. Textile Mercury, **80**, #2086, Silk and Art Suppl., 80; Rayon, 1929, **8**, #8, 7, 38; abst. C. A. 1929, **23**, 5316.
9. C. Mullin, Rayon, 1929, **8**, 20; abst. C. A. 1929, **23**, 1753.
10. C. Mullin, Silk Journal, 1927, **3**, #32, 58.

acetate silk, embossed and metallized effects, and rubberized celanese, and has pointed out the faults of rayon in general[1].

It is claimed[2] that the viscosity is greatly effected by allowing the acetylating bath to stand for 2 hours or more in a dry atmosphere with or without the condensing agent. An initial water content of the reagents in the bath (acetic anhydride to acetic acid) which disappears on standing, was found to give a viscosity of the acetylated products of 65 (relative measure) if the bath was immediately used, and 277 if used after 24 hours standing. T. Nakashima has given detailed methods for the production of cellulosexanthoacetic acid[3], and cellulosexanthamides[4]. It was found that when viscose after purification by treatment with acetic acid, was treated with sodium chloroacetate, sodium cellulose-xanthoacetate separated slowly as a jelly and was precipitable by alcohol or salt solution. Addition of dilute sulfuric acid to the aqueous solution precipitated cellulosexanthoacetic acid, which was stable at 105° but decomposed slowly in alkaline solution. In contrast to cellulose xanthate, brief boiling with dilute sulfuric acid caused no decomposition. Analysis of the products obtained by the action of varying amounts of sodium chloroacetate was based on the determination of sulfur in the portions decomposable and non-decomposable in this way, total sulfur, and sodium, and the proportion of xanthoacetic acid formed found to increase with the amount of sodium chloroacetate used. A product the composition of which approximated to $C_{12}H_{19}O_9.O.CS.S.CH_2.CO_2Na$ was obtained when 2 mols. of chloroacetate were used.

1. C. Mullin, Rayon, 1929, **9**, #3, 7.

2. Naamlooze Vennootschap Nederlandsche Kunstzijdefabriek, Holl. P. 19509; abst. C. A. 1929, **23**, 2822.

3. Z. angew. Chem. 1929, **42**, 546; J. S. C. I. 1929, **48**, 799-A; see also Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 103; abst. J. S. C. I. 1929, **48**, 430-A.

4. Z. angew. Chem. 1929, **42**, 643; J. S. C. I. 1929, **48**, 799-A. See also Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 109; abst. J. S. C. I. 1929, **48**, 430-A.

The C. Nash molding mixture comprises a resin of the urea-formalin type, a filler as wood flour, and cellulose acetate[1]. In the preparation of selenium cells[2], the electrodes are formed of thin sheet metal, preferably with interfacing spike-like fingers, and are either imbedded in insulating material as cellulose acetate, or placed between a pair of insulating plates, one of which, at least, must be translucent, preferably of glass. C. Newby[3] has described the methods of coloring cellulose acetate lacquers, and claims one difficulty (as compared with cellulose nitrate) is to find commercially suitable high-boiling solvents or plasticizers. Acetone and methyl acetone are the most important solvents. Coloring agents may be classified: (1) pigments and lakes; (2) dyes; (3) metallic and colored bronzes. Pigments are more widely used than dyes. The method of preparation of pigment enamels is described in some detail, particularly with regard to the method of mixing the pigment with the acetate solution, and the maturing of the medium before and after coloring. Dyes cannot often be used in place of pigments but in some cases can be used in conjunction with a pigment. Various difficulties arise in the preparation and use of such enamels. For a really genuine black enamel, however, a soluble dye is essential. The various methods of use of metal powders for coloring a cellulose acetate medium are described.

The Non-Inflammable Film Co.[4] method of forming composite sheets of cellulose acetate and glass consists in pretreating glass sheets with gelatin to increase their adherency, softening a cellulose acetate sheet with a volatile solvent, then applying pressure and heat to the contacted sheets. Cellulose acetate may be partially hydrolyzed for the production of films and filaments by adding, in addition

1. U. S. P. 1721742; abst. C. A. 1929, **23**, 4784. See also Bakelite Corp., F. P. 643438; abst. C. A. 1929, **23**, 1517.
2. J. Neale, E. P. 317158; abst. C. A. 1930, **24**, 1804. Cf. F. P. 655034 and U. S. P. 1728073; abst. C. A. 1929, **23**, 3634, 5119.
3. J. Soc. Dyers Colourists, 1929, **45**, 104; J. S. C. I. 1929, **48**, 443-B.
4. Can. P. 291026.

to the water necessary to combine with the free acetic anhydride present, more than 40 parts by weight of water for each 100 parts dry cellulose originally acetylated, the temperature being kept under 40°[1].

In dry spinning acetate silk[2], 1-5% calculated on the weight of cellulose acetate, of vegetable or animal fats or oils are added to the spinning solution, olein, olive oil, cocoanut oil, butter fat, beef suet and bone oil being suitable. As an electrical resistance unit[3], it has been proposed to mix carbon with cellulose acetate as a binder. S. Ogden[4] takes cellulose specially prepared[5], which is treated with acetic acid and dried by heat, the partially acetylated product being then further acetylated with acetic anhydride in the usual way.

F. Ohl[6] has called attention to the fact that although a greater part of the acetate rayon is produced by the dry spinning process, a rayon of considerably higher quality and tensile strength can be obtained by the wet-spinning method, a tensile strength of 3 g. per denier being not unusual. The practical difficulty of the wet-spinning method undoubtedly lies in the spinning bath. The variable factors in the spinning bath are discussed. The following points, without regard to cost, are important with reference to the spinning bath: it must allow the greatest stretching of the filaments without injury to the coagulability; the coagulation should not involve a shriveling of the filaments; the components of the precipitation bath must exert an appreciable swelling action on the acetate and must be easily removed from the filaments by washing. Acetone, glycol acetate, ammon-

1. N. V. Nederlandsche Kunstzijdefabriek, F. P. 661964; abst. C. A. 1930, **24**, 499.
2. N. V. Nederlandsche Kunstzijdefabriek, F. P. 661992; abst. C. A. 1930, **24**, 500.
3. Naamlooze Vennootschap Philips' Gloeilampen-fabrieken, F. P. 653880; abst. C. A. 1929, **23**, 3636.
4. E. P. 310563; abst. J. S. C. I. 1929, **48**, 513-B; Silk Journal, 1929, **6**, #63, 68; C. A. 1930, **24**, 962.
5. According to S. Ogden, E. P. 246746; abst. J. S. C. I. 1926, **45**, 975-B; C. A. 1927, **21**, 495.
6. Kunstseide, 1929, **11**, 434; abst. C. A. 1930, **24**, 1973.

ium thiocyanate and calcium thiocyanate are mentioned as desirable constituents of the bath. Only neutral or weakly acid baths are used. The extensibility of the wet rayon is to a large degree (90%) elastic, while with dry spun rayon it is not more than 5% elastic. This condition may be modified by adding softening agents (cyclohexanone, cyclohexanol) to the spinning bath. The presence of small quantities of sulfuric acid in the cellulose acetate results in poor filaments. Only acetone is used as a solvent.

In the W. Ormandy process[1], acetone is recovered from gases in the manufacture of artificial silk by absorption in inorganic acids (sulfuric acid) of 110-130° Tw., the acid being diluted to 50% by weight, before removal of the acetone. The J. Paisseau decorative material is based upon forming gas bubbles within a transparent or translucent mass as cellulose acetate[2], and containing a pearl essence or other brilliant solid particle. The mass is so pressed as to flatten the bubbles thus formed, and the pressure maintained to facilitate absorption of the gas contained in the bubbles by the mass. E. Palau[3] has given a history of the acetylcellulose silk art, claiming 3% of the world's silk produced artificially is by the acetate process, and that acetate silk production is growing because it is less hygroscopic and loses only 25% of its resistance when wetted, as against 75% for the viscose process.

In calendering or ironing fabrics comprising cellulose acetate or other organic cellulose derivatives[4], pressing without appreciably affecting the luster is brought about by subjecting the fabric while damp to the action of a surface such as a calender or iron warmed to somewhat below 100° until the fabric is substantially dry, then completing the pressing by use of a surface warmed to above 100°.

1. F. P. 671418; abst. C. A. 1930, **24**, 2295.
2. U. S. P. 1737943; abst. C. A. 1930, **24**, 993. See E. Heuch, D. R. P. 113114. E. Heuch and J. Paisseau, F. P. 416696 and 471581. Paisseau-Feil, F. P. 407092; F. P. Addn. 12922, 13035, 18507. F. P. 599834; abst. Chem. Zentr. 1926, I, 2860.
3. Quim. Ind. 1929, **70**, 276; abst. C. A. 1930, **24**, 957.
4. C. Palmer, U. S. P. 1732340; abst. C. A. 1930, **24**, 249.

C. Palmer and W. Whitehead[1] have shown details and mechanical features for the continuous production of extruded filaments and twisted threads from cellulose acetate solutions. When "semi-moist" cellulose acetates of low viscosity are mixed with solid solvents or gelatinizing agents of high boiling point in the absence of volatile organic solvents[2], valuable plastic compositions result.

In a mathematical exposition of the viscosity and elasticity of sols by B. Rabinowitsch[3], it was found that solutions of acetylcellulose, nitrocellulose and rubber gave deviations from Poiseuille's law, while gelatin substantiated the law. In the production of composite sheet material for making boxes or cartons, L. Rado[4] coats pastboard with a pellicle of cellulose acetate, then with a water-repellent material as celluloid, or, if tubes are to be formed[5], takes aluminum foil, coats one or both sides with cellulose acetate, secured to the metal foil, if necessary, by an adhesive as gelatin. It is claimed[6] that when an amino compound of the anthraquinone series as 1-aminoanthraquinone is condensed with a halohydrin in the presence of an acid-binding agent, with or without a solvent or diluent, products are obtained useful for dyeing acetate silk.

E. Orioli[7] produces sulfuric acid esters of cellulose (cellulose sulfates) by using sulfuric acid with a fatty acid in the presence of a fatty acid anhydride acting as a dehydrating agent without formation of an appreciable amount of organic ester. This reads like cellulose acetate manufacture by patent circumlocution. In a succeeding patent[8], organic esters of cellulose are alleged to be pre-

1. U. S. P. 1731317; abst. C. A. 1930, **24**, 239; J. S. C. I. 1929, **48**, 976-B. See E. P. 198023; abst. J. S. C. I. 1923, **42**, 765-B.
2. W. Plinatus, E. P. 305238; abst. C. A. 1929, **23**, 4819. Swiss P. 142752.
3. Z. physik. Chem. 1929, **145**-A, 1.
4. E. P. 305098; abst. C. A. 1929, **23**, 4785. F. P. 650432.
5. E. P. 312262; abst. C. A. 1930, **24**, 933.
6. G. Reddelien and W. Müller, U. S. P. 1717809; abst. C. A. 1929, **23**, 4081.
7. F. P. 660924; abst. C. A. 1930, **24**, 239.
8. F. P. 660925; abst. C. A. 1930, **24**, 239. Compare Can. P. 286538; abst. C. A. 1929, **23**, 1504.

parable by treating the sulfuric acid esters with a fatty acid anhydride without employment of a catalyst. To impart a pearly luster to wood, paper or cloth[1], it is advised to first apply a rubber solution and then an overlying coating of a pearly substance incorporated in acetylcellulose. In the J. Robertson compound glass manufacturing process[2], a coating of gelatin in phenol is applied to and allowed to set on the glass sheet, and its surface then softened by a bath of ethyl or propyl alcohol. A cellulose acetate sheet, preferably coated with gelatin or celluloid, is then sandwiched between the glass sheets, and heat and pressure applied.

In the manufacture of artificial silk[3], acetylcellulose and acrylic acid esters, vinyl esters or ethers, or styrol, are separately dissolved in non-miscible solvents, and the mixture of solutions so obtained spun into filaments, polymerization of the unsaturated organic compound being completed when necessary. R. Roland[4] forms flexible sheets for automobile curtain windows of acetylcellulose 25, alcohol 25, and 10 each of chlorbenzene, tetrachlorethane, benzyl benzoate, triacetin and dichlorhydrin. K. Roos alone[5], and in conjunction with H. Friese[6], has discussed the production of cellulose acetate silk, and reviewed the various processes which have been brought forward.

G. Rudolph[7] has didscussed the possibilities of dyeing acetate rayon, and the formation of two, three and four color effects. The Ruth-Aldo Co.[8] subject cellulose which

1. Regensburger & Co., Kommandit-Ges., E. P. 315385; abst. C. A. 1930, **24**, 1712.
2. E. P. 321157; abst. Brit. Plastics, 1930, **1**, 447; J. S. C. I. 1930, **49**, 13-B. F. P. 662816. D. R. P. 535109.
3. Roehm & Haas A.-G. and R. Herzog, E. P. 311784; abst. J. S. C. I. 1930, **49**, 985-B.
4. U. S. P. 1713482; abst. C. A. 1929, **23**, 3343; Plastics, 1929, **5**, 572. E. P. 318818; abst. C. A. 1930, **24**, 2600. Can. P. 283385. F. P. 667792; abst. C. A. 1930, **24**, 1217. Swiss P. 143411.
5. Jentgen's Rayon Review, 1929, **1**, 187.
6. Kunstseide, 1929, **11**, 455; abst. C. A. 1930, **24**, 1973.
7. Kunstseide, 1929, **11**, 261; abst. C. A. 1929, **23**, 4823. Rayon, 1929, **9**, #9, 14, 16, 41; abst. C. A. 1930, **24**, 502.
8. E. P. 303134; abst. Silk Journal, 1929, **5**, #59, 74; J. S. C. I. 1929, **48**, 892-B; C. A. 1929, **23**, 4571.

is to be used for esterification purposes to a pre-treatment with acetic acid vapors and a small quantity of halogen or halogen halogenide at a temperature not exceeding 65°, and preferably between 20-40°, claiming the so treated cellulose becomes more reactive, while the presence of the residual halogen enables the quantity of sulfuric acid used in the acetylation bath to be considerably reduced. In a modification of this process[1], the treated cellulose is acetylated in at least four stages in order to keep down the reaction temperature. It is recommended to carry out the acetylation in a rotating hollow body[2], the walls of which are unevenly distributed with respect to the axis of rotation.

Or[3], the cellulose acetate may be made by a complete process comprising oxidation of the cellulose in the form of cotton linters or wood pulp by means of an alkaline oxidizing agent containing a moderating agent[4]; pretreatment with a stream of acetic acid vapor or with one or more halogens[5], in such a manner that a state of equilibrium is regulated by the law of mass action[6], the catalyst being sulfuric acid alone or in association with a halogen[7], this being followed by saponification by a two-stage process, comprising the addition of an aqueous solution of formic or acetic acids followed by HCl, with or without HF[8], and finally precipitating the acetate in water or other floc-

1. Ruth-Aldo Co., Inc., E. P. 303135; abst. J. S. C. I. 1930, **49**, 368-B; Silk Journal, 1929, **5**, #59, 74.

2. Ruth-Aldo Co., Inc., E. P. 303099; abst. Silk Journal, 1929, **5**, #59, 74; J. S. C. I. 1929, **48**, 1011-B; Brit. Plastics, 1930, **1**, 330; C. A. 1929, **23**, 4571. Can. P. 292025. See also E. P. 282791; abst. J. S. C. I. 1929, **48**, 429-B.

3. Ruth-Aldo Co., Inc., E. P. 305096; abst. J. S. C. I. 1930, **49**, 900-B; Brit. Plastics, 1930, **2**, 229; Silk Journal, 1929, **5**, #60, 66; C. A. 1929, **23**, 4819. See I. G. Farbenindustrie, E. P. 305661; abst. Brit. Plastics, 1930, **2**, 100. Compare E. P. 303098; abst. C. A. 1929, **23**, 4571. Ital. P. 256209.

4. E. P. 282794. U. S. P. 1826718. D. R. P. 505222. Can. P. 315966.

5. E. P. 303134; abst. C. A. 1929, **23**, 4571.

6. E. P. 282788; abst. C. A. 1928, **22**, 3988.

7. E. P. 282793; abst. C. A. 1928, **22**, 3988. E. P. 303135; abst. C. A. 1929, **23**, 4571. Belg. P. 352207.

8. Ruth-Aldo Co., Inc., and H. Barthelemy, E. P. 303098; abst. C. A. 1929, **23**, 4571; J. S. C. I. 1930, **49**, 53-B; Silk Journal, 1929, **5**, #59, 74.

culating agent. The process is carried out in a rotating apparatus[1].

I. de Introini[2] renders nitro- and acetyl-cellulose solutions less viscid and more homogeneous by adding gall or bile, either alone or dissolved in harmonious solvents. In another method for cellulose acetate formation, cellulose sulfates are first formed by heating cellulose in the presence of sulfuric acid and an aliphatic acid anhydride under such conditions that no appreciable amount of acetylcellulose is formed[3], this cellulose sulfate being then decomposed into the acetate[4] by submission of the mass to an excess of anhydride without the addition of a catalyst. The Ruth-Aldo Co. use an aqueous solution of hydrofluoric acid dissolved in acetic acid as the catalyst in cellulose acetylation[5].

L. Rutstein[6] has devised a method for phonograph record formation embracing 100 rotten stone, 100 finely ground record mass, 75 china clay, 40 mica, 5 lamp black, 10 cotton flock, 10 orange shellac and 80 of cellulose acetate in the plastic condition. Iron oxide[7] may be added to the composition. In the C. Ruzicka process for cellulose acetylation, glacial acetic acid is treated with dry chlorine at below 30° in the presence of acetic anhydride and/or one or more compounds of acetic or formic acids. Dry cellulose is then treated with this chlorinated acid below 50°, and when chlorination and hydration of the cellulose have pro-

1. E. P. 282791; abst. C. A. 1928, **22**, 3989. Belg. P. 352205. Ital. P. 256788.
2. E. P. 307392; abst. C. A. 1929, **23**, 5317.
3. Ruth-Aldo Co., Inc., E. P. 303493; abst. Silk Journal, 1929, **5**, #59, 76. Can. P. 286538; abst. C. A. 1929, **23**, 1504. Can. P. 286539; abst. C. A. 1929, **23**, 1504. Can. P. 291434.
4. Ruth-Aldo Co., Inc., and E. Orioli, E. P. 303491; abst. Silk Journal, 1929, **5**, #59, 76; C. A. 1929, **23**, 4571. Belg. P. 352204.
5. Ruth-Aldo Co., Inc., E. P. 303136; abst. Silk Journal, 1929, **5**, #59, 74; Brit. Plastics, 1930, **1**, 447; J. S. C. I. 1930, **49**, 53-B. E. P. 303137; abst. Silk Journal, 1929, **5**, #59, 74. Can. P. 287750. Can. P. 291435. E. P. 282788 & 282789 are referred to. U.S.P. 1839912.
6. U. S. P. 1727039; abst. Plastics, 1930, **6**, 214; C. A. 1929, **23**, 5284; Brit. Plastics, 1929, **1**, 285.
7. U. S. P. 1727040; abst. Plastics, 1930, **6**, 216; C. A. 1929, **23**, 5284; Brit. Plastics, 1929, **1**, 285.

ceeded to the required stage, the mass is acetylated at 30° or lower, zinc chloride or sulfuryl chloride being used as catalyst[1]. Instead of acetic or formic acids, propionic or butyric acids may be used[2], a mixed formo-propionate, formo-butyrate, aceto-propionate or aceto-butyrate mixed cellulose ester being formed[3].

C. Ryley, C. Palmer and S. Welch have assigned to the Celanese Corporation[4] a method for dry-spinning and winding of cellulose acetate threads, by treating the filaments with paraffin oil, olive oil or other suitable lubricant, which facilitates the winding. In the swelling of cellulose acetate in single organic liquids[5], the degree of swelling in a number of them has been measured, all the solvents and swelling media having relatively high values of molecular polarization and dipole moment. Substances which are free from or poor in dipoles are neither cellulose acetate solvents nor swelling agents. With binary liquid mixtures where both components are polar[6], no simple relation between swelling and polarization could be recognized. Copious data are listed in an attempt to show the relations between swelling, molecular polarization, vapor pressure and viscosity of cellulose acetate solutions in binary liquid mixtures where one or both of the components are polar.

I. Sakurada[7] has given methods of preparation and purification of celluloseglycollic acid and its estimation. Celluloseglycollic acid is soluble in water and in organic solvents, not saponified by hot acid or alkali, and sodium cel-

1. E. P. 303432; abst. J. S. C. I. 1929, **48**, 203-B; C. A. 1929, **23**, 4571.
2. C. Ruzicka, E. P. 316593; abst. Brit. Plastics, 1929, **1**, 284; J. S. C. I. 1929, **48**, 892-B.
3. C. Ruzicka, E. P. 316594; abst. C. A. 1930, **24**, 1979.
4. U. S. P. 1725829; abst. C. A. 1929, **23**, 5049.
5. I. Sakurada, Kolloid-Z. 1929, **48**, 277; abst. J. S. C. I. 1929, **48**, 713-B.
6. I. Sakurada, Kolloid-Z. 1929, **49**, 178; abst. J. S. C. I. 1929, **48**, 1380-A. Cf. Kolloid-Z. 1929, **49**, 52; abst. J. S. C. I. 1929, **48**, 1234-A.
7. Z. angew. Chem. 1929, **42**, 640; abst. C. A. 1929, **23**, 4340. See also J. S. C. I. (Japan) 1928, **31**, 67; abst. C. A. 1928, **22**, 1849; J. S. C. I. 1929, **48**, 799-A.

lulose glycollate is water-soluble and miscible with viscose. It was found[1] that celluloseglycollic acid is best prepared by soaking cellulose in 20% NaOH solution, then treating with concentrated cold sodium monochloracetate solution. G. Sandor[2] has published directions for differentiating between films of cellon (cellulose acetate) and cellophane (hydrated cellulose), based upon a distinct blue fluorescence of cellon under filtered ultraviolet light, with no fluorescence with cellophane. A simpler test would be to add a solvent as acetone when cellon dissolves, and cellophane is unaffected.

H. Sauget[3] adds to cellulose acetate intended for phonograph (gramophone) records at least 5% gum lac to lower to the temperature necessary to plasticize. The Schering-Kahlbaum A. G.[4] produce anhydrous formic acid by treating the aqueous acid with phthalic anhydride or a dehydration product or boric or phosphoric acid, and distilling the formic acid. The Silver Springs Bleaching & Dyeing Co.[5] claim that saponification of cellulose acetate does not take place where mixed fabrics containing the same are treated with caustic potash of not less than 80° Tw. strength. R. Spelling[6] produces inexpensive acetate filaments by utilizing waste film and film cuttings freed from their chemical coatings, the viscosity of the solution being augmented if too low, by adding a known quantity of new acetate spinning solution.

A paint has been put forward as suitable for use on sheet materials containing rubber[7], by dissolving dammar

1. I. Sakurada, Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 96; abst. J. S. C. I. 1929, **48**, 430-A.
2. Z. angew. Chem. 1929, **42**, 1108; abst. C. A. 1930, **24**, 1214; Rayon Record, 1930, **4**, 163; J. S. C. I. 1930, **49**, 235-B; Brit. Plastics, 1930, **1**, 498.
3. F. P. 670235; abst. C. A. 1930, **24**, 1948.
4. E. P. 308731; abst. C. A. 1930, **24**, 380; J. S. C. I. 1930, **49**, 361-B. F. P. 672161; abst. C. A. 1930, **24**, 2144.
5. E. P. 309280. Specification 295488 is referred to.
6. E. P. 311368. Specifications 182488 and 245078 are referred to.
7. P. Schidrowitz and D. Burke, E. P. 304334; abst. C. A. 1929, **23**, 4835.

or wax-free shellac with cellulose acetate in a high boiler as ethyl lactate or ethyl benzoate, to which pigments and oils may be added. A cellulose acetate dye giving red to bluish-red shades results by treating hydroxyanthraquinone with ethylene chloride[1], when dark crystalline compounds are obtained. In the insulating electric conductors of G. Schnable[2], material such as wire is provided with a baked, laminated insulation, one layer of which is formed from cellulose acetate and a synthetic resin, to which is added a solid hydrocarbon as ozokerite and castor oil.

Scottish Dyes[3] acetylate cellulose in the presence of pyridine and sulfur trioxide, products being obtained containing up to 56% acetyl group. Diluents as acetic acid, chloracetic acid and phenyl chloride may be used. They dye cellulose acetate with ethereal salts of vat dyes[4], the material being impregnated with the salt at a temperature of 50-80° for 0.5-1 hour, this treatment being followed by development of the dye. In an example, acetate silk is dyed with Soledon jade green and developed with sodium nitrite or ferric chloride in HCl.

In the removal of dyes from cellulose acetate rayon, addition of calcium thiocyanate does not give perfectly satisfactory results, it being better to print with sodium sulfoxylate[5] to which is added a benzene derivative containing one or more hydroxyl groups as resorcinol, or aromatic or aliphatic acids containing an alcohol group as lactic or glycollic acids, which do not react with the reducing agent. Phenol should not be used because it exerts too strong a solvent action on the fiber. Dyes which are de-

1. R. Schmidt and R. Berliner, U. S. P. 1706498; abst. C. A. 1929, **23**, 2304; J. S. C. I. 1929, **48**, 891-B. See E. P. 284242; abst. J. S. C. I. 1929, **48**, 637-B.
2. U. S. P. 1720749; abst. C. A. 1929, **23**, 4283.
3. F. P. 668028; abst. Cellulose, 1930, **1**, 127; C. A. 1930, **24**, 1507. E. P. 310556; abst. C. A. 1930, **24**, 723.
4. Scottish Dyes, Ltd., F. P. 685351; abst. C. A. 1930, **24**, 6033.
5. Scheuer, Lauth & Cie and L. Diserens, Bull. soc. ind. Mulhouse, 1929, **95**, 349; Sealed Note 2662, June 23, 1926; abst. C. A. 1929, **23**, 4817; J. S. C. I. 1929, **48**, 751-B.

stroyed by reduction are unaffected by hyposulfite NF, alone when fixed on acetate rayon, but are very deeply degraded by the action of colored removing pastes consisting of basic dyes dissolved in resorcinol, hyposulfite NF and tannin. Addition of anthraquinone or its derivatives is practically without effect, showing that the action is not due to catalysis of the basic dye similar to that produced by Cetopaline, Patent Blue or Nitroalizarin in the removal of naphthylamine bordeaux. A large number of the Duranol, Ionamine, Acetonine and Setacyl dyes can be removed by addition of 5-10% resorcinol. The function of the latter is considered to be partly a cellulose acetate solvent; but that cannot be its sole function for solvents such as acetone and phenol do not give a good white. It is considered highly probable that resorcinol reacts with the cellulose acetate in a manner similar to acetic anhydride and phenols. A. Wolff[1] claims the addition of resorcinol gives a better white and with a larger number of dyes than calcium thiocyanate, but the fiber is seriously impaired unless the amount of resorcinol be reduced to about 20 gm. per kgm. of color, and the results are then no better than those obtained with calcium thiocyanate.

N. Senda and Y. Uyeda[2] have studied the effects of various factors such as time and amount of acetic anhydride, on the acetolysis of cellulose from a tissue paper of 5.53% moisture content and 0.31% ash, and find that in the acetolysis, removal of water-soluble and alcohol-soluble substances from the gelatinous products formed by pouring the acetylated cellulose into water gives but 37.5% cellobiose octaacetate of the theoretical, with cotton wadding 27.8%, sulfite pulp 11.5% and straw 9.7%. A. Shapiro[3] produces acetic anhydride by acting with HCl instead of sulfuric acid upon a mixture of acetamide and glacial acetic acid.

1. A. Wolff, Bull. soc. ind. Mulhouse, 1929, **95**, 352; abst. C. A. 1929, **23**, 4817; J. S. C. I. 1929, **48**, 751-B.
2. Cellulose Ind. 1929, **5**, 29; abst. C. A. 1929, **23**, 4817; J. S. C. I. 1929, **48**, 319-B.
3. Russ. P. 58598, Addn. to Russ. P. 17216; abst. C. A. 1931, **25**, 1264.

In his studies of alkali-cellulose prepared from cellulose acetate, V. Sharkov[1] finds that when prepared by the method of H. Pringsheim and A. Aronowsky[2], after careful washing with water and drying to constant weight at 110° contained 13.11% NaOH as compared with 12.92% required by the formula $2C_6H_{10}O_5.NaOH$, the discrepancy being accounted for by the difficulty of washing out the last tracts of sodium acetate, and hence the existence of the above compound is considered to be proved. He has also shown[3] that *b*- and *v*-cellulose have different swelling properties in caustic soda solutions.

In the fabrication of rayon pile fabrics[4], a weft of viscose rayon is floated at certain parts as indicated by rectangles, a second weft of cellulose acetate filaments being also floated at certain parts and, one weft forming the ground at those parts of the fabric where the other is being floated. Adsorption and desorption isotherms of cellulose acetate have been determined[5], and it has been found that the amount of water absorbed per gram increases at a given temperature, with the vapor pressure to a maximum value for saturation, and the adsorption of water is progressively lowered by any process which degrades the cellulose, but is considerably increased by mercerization. De-esterified cellulose acetate gives similar results.

In the manufacture of laminated glass[6], the edges of a laminated plate made up of alternating sheets of glass and cellulose acetate are sealed by immersing them in a bath of a pyroxylin plastic solvent as tolyl phosphate, and

1. Zhur. Prikladnoi Khim. 1929, **2**, 775; abst. C. A. 1930, **24**, 1972; J. S. C. I. 1930, **49**, 896-A.
2. Berichte, 1922, **55-B**, 1414; abst. C. A. 1922, **16**, 3878.
3. Zhur. Prikladnoi Khim. 1929, **2**, 749; abst. C. A. 1930, **24**, 1973. Cf. Zhur. Prikladnoi Khim. 1929, **2**, 579; abst. C. A. 1930, **24**, 956.
4. F. Shepherd & Cords, Ltd., E. P. 313992; abst. Silk Journal, 1929, **6**, #65, 80.
5. S. Sheppard and P. Newsome, J. Physical Chem. 1929, **33**, 1817; abst. J. S. C. I. 1930, **49**, 28-A.
6. J. Sherts and R. Hamill, U. S. P. 1781084; abst. J. S. C. I. 1931, **50**, 633-B.

heating the solvent under pressure until the cellulose acetate softens and is forced into the joints. In the chlorination of acetic acid E. Shilov[1] has confirmed and extended the work of H. Brückner[2], recently disputed by O. Magidson[3], it having been found that when glacial acetic acid is treated with chlorine in the presence of a mixed catalyst of iodine, phosphorus and phosphorous pentachloride, a yield of 75-90% of monochloracetic acid is obtained.

In a series of inventions granted to the Silver Springs Bleaching & Dyeing Co. and A. Hall[4] are described mercerization of textiles containing both viscose and cellulose acetate which is effected with caustic potash of sp. gr. 1.4-1.5, the excess alkali being removed by washing with water at 10-20°. Saponification of the cellulose acetate is said not to take place, and the soft handle and luster of the viscose rayon remains unchanged. They deluster cellulose acetate materials[5] by treatment so as to absorb the leuco-compounds of anthraquinone and such of its derivatives as are colorless in the fully oxidized state, which are then suitably oxidized, the fully oxidized anthraquinone being thereby deposited within the silk which thus becomes reduced in luster, anthraquinone and 2-chloranthraquinone being particularly suitable. Or the acetate silk may be treated with aqueous suspensions of esters[6], as ethyl oxalate, then with ammonia, whereby oxamide is formed within the material, thus reducing the luster and giving to it a scroop handle. They produce black dyeings on acetate silk by impregnation with a solution or dispersion of

1. J. Chem. Ind. (Russia) 1929, **6**, 538; abst. C. A. 1930, **24**, 827.
2. Z. angew. Chem. 1927, **40**, 973; abst. C. A. 1927, **21**, 3345. Z. angew. Chem. 1928, **41**, 226; abst. C. A. 1928, **22**, 3819.
3. O. Magidson, I. Zilberg and N. Preobrazhenskii, J. Chem. Ind. (Moscow) 1928, **5**, 528; abst. C. A. 1928, **22**, 4105.
4. E. P. 309280; abst. J. S. C. I. 1929, **48**, 640-B.
5. Silver Springs Bleaching & Dyeing Co., Ltd., and A. Hall, E. P. 316169; abst. J. S. C. I. 1929, **48**, 938-B; Silk Journal, 1929, **6**, #66, 68; C. A. 1930, **24**, 1750.
6. Silver Springs Bleaching & Dyeing Co., Ltd., and A. Hall, E. P. 316638; abst. J. S. C. I. 1929, **48**, 938-B; Silk Journal, 1929, **6**, #66, 70; C. A. 1930, **24**, 1992.

α-naphthylamine which is then treated with an aqueous solution of nitric acid[1]; or 2.4-dinitrodiphenylamine is applied in a dye liquor or printing paste, and reduced simultaneously with or subsequent to its application to the corresponding diamino compound[2], which is then subjected to oxidation.

J. Simonin[3] has described a cellulose xanthacetate obtained by converting cellulose into viscose which is then neutralized with acetic acid and an aqueous solution of sodium chloracetate then added. Finally the solution is treated with weak sulfuric acid and the cellulose ester precipitated in shred form. To imitate suede leather[4] the smooth side of a velour cloth of fine texture is coated with a cellulose acetate solution to form a flexible backing. In the production of hollow rayon[5], a preliminary fiber made of sugar, sulfur, glue, rosin or casein, is covered with a thin film of cellulose acetate solution, and after coagulation of the coating, the preliminary fiber is dissolved out.

The Societe Anon. des Distilleries des Deux-Sevres[6] extract diluted acetic acid with an acetic acid solvent (butyl acetate) and the solution obtained charged into a surface-heated column containing an entrainer (petroleum hydrocarbon mixture, b. pt. 99-101°) which forms with acetic acid a binary azeotropic mixture capable of separation into layers. To produce anhydrous formic acid[7], the dilute acid is distilled with *iso*butyl formate as entraining

1. Silver Springs Bleaching & Dyeing Co., Ltd., and A. Hall, E. P. 321034; abst. C. A. 1930, **24**, 2615; J. S. C. I. 1930, **49**, 54-B; Silk Journal and Rayon World, 1930, **6**, #69, 62.
2. Silver Springs Bleaching & Dyeing Co., Ltd., and A. Hall, E. P. 322893; abst. C. A. 1930, **24**, 2897; Rayon and Synthetic Yarn Journal, 1931, **12**, #3, 58.
3. Rev. gen. mat. plastique, 1929, **5**, 507.
4. C. Simpson, E. P. 306693; abst. C. A. 1929, **23**, 5349. Compare E. P. 291890; abst. C. A. 1929, **23**, 1304.
5. W. Snelling, U. S. P. 1713679; abst. J. S. C. I. 1929, **48**, 639-B.
6. E. P. 312046; abst. J. S. C. I. 1930, **49**, 232-B; C. A. 1930, **24**, 863. F. P. 668935; abst. C. A. 1930, **24**, 1651.
7. F. P. 667031; abst. C. A. 1930, **24**, 1123. E. P. 303742; abst. C. A. 1929, **23**, 4484.

material, and with a diluent liquid containing ammonium formate to prevent the formic acid from distilling over with the azeotropic mixture. The formic acid and diluent is then distilled with entraining substances as benzene, toluene, xylene, butyl chloride. They concentrate acetic acid[1] by extracting the acid from its aqueous solutions by heating in a dehydrating column with acetic acid vapors from the distillation column. Or the acetic acid extraction is carried out by the action of solvents on dilute vapors of the acid instead of aqueous liquids, to avoid contamination by substances contained therein. In another method[2] the acid is extracted from its aqueous solutions by a solvent having a boiling point above that of acetic acid but under 150° as amyl acetate. Where acetic acid is extracted from pyroligneous acid[3], *C*-alkylated cresols are used as *C*-butylcresol obtained by condensing ordinary cresol with butyl alcohol in presence of zinc chloride. In the concentration of acetic acid[4], a petroleum fraction boiling at 114-116° is added to a mixture of dilute acetic acid in amyl acetate and distilled, the amyl acetate being un-vaporized. Or[5], dilute acetic solutions are passed countercurrentwise to an extracting medium insoluble in the solvent present in the solution, being treated through a multiple-stage apparatus (which is described), the acid obtained being especially applicable for cellulose acetation.

1. F. P. Addn. 34574 and 34691 to F. P. 651528; abst. C. A. 1930, **24**, 1392.
2. F. P. 651528; abst. C. A. 1929, **23**, 3234. E. P. 296974; abst. C. A. 1929, **23**, 2449.
3. E. P. 316284; abst. J. S. C. I. 1930, **49**, 452-B. E. P. 316287; abst. C. A. 1930, **24**, 1700; J. S. C. I. 1930, **49**, 880-B. F. P. Addn. 37056 to 668935; abst. C. A. 1931, **25**, 970. F. P. 668935; abst. C. A. 1930, **24**, 1651. E. P. 331637; abst. C. A. 1931, **25**, 116. E. P. 312046; abst. C. A. 1930, **24**, 863. F. P. 679442; abst. C. A. 1930, **24**, 3898. F. P. 679418; abst. C. A. 1930, **24**, 3858.
4. E. P. 317462; abst. J. S. C. I. 1930, **49**, 602-B; C. A. 1930, **24**, 2143. Compare E. P. 296974; abst. J. S. C. I. 1929, **48**, 349-B; C. A. 1929, **23**, 2449. F. P. Addn. 37269 to 651528; abst. C. A. 1931, **25**, 2439. F. P. 651528; abst. C. A. 1929, **23**, 3234. F. P. Addn. 35750 to F. P. 651528; abst. C. A. 1930, **24**, 4052.
5. F. P. 671482; abst. C. A. 1930, **24**, 2143. E. P. 307868; abst. C. A. 1930, **24**, 129.

The dyeing properties of cotton may be modified without changing the fiber structure[1] by treatment with an aliphatic or aromatic isocyanate as phenyl, naphthyl or nitrophenyl isocyanate with or without a catalyst as zinc chloride or pyridine. By this treatment, wool is said to lose its affinity for acid wool dyes, cotton becomes immune to substantive dyes and less easily dyed by acetate silk dyes such as insoluble azo colors and aminoanthraquinones. Or the cellulose may be treated with maleic anhydride[2] to obtain a product which has little affinity for direct dyes but strong affinity for basic. Azo dyes may be prepared by the union of diazotized salts of unsulfonated *o*-aminophenols with unsulfonated aromatic compounds containing hydroxyl or amido groups, and, if necessary, saponifying, alkylating or acylating. Thus, the *p*-toluenesulfonic ester of *o*-aminophenol is diazotized with sodium aniline methane sulfonate. The product is saponified, the dye obtained dyeing acetate silk yellow[3]. Colored effects on mixed cloths containing acetate silk are obtained by treating the fiber with the alkali salt of a 1-hydroxynaphthalene-4-arylketone, steaming and developing with diazo compounds[4].

In dyeing cotton[5], or producing variegated effects on mixed goods of cotton and acetate silk, fast dyeings are obtained by treatment with naphthols or coupling components having salts stable to steam, drying, steaming and developing with diazo compounds. In the immunization of vegetable fibers to direct dyes[6], cotton is first impregnated with copper sulfate solution, then dried, and acetylated with acetic anhydride at 100°, immunization being

1. Soc. Chem. Industrie in Basle, E. P. 317019; abst. J. S. C. I. 1930, **49**, 1106-B; C. A. 1930, **24**, 1992. Cf. P. Goissedet, E. P. 130277; abst. J. S. C. I. 1919, **38**, 714-A.
2. Soc. Anon. Pour L'ind. Chim. a Bale, F. P. 677493; abst. C. A. 1930, **24**, 3112.
3. F. P. 683955; abst. C. A. 1930, **24**, 5164.
4. F. P. 666352; abst. C. A. 1930, **24**, 1522.
5. Soc. Anon. pour L'Ind. Chim. a Bale, E. P. 303179; abst. C. A. 1929, **23**, 4579. D. R. P. 521200.
6. 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.

complete in less than an hour. Acetic acid or its esters may be obtained by treating cellulosic vegetable substances at a low temperature[1] by dilute alkali solutions so as to transform the complex acetyl derivatives into metallic acetate.

Cellulose butyrates, as the tri*iso*butyrate and tributyrate[2], may be prepared by submitting cellulose to the regulated action of a chlorine derivative of acetic acid in the presence of a solvent, as butyric acid or acetone, at a low temperature, and esterifying at 15-25° in the presence of 66° Be. sulfuric acid and an appropriate solvent. Mixed cellulose esters result (acetobutyrates) by treating cellulose with chloracetic acid in the presence of acetic or butyric acids as solvent, then esterifying with a mixture of butyric anhydride and acetic anhydride in the presence of vitriol[3].

In the concentration of crude acetic acid to absolute strength[4], the vapors from the retort pass into a horizontal calcium chloride absorber provided with rotating vertical plates. In another method for the production of acetic acid[5], methyl alcohol is caused to react with formamide under suitable conditions to obtain acetamide which is then converted into acetic acid in known manner. In the manufacture of gas masks[6] one or more layers of a coating formed of drying oil and cellulose acetate is applied to cloth used for protection against noxious gases. Cellulose acetates, sulfacetates, phosphoacetates and formylacetates are saponified in solution with phenols or polyphenols (phenol, resorcinol, sodium phenate, cresolate, resorcinate), es-

1. Soc. Chim. des Derives du Pin and G. Darzens, F. P. 670285; abst. C. A. 1930, **24**, 1868.
2. Soc. des Brevets Etrangers Lefranc et Cie, F. P. 686906; abst. C. A. 1931, **25**, 812. F. Addn. 38980 to 686906.
3. Soc. des Brevets Etrangers Lefranc et Cie, F. P. 687169; abst. C. A. 1931, **25**, 813.
4. Soc. des Etablissements Barbet, F. P. Addn. 36953 to F. P. 649121; abst. C. A. 1931, **25**, 1071. F. P. 649121; abst. C. A. 1929, **23**, 2722.
5. Soc. Francaise de Catalyse Generalisee, F. P. 700774; abst. C. A. 1931, **25**, 3669. F. Addn. 38577.
6. Soc. Chim. du Caoutchouc (Soc. Anon.), F. P. 651522; abst. C. A. 1929, **23**, 3284.

ters treated in this manner being modified as to their solubilities, so that films and filaments prepared therefrom take on superior mechanical properties[1].

In compound glass manufacture[2], plastic cellulose acetate is softened by immersion in a bath of benzyl alcohol, then placed between two glass sheets free from air-bubbles, and the composite sheet united by gentle pressure. In the production of acetic anhydride and acetaldehyde[3], vapors from the dissociation of ethylene diacetate are led through a suspension or solution or organic salts (potassium acetate) in a mixture of ethylidene diacetate and acetic anhydride, so as to remove hydrochloric acid or other polymerizing agent. Cellulose butyrate[4] and acetobutyrate[5] are produced when cellulose is treated with acetic acid as previously outlined[6], and is then further esterified by application of butyric or *iso*butyric anhydride or their mixtures (cellulose aceto-*n*-butyro*iso*butyrate as example), with or without a diluent or solvent of the product formed. New crotonates of cellulose are prepared[7] by submitting cellulose tricrotonate in a solvent mixture containing water in the presence of saponifying catalysts as mineral acids or sulfonic acids. Cellulose butyrates soluble in alcohol[8] may

1. Soc. des Usines Chimiques Rhone-Poulenc, E. P. 321648; abst. C. A. 1930, **24**, 2882; J. S. C. I. 1930, **49**, 99-B; Rayon Record, 1930, **4**, #20, 1062; Cellulose, 1930, **1**, #7, 198; Silk Journal and Rayon World, 1930, **6**, #69, 64. See E. P. 318250; abst. C. A. 1930, **24**, 2290. E. P. 21016, 1914. Swiss P. 140727. D. R. P. 539471.

2. Soc. des Usines Chimiques Rhone-Poulenc, E. P. 316955; abst. C. A. 1930, **24**, 1951; J. S. C. I. 1930, **49**, 1029-B; Brit. Plastics, 1930, **2**, #19, 322. E. P. 305189; abst. J. S. C. I. 1929, **48**, 679-B.

3. *Ibid.* E. P. 318960; abst. C. A. 1930, **24**, 2473; J. S. C. I. 1930, **49**, 939-B. F. P. 674392; abst. C. A. 1930, **24**, 2474. E. P. 238825; abst. C. A. 1926, **20**, 1995. Aust. P. 114018, 117047. F. P. 506659. D. R. P. 292818, 293070. D. R. P. 527873.

4. *Ibid.* F. P. 684273; abst. C. A. 1930, **24**, 5495.

5. *Ibid.* E. P. 321575; abst. C. A. 1930, **24**, 2882; J. S. C. I. 1930, **49**, 53-B; Brit. Plastics, 1930, **1**, #10, 447. F. P. 684274; abst. C. A. 1930, **24**, 5496.

6. *Ibid.* E. P. 237567; abst. C. A. 1926, **20**, 1522; J. S. C. I. 1926, **45**, 49-B.

7. *Ibid.* F. P. 684759; abst. C. A. 1930, **24**, 5496.

8. *Ibid.* F. P. 685637; abst. C. A. 1930, **24**, 6013. For manufacture of films, see E. P. 318250; abst. Brit. Plastics, 1931, **2**, #21, 433.

be similarly made. Cellulose acetate soluble in aqueous or anhydrous phenols or polyphenols, is saponified by submitting, dissolved in the phenols, to the action of alkali compounds, as dissolved alkali phenates[1].

To produce hollow or bubble-containing filaments[2], a solution of cellulose acetate in acetone is applied as a film or coating to one or more threads, and then, either by application of heat or reduction of pressure, gas development is caused to take place while the material is on the support. Cellulose monochloracetate may be similarly treated[3]. Acetic acid may be prepared by passing CO and H over catalysts of nickel, cobalt, chromium, iron or copper phosphates, silicates and borates[4]. In the dry-spinning of acetate silk[5] below the boiling point of the solvent, the temperature is kept reduced until after it leaves the spinning nozzles. An acetone solution of cellulose acetate is kept below 56° before it leaves the spinning nozzles and is then submitted to a temperature of 100-140°. A special candle-shaped filter used has been described[6].

In the production of acetate filaments, the untwisted threads in the wound form as received from the spinning machine are first subjected to a sizing treatment[7] whereby the individual filaments are agglutinated, thus permitting the threads to be used for weaving or knitting. The bobbins, reels or cakes are assembled in a creel, the threads

1. Soc. des Usines Chimiques Rhone-Poulenc, F. P. 676631; abst. C. A. 1930, **24**, 3112.
2. *Ibid.* E. P. 318970; abst. C. A. 1930, **24**, 2603. Aust. P. 117486.
3. Soc. des Usines Chim. Rhone-Poulenc, H. Gault and F. Bidaud, E. P. 318908; abst. C. A. 1930, **24**, 2882; J. S. C. I. 1929, **48**, 1011-B; Brit. Plastics, 1930, **1**, #8, 330. F. P. 672220; abst. C. A. 1930, **24**, 2290.
4. Soc. Francaise de Catalyse Generalisee, F. P. Addn. 36719 to F. P. 681958; abst. C. A. 1931, **25**, 970. F. P. 681958; abst. C. A. 1930, **24**, 4306. F. P. Addn. 37720 to F. P. 681958; abst. C. A. 1931, **25**, 4558. E. P. 338329.
5. La Societe Syntheta A. G., F. P. 667990; abst. C. A. 1930, **24**, 1510.
6. La Societe Syntheta A. G., F. P. 667991; abst. C. A. 1930, **24**, 1510.
7. Sondermann & Co., E. P. 297778; abst. Silk J. 1929, **6**, #67, 72.

suitably separated being then conducted through a sizing apparatus and dried[1]. H. Stadlinger[2] has discussed the importance of combining nitrocellulose with cellulose acetate in the lacquer industry, and C. Staud[3] the technology of cellulose acetate in its relation to solvents and plasticizers. In the glueing of leather and similar materials[4], powdered cellulose acetate with suitable softeners are placed between the surfaces to be cemented, and heat and pressure applied. Cellulose esters of phthalic acid, and mixed esters with acetic, propionic, butyric, crotonic, lauric, palmitic and stearic acids have been described[5], an example being cellulose phthalate or cellulose aceto-phthalate, dissolving in the usual inexpensive solvents.

Cellulose and resins are acetylated together, the combined acetated cellulose and acetated resin being employed as a thermoplastic composition for molding[6]. In the manufacture of concentrated acetic acid by extracting the superheated vapor of dilute acetic acid with a water-insoluble organic solvent of higher boiling point than acetic acid[7], trichlorethylene, wood tar, quinoline, dimethylaniline, anthracene oil is used[8]; or the acetic acid may be distilled at successively decreasing pressures[9]. The acid may also be

1. Sondermann & Co., E. P. 318211, Addn. to E. P. 297778; abst. Silk J. 1929, **6**, #67, 72.
2. Chem. Ztg. 1929, **53**, 377; abst. C. A. 1929, **23**, 4570.
3. Paint, Oil & Chem. Rev. 1929, **88**, #19, 9; Am. Paint. J. 1929, **14**, #4, 22; abst. C. A. 1930, **24**, 514.
4. W. Stelkens, E. P. 314867; abst. C. A. 1930, **24**, 1542; J. S. C. I. 1930, **49**, 1081-B.
5. R. Stinchfield, U. S. P. 1704306; abst. C. A. 1929, **23**, 2033; Plastics, 1930, **6**, #2, 91.
6. E. de Stubner, F. P. 660877; abst. C. A. 1930, **24**, 252.
7. H. Suida, Can. P. 292128. Aust. P. 116727; abst. C. A. 1930, **24**, 2756. U. S. P. 1703020; abst. C. A .1929, **23**, 1909; J. S. C. I. 1929, **48**, 317-B. E. P. 255047; abst. J. S. C. I. 1927, **46**, 316-B. Cf. F. P. 639112; abst. C. A. 1929, **23**, 608. F. P. Addn. 33971 to F. P. 593091; abst. C. A. 1929, **23**, 4230. E. P. 296172; abst. C. A. 1929, **23**, 2449.
8. *Ibid.* E. P. 303494, 303495; abst. C. A. 1929, **23**, 4711; J. S. C. I. 1930, **49**, 361-B. F. P. 662391; abst. C. A. 1930, **24**, 381. Aust. P. 117057; abst. C. A. 1930, **24**, 3250. Can. P. 292129. Aust. P. 116727; abst. C. A. 1930, **24**, 2758. D. R. P. 542354.
9. *Ibid.* U. S. P. 1715313; abst. C. A. 1929, **23**, 3478. U. S. P. 1621441; abst. C. A. 1927, **21**, 1464. U. S. P. 1624810; abst. C. A. 1927, **21**, 1819.

extracted with diethyl or dibutyl phthalates[1], or[2], carbon tetrachloride or dichlorethane.

In an investigation of the acetylated products of wood, H. Suida and H. Titsch[3] esterifying in the presence of pyridine or dimethylaniline for 15-35 days at 100° gave products containing 30.1-35.2% acetic acid[4]. With the method of W. Fuchs[5], the acetyl content is of the order of 36-38% and not 41% as stated by O. Horn[6]. Non-splintering glass sheets are produced by the J. Talbot process[7] by sealing a single pane of glass between cellulose acetate sheets, then sealing the edges by means of an acetate lacquer. J. Taylor[8] has described the manufacture of "Triplex" and other types of safety glass, and described a glass-like substitute prepared by condensing phthalic anhydride, urea and glycerol. Celloglass is a wire netting coated with cellulose acetate (see p. 155, n. 1; p. 555, n. 7). In joining glass sheets with an intervening cellulose acetate film, J. Thornton[9] softens the acetate surface with solvent, the glass having previously been lightly treated with hydrofluoric acid or sodium silicate and gives a roughened surface and increased adhesion.

Cigars have been described as manufactured by forming the wrapper with a mixture of comminuted tobacco in a cellulose acetate lacquer[10]. Patentee does not guarantee the taste. In an investigation of the diffraction of cathode rays, G. Thompson finds beaten foils, thinned down chemically, to be inferior for quantitative work to those produced

1. H. Suida, F. P. 658960; abst. C. A. 1929, **23**, 5195. Can. P. 286812.
2. *Ibid.* Aust. P. 116377; abst. C. A. 1930, **24**, 2473. F. P. 662402; abst. C. A. 1930, **24**, 381; E. P. 303494; abst. C. A. 1929, **23**, 4711.
3. Monatsch. 1929, **53-54**, 687; abst. C. A. 1930, **24**, 5481.
4. Ber. 1928, **61-B**, 1599; abst. C. A. 1928, **22**, 4807.
5. Ber. 1928, **61-B**, 948; abst. C. A. 1928, **22**, 2744.
6. Ber. 1928, **61-B**, 2542; abst. C. A. 1929, **23**, 1886.
7. E. P. 313273; abst. C. A. 1930, **24**, 938; J. S. C. I. 1929, **48**, 645-B; Brit. Plastics, 1929, **1**, #4, 153.
8. Brit. Plastics, 1929, **1**, 206.
9. E. P. 308117; abst. C. A. 1930, **24**, 215.
10. W. Thiele, U. S. P. 1716250; abst. C. A. 1929, **23**, 3807.

by cathode sputtering on cellulose acetate[1]. S. Tootal[2] describes dyes for domestic and laundry use in dyeing materials comprising cellulose acetate, which are prepared by suspending an insoluble dye such as Duranol Violet or Artisil Direct Red 2 BL, in a state of fine subdivision in a solid but soluble form of gelatin and glycerol.

In a study of orientation and pseudo-crystallization in stretched colloidal gels, J. Trillat[3] made X-ray spectograms along the three axes of stretched and unstretched cellulose acetate and nitrate films. Unstretched films gave amorphous rings in all directions indicating random molecular orientation, whereas with stretched films, equatorial reinforcement of the diffraction ring was observed in two of the three dimensions studied, indicating that long molecular chains were oriented by the stretch. The G. Truempler acetate plastic compositions[4] are prepared by making a paste with volatile solvents of cellulose acetate and softeners, then heating to drive off the volatile solvent, thus leaving a loose mass which is dried and pulverized and can be molded while hot. A water-miscible solvent as diacetone alcohol is prfeerred[5].

Y. Tsuzuki[6] is authority for the statement that starch may be readily acetylated by acetic anhydride in presence of lithium, sodium, or calcium thiocyanate or iodide, but the product differs from that previously described[7] in that it disperses only slowly in organic media, forming highly viscous solutions. Acetylation of dextrose and galactose with acetic anhydride and dry sodium thiocyanate yields *b*-penta-acetylglucose and *b*-penta-acetylgalactose.

1. Proc. Roy. Soc. 1929, A-**125**, 352.
2. E. P. 314149; abst. C. A. 1930, **24**, 1226.
3. Compt. rend. 1929, **188**, 1246; abst. J. S. C. I. 1929, **48**, 763-A.
4. F. P. 668124; abst. C. A. 1930, **24**, 1476.
5. F. P. 668125; abst. C. A. 1930, **24**, 1528.
6. Bull. Chem. Soc. Japan, 1929, **4**, 21; abst. J. S. C. I. 1929, **48**, 428-A; C. A. 1929, **23**, 2425. Bull. Chem. Soc. Japan, 1929, **4**, 153; abst. C. A. 1930, **24**, 260.
7. Bull. Chem. Soc. Japan, 1928, **3**, 276; abst. J. S. C. I. 1929, **48**, 175-A.

In the U. S. Industrial Alcohol Co. patented process[1], cellulose acetate produced by acetylation of cellulose under pressure, with or without a catalyst, in a medium of liquid sulfur dioxide, is discharged from the reaction vessel so that the SO_2 is abruptly liberated as gas, thus disrupting the ester with production of a light and fluffy product. An apparatus for effectuating the invention has been illustrated[2]. They remove acetic acid in the anhydrous state from its solutions by treatment with a liquid which does not form an azeotropic mixture with the anhydrous acid[3]. Instead of a single solvent, a mixture of solvents may be used[4].

The after process of hydrolysis of cellulose acetate may be modified[5] by carrying the treatment out in solution with the aid of sulfuric acid, and in the presence of a quantity of water not less than 50% that of the cellulose originally taken, and is continued at about 20° until the viscosity in an acetone solution of the hydrolyzed acetate is at least 1.5 times the minimum viscosity, this requiring several days treatment[6]. Meanwhile[7] the reaction mass is thoroughly agitated by means of a mechanical whirling device, and the operation preferably carried out by means of a revolving drum having an acid-resisting wall or lining and traversed with bars or beams fixed to the inner wall in such manner that they exert a cutting action on the heart of the reaction mass[8].

1. E. P. 306531; abst. C. A. 1929, **23**, 5041; J. S. C. I. 1930, **49**, 609-B; Silk J. 1929, **6**, #61, 72; Brit. Plastics, 1930, **2**, #15, 135. Can. P. 292842. F. P. 667978; abst. Cellulose, 1930, **1**, #4, 125; C. A. 1930, **24**, 1508. Belg. P. 270223, 357748. Ital. P. 276787.

2. F. P. 686491, 686492; abst. C. A. 1931, **25**, 591. Belg. P. 366142, 366143. L. Burghart, U. S. P. 1822563, 1839295; abst. C. A. 1931, **25**, 5990.

3. U. S. Industrial Alcohol Co., Can. P. 289093.

4. *Ibid.* Can. P. 293404.

5. Naamlooze Vennootschap Nederlandsche Kunstzijdefabriek, E. P. 292398; abst. C. A. 1929, **23**, 1504; J. S. C. I. 1928, **47**, 637-B.

6. S. Vles, E. P. 310434; abst. C. A. 1930, **24**, 723; J. S .C. I. 1929, **48**, 594-B; Silk J. 1929, **6**, #63, 68.

7. Verein fur Chemische Industrie, A.-G., E. P. 317088; abst. C. A. 1930, **24**, 1979. D. R. P. 521125.

8. *Ibid.* E. P. 303485; abst. C. A. 1929, **23**, 4571; Silk J. 1929, **5**, #59, 76. F. P. 662790; abst. C. A. 1930, **24**, 499.

In order to obtain a non-fraying rayon of soft feel[1], the bundle of filaments constituting the thread is not twisted, but so treated as to effect permanent adherence of the filaments in such manner that at various parts of the bundle, different filaments are caused to adhere. The method is applicable in particular to cellulose acetate filaments.

According to directions set forth by A. Wacker, a primary solution of cellulose acetate[2] is squirted into a precipitating bath[3], the acetone-soluble ester being then treated with an acid salt of a metal of Groups I or II of the Periodic System[4] containing water of crystallization, until partial hydration has been carried to the point desired. The waste acetic acid obtained is rejuvenated by distillation in the presence of an acetic acid ester boiling within 10° of absolute acetic acid[5].

In making multicolor photographic screens[6], a cellulose acetate film 0.0055 inch thick[7] is coated by an apparatus described[8], with a fine layer of collodion which may be coated green, and a series of fine parallel lines printed on the film at an angle of 67° to the latter's edge by an engraved steel roller[9]. The film is made on a described

1. S. Vles and D. Van der Want, E. P. 306050; abst. Silk J. 1929, **5**, #60, 70.

2. E. P. 313974; abst. C. A. 1930, **24**, 1218; J. S. C. I. 1930, **49**, 985-B; Silk J. 1929, **6**, #65, 78. F. P. 675947; abst. C. A. 1930, **24**, 2882. F. P. 649623. Ital. P. 268794. Norw. P. 46521. Swiss P. 143667.

3. E. P. 291001; abst. C. A. 1929, **23**, 1267; J. S. C. I. 1929, **48**, 750-B. D. R. P. 488528; abst. C. A. 1930, **24**, 2291. E. P. 325209; abst. J. S. C. I. 1930, **49**, 414-B. F. P. 661935; abst. C. A. 1930, **24**, 499. Norw. P. 47806. Swiss P. 139514. D. R. P. 510425; abst. C. A. 1931, **25**, 1082. Holl. P. 24111.

4. Can. P. 292845.

5. F. P. 661343; abst. C. A. 1930, **24**, 381. E. P. 298137; abst. C. A. 1929, **23**, 2724. Can. P. 291049. Swiss P. 134111. Norw. P. 46437.

6. Versicolor Dufay (Compagnie d'Exploitation des Procedes de Photographie en Couleurs L. Dufay), E. P. 322432.

7. E. P. 243032; abst. Ann. Rep. S. C. I. 1926, **11**, 618. E. P. 281803; abst. J. S. C. I. 1928, **47**, 187. E. P. 287635; abst. J. S. C. I. 1928, **47**, 444-B. E. P. 301439; abst. J. S. C. I. 1929, **48**, 203-B.

8. E. P. 321222.

9. E. P. 20111, 1908; abst. J. S. C. I. 1909, **28**, 544. E. P. 217557; abst. Ann. Rep. S. C. I. 1925, **10**, 578.

machine[1] for treating a long strip of dyed cellulose acetate, having a resist pattern printed thereon for the production of either two-color or multi-color screens.

Acetate silk is produced at winding speeds of the order of 600 feet per minute by heating the air in the spinning cell to 140°, using an acetone solution. The spinning nozzles and the walls of the cells in which they are located are water-cooled[2]. A piston pump for solutions of cellulose acetate has been described by A. Maurer[3].

In polychrome filter formation, A. Wade[4] has patented the step of applying to a cellulose acetate film, a solution of collodion, *after* the application of the dye. A. Wahl and J. Rolland[5] have detailed the composition of commercial artificial silks; A. Weber[6] a process for the surface treatment of celluloid articles by spraying them with a cellulose acetate solution; and A. Weith and O. Holzmann[7] a molding mixture of cellulose acetate and Bakelite.

G. Whitby and W. Gallay[8] have given some experimental results for the relative viscosity (i.e. viscosity referred to viscosity of the pure solvent at the same temperature) and the percentage volume occupied by the disperse phase (calculated from Hatschek's equation for the viscosity of emulsoids) of solutions of cellulose acetate in phenylethyl alcohol, benzyl alcohol, acetone and cyclohexanone. The measurements with cellulose acetate were carried out on sols of different concentrations and it was found that, for sols with a relative viscosity of 4 or less, temperature had

1. E. P. 322454.
2. Syntheta, A.-G., E. P. 323031; abst. Rayon Record, 1930, **4**, #6, 338.
3. D. R. P. 518100; abst. C. A. 1931, **25**, 2567.
4. F. P. 667253. L. Dufay, U. S. P. 1805361.
5. Rev. Gen. Mat. Col. 1929, **33**, 1; abst. J. S. C. I. 1929, **48**, 167-B.
6. A. Weber, H. Hoppner, Jr., and H. Weich, E. P. 316276; abst. J. S. C. I. 1929, **48**, 1011-B.
7. U. S. P. 1720192; abst. Plastics, 1930, **6**, #2, 89.
8. Trans. Roy. Soc. Canada, 1929, iii, **23**, 1; abst. J. S. C. I. 1929, **48**, 374-A; C. A. 1929, **23**, 2089.

a comparatively small effect on the viscosity relative to that of the solvent at the same temperature. This conclusion is in accord with data published by E. Mardles[1]. The viscosity of cellulose acetate when peptized in acetone shows an increase in viscosity as hydrolysis proceeds[2], but when peptized in formic acid, no appreciable change in viscosity results with decrease in acetyl content (see p. 860, n. 5).

J. White[3] provides conductors, as telephone switchboard cables, with a nonwaterproof insulating material as cotton coated with an acetone solution of cellulose acetate, free from electrolytic material. Cellulose acetate yarns may be dyed[4] by treatment with a water-insoluble color, as methylaminoanthraquinone, dissolved in ethylene dichloride and trichlorethylene.

Wolff & Co.[5] cement viscose foils with a cellulose acetate lacquer juxtaposed by means of a mixture of an adhesive bath for the coating, including a solvent for the lacquer coating. Paraffin, Japan wax, carnauba, ceresine or lanolin may be added[6]. Thermoplastic cellulose acetate fabrics may be made of decreased permeability[7], by subjecting the fabric to heat and pressure to flatten the filaments in the fabric in one direction. In a method for cellulose carboxylate manufacture[8], cellulose is acetylated

1. J. C. S. 1923, **123**, 1951. See G. Whitby, J. McNally and W. Gallay, Trans. Roy. Soc. Canada, 1928, **22**, 27; abst. C. A. 1928, **22**, 2079.

2. K. Werner and H. Engelmann, Z. angew. Chem. 1929, **42**, 438; abst. C. A. 1929, **23**, 4569; J. S. C. I. 1929, **48**, 468-B.

3. U. S. P. 1725773; abst. C. A. 1929, **23**, 4983.

4. W. Whitehead, U. S. P. 1738978; abst. C. A. 1930, **24**, 973; J. S. C. I. 1930, **49**, 101-B. E. P. 282036; abst. J. S. C. I. 1929, **48**, 169-B.

5. E. P. 316574; abst. J. S. C. I. 1930, **49**, 1105-B; Brit. Plastics, 1931, **2**, #20, 376.

6. Wolff & Co., R. Weingand and F. Spiecker, E. P. 309017; abst. J. S. C. I. 1930, **49**, 11-B. E. P. 318166, Addn. to 309017.

7. T. Woodman and W. Dickie, U. S. P. 1716255; abst. C. A. 1929, **23**, 3818.

8. B. Wylam, J. Thomas and Scottish Dyes, Ltd., E. P. 310556; abst. J. S. C. I. 1929, **48**, 594-B.

with "pyridine sulfuric acid" to which chloracetic ester, chlorbenzene, chlortoluene and chlorxylene are added as diluents during the esterification process. G. Zemplen[1] has hydrolyzed various acetylated sugars, including mannitol from the hexa-acetate, *b*-glucosan from the triacetate, thio*iso*trehalose from the octo-acetate, and *a*-methylmannoside from the tetra-acetate.

Several anonymous papers on cellulose acetate technology have appeared[2].

Organic Cellulose Esters Art. 1930 Progress. A remarkably extensive literature of patents and literary contributions has accumulated during this year, especially in the cellulose ether art (see pp. 214-256) and compounds of cellulose other than the acetates, as the mixed esters of which acetic acid is usually one of the radicals. The contributions—exceeding five hundred in number recorded herein—are indicative of the intensive research progressing both from the theoretical viewpoint and commercial exploitation.

In an investigation undertaken to find the most suitable wrapper for tobacco and food products[3], vapor transmission through cellulose acetate was studied, the method used being to cover a bottle containing water or other liquid with the acetate film and determine the evaporation after varying periods. In laminated glass manfacture[4], a

1. G. Zemplen and E. Pacsu, Ber. 1929, **62**-B, 1613; abst. J. S. C. I. 1929, **48**, 911-A.

2. Abel's Phot. Weekly, 1929, **44**, 170. Amer. Silk Journ. 1929, **48**, #1, 54. Amer. Silk Journ. 1929, **48**, #9, 54. Chem. & Met. Eng. 1929, **36**, 671. Chem. & Met. Eng. 1929, **36**, 749. Filmtechnik, 1929, **5**, 121. Jentgen's Artificial Silk Review, 1929, **1**, #3, 149. Plastics, 1929, **5**, 109, 110, 439, 441, 679. Molded Products (Plastics), 1929, **3**, #5, 283. Radiology, 1929, **13**, 369. Rayon, 1929, **8**, #8, 14. Rayon 1929, **9**, #2, 32, 34. Silk J. and Rayon World, 1929, **5**, #59, 54, 55. Silk J. and Rayon World, 1929, **6**, #65, 51. Textile World, 1929, **75**, 3881. Textile World, 1929, **76**, 1755, 2841, 3097, 4629.

3. A. Abrams and W. Chilson, Paper Trade J., 1930, **91**, 175.

4. Acetex Safety Glass, Ltd., and W. Johnston, E. P. 330265; abst. C. A. 1930, **24**, 5958; British Plastics, 1930, **2**, #16, 185; Kunst. 1931, **21**, 93. Can. P. 299073. U. S. P. 1809276.

sheet of acetylcellulose solvated with triacetin is interposed between two sheets of glass, the sheets are pressed together by means of compressed air, and finally subjected to steam under pressure at a temperature under the boiling point of the solvent used. Triacetin boils at about 258°. In acetic anhydride production[1], concentrated acid is treated with carbonyl chloride (phosgene) in presence of about 10% aluminum chloride, magnesium or copper acetates, bismuth or cadmium oxide, chloride or acetate.

In coloring cellulose acetate silk[2], the latter is dyed with dischargeable dyes which are discharged with hyposulfite, and for printing, a mordant is used composed of glycerol, zinc nitrate and phenol or resorcinol, cyclohexanol, *p*-toluenesulfonamide or *p*-toluenesulfonanilide, the fibers being softened for spinning by means of olive oil, olein, cocoanut fat, butter fat or earthnut oil[3]. In the partial hydration of acetated cellulose[4], a temperature under 45° is recommended to obtain films and filaments or maximum strength and tenuity, 35-40° being the preferred range[5].

An arc welding electrode has been described[6] in which the coating of the electrode is provided with a film impermeable to moisture made with acetylcellulose, so as to prevent hygroscopic action on the components of the coating. In the ornamentation of pencils and other similar articles[7], a transfer having a backing of aluminum or other metal foil is applied to the article, the adherence being secured by the use of cellulose acetate lacquer containing gelatin and sodium lactate.

1. A. G. f. Stickstoffdünger, E. P. 328572; abst. C. A. 1930, **24**, 5309; J. S. C. I. 1930, **49**, 705-B. F. P. 669150; abst. C. A. 1930, **24**, 1652. Belg. P. 372319. Ital. P. 276630. Norw. P. 48842.
2. C. Alabouvette, F. P. 662243; abst. C. A. 1930, **24**, 510.
3. Algemeene Kunstzijde Unie N. V., Swiss P. 140049.
4. *Ibid.* Swiss P. 140726, Addn. to Swiss P. 134955.
5. *Ibid.* Swiss P. 141037; abst. Chem. Zentr. 1931, II, 3061. See Swiss P. 133809.
6. Alloy Welding Process, Ltd., Can. P. 299706.
7. Anglo Pencil Co., Ltd., and M. Smith, E. P. 326882; abst. C. A. 1930, **24**, 4945.

The jelly strength of the reversible gel composed of acetylcellulose and benzyl alcohol[1], as determined by the Smith apparatus in 10% ester solution at 10° becomes almost constant after cooling 5-6 hrs., while the values of the different samples were inversely proportional to viscosity. On drying solutions of acetylcellulose in a mixture of equal parts of Anon and acetone on a glass plate, thin films were obtained which had a tensile strength of 6-7 kgm. per sq. mm. The R. Arnot adhesive film and sheet is prepared by combining synthetic resins in the reactive state with cellulose acetate[2], paper, cloth or asbestos paper being impregnated with the resin, upon which is superposed a plurality of coats of cellulose ester. In 1930 N. Artem'ev[3] presented a comprehensive review of the methods for the catalytic production of acetic anhydride described in the patent and technical literature.

Non-splintering glass may be produced by uniting sheets of glass by means of cellulose acetate incorporated with dialkyl (dimethyl, diethyl, dipropyl) esters of itaconic acid[4]. In the dyeing of regenerated cellulose material[5], especially a range of blue shades, secondary diazo dyes obtained by coupling the diazo compound of a sulfonated or carboxylated-*p*-nitroarylamine with an aminonaphthol sulfonic acid, as *p*-nitraniline-*o*-sulfonic acid, *m*-amino-*p*-cresol methyl ether and 1.8.4-aminonaphthol sulfonic acid. If the latter is used[6] with reduction of the nitro group, a

1. T. Araki and M. Kusagawa, J. S. C. I. Japan, 1930, **33** (suppl. binding), 267; abst. C. A. 1930, **24**, 4929; J. S. C. I. 1930, **49**, 1022-B; Brit. Plastics, 1030, **2**, #19, 322; Cellulose, 1930, **1**, #8, 221.
2. E. P. 333194; abst. C. A. 1931, **25**, 566. See U. S. P. 1771553. E. P. 290327.
3. J. Chem. Ind. (Moscow), 1930, **7**, 1575; abst. C. A. 1931, **25**, 4222.
4. 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. See also E. P. 254668, 264550.
5. J. Baddiley and British Dyestuffs Corp., Ltd., U. S. P. 1757158. E. P. 287609, addn. to E. P. 283319; abst. Chem. Zentr. 1928, II, 603. Cites E. P. 19743, 1892; 4767, 4768, 11364, 23992, 1909.
6. *Ibid.* U. S. P. 1757501. E. P. 287214; abst. Chem. Zentr. 1928, I, 2997.

greenish-black shade results. For other shades[1], it is recommended to use a diazotized amino compound, *b*-naphthylamine with 2-amino-5-naphthol-7-sulfonic acid (scarlet); *p*-aminoacetanilid with 2-phenylamino-5-naphthol-7-sulfonic acid (violet); dehydrothio-*p*-toluidinesulfonic acid with 2-phenylamino-5-naphthol-7-sulfonic acid (crimson); *p*-chloraniline with 5-hydroxy-2.2′-dinaphthylamine-7-sulfonic acid (red); aniline with 2-benzoylamino-5-naphthol-7-sulfonic acid (orange); and 2-naphthylamine-6.8-disulfonic acid with 2-benzoylamino-5-naphthol-7-sulfonic acid (pink). Where the middle component is *a*-naphthylamine or *m*-amino-*p*-cresol methyl ether[2], and the end component 2-ethylamino (or amino or phenylamino)-5-naphthol-7-sulfonic acid coupled alkaline, shades of blue result. In the E. Badger & Sons Co. method of acetic anhydride production[3], anhydrous sodium acetate, sulfur chloride or sulfuryl chloride and chlorine are fed to a batch reaction chamber surrounded by a cooling jacket, the temperature preferably maintained below 10°.

In obtaining prints in natural colors in which a light-sensitive layer coated over a multi-color screen on a transparent support is printed through the support from a negative associated with a multi-color screen[4], it is recommended to print the screen on an acetyl- or nitro-cellulose support. An apparatus especially applicable to the mixing of cellulose acetate has been granted patent protection[5], comprising a jacketed vessel the inner lining of which is formed without rivet holes, joints or recesses. A molding mixture has been put forward consisting of an urea-alde-

1. J. Baddiley and British Dyestuffs Corp., Ltd., U. S. P. 1757502. E. P. 280320; abst. Chem. Zentr. 1928, I, 1334.
2. *Ibid.* U. S. P. 1757503. E. P. 287609; abst. Chem. Zentr. 1928, II, 603.
3. E. P. 333991; abst. C. A. 1931, **25**, 715; J. S. C. I. 1930, **49**, 1058-B. U. S. P. 1819563.
4. T. Baker, E. P. 337040. Cites E. P. 282980, 322454, 328336, 337041.
5. Baker Perkins, Ltd., and R. Webb, E. P. 333993; abst. Brit. Plastics, 1930, **2**, #18, 278.

hyde type of resin with acetylcellulose and wood flour as filler[1].

Dyes suitable for coloring cellulose acetate are formed by causing an aldehyde as benzaldehyde to act in presence of ammonium bisulfite on 1.4.5.8-tetra-, 1.4-, 1.5- or 1.8-di-aminoanthraquinone[2], such as 1-methylamino-, 1-phenylamino-4-amino-, 1.5-diamino-4-phenylamino-, or 1.5-diamino-5-8-diphenylamino-anthraquinone, which dye orange, red, blue or violet. Organosols of cellulose acetate are prepared[3] by combining the ester with a small proportion of cholesterin or sodium glycollate, and are recommended for artificial filament formation.

The L. Bartelstone method of laminating[4] comprises two panes of glass, an intervening sheet of celluloid, intermediate transparent films of a camphor-free acetylcellulose, the whole unified by simultaneous heat and pressure. Cellulose sulfacetates are removed from primary acetylating mixtures by the addition of dilute acetic acid containing HF and HCl as saponifying catalyst[5], in such proportion that the quantity of H. ions carried by these acids is equal to or higher than the H. ions carried by the sulfuric acid used in acetation. To facilitate their esterification[6], cellulose fibers are softened by submission to the combined vapors of acetic acid with Cl or Br. The catalyst may be HF associated with a small quantity of nitric acid[7], and the cellulose may be partially transformed into oxycellulose (which will result in the formation of a weak product),

1. Bakelite Corp., E. P. 327969; abst. Brit. Plastics, 1930, **2**, #15, 135; J. S. C. I. 1930, **49**, 677-B; Chem. Zentr. 1930, II, 1454.
2. O. Bally and P. Grossmann, U. S. P. 1777953; abst. C. A. 1930, **24**, 6030.
3. I. Barbieri de Introini, F. P. 664588; abst. Kunst. 1931, **21**, 213.
4. Can. P. 305295. F. P. 666396.
5. H. Barthelemy, F. P. 660376; abst. C. A. 1930, **24**, 238. See also F. P. 638900; abst. C. A. 1930, **23**, 513. F. P. 660377; abst. C. A. 1930, **24**, 238.
6. *Ibid.* F. P. 660393; abst. C. A. 1930, **24**, 238. F. P. 660394; abst. C. A. 1930, **24**, 238.
7. *Ibid.* F. P. 660411; abst. C. A. 1930, **24**, 238.

rise of temperature above 26° being avoided[1]. Or the cellulose may be pretreated with a small amount of nitric acid[2] which serves to facilitate formation of cellulose acetates of very low viscosity.

Containers are protected against the action of gasoline, oils, alcohols and other cellulose ester nonsolvents[3] by a coating of cellulose acetate and a formophenolic substance. In 1930 appeared a comprehensive article on the general subject of pretreatment and esterification of cellulose[4], with tables, graphs and photomicrographs. In the micro-

1. H. Barthelemy, F. P. 662265; abst. C. A. 1930, **24**, 499.
2. F. Becker, H. Heimann and A. Bayerl, U. S. P. 1780151; abst. C. A. 1931, **25**, 204; Plastics, 1931, **1**, #3, 175.
3. R. Behin, F. P. 654238; abst. C. A. 1929, **23**, 3783; Chem. Zentr. 1929, II, 500.
4. A. Bernoulli, M. Schenk and W. Hagenbuch, Helv. Chim. Acta, 1930, **13**, 534; abst. C. A. 1930, **24**, 6003; J. S. C. I. 1930, **49**, 1168-A. From a study of the swelling of cellulose in alkaline solutions, the acetylation of cellulose with acetic acid and anhydride, and the inter-relation of these, it is concluded that there are three successive stages in the acetylation, viz., $C_{24}H_{39}O_{20}Ac$, cellulose monoacetate ($C_6H_9O_5Ac$), and triacetate ($C_6H_9O_5Ac_3$). In general, however, the intermediate stages are not well-defined. In the case of viscose, the affinity for substantive dyes decreases as acetylation proceeds and disappears completely at 42-44% (as AcOH). This is also the point at which complete gelatinisation in acetic anhydride, and also the complete disappearance of swelling in water, occur. The disappearance of these properties as the triacetate stage is approached points to the need of a definite number of hydroxyl groups for their existence. The swelling of viscose in sodium hydroxide solution, determined by the direct measurement of individual threads, shows maxima at alkali concentrations of 0.5*N*, 2.75*N*, and 6*N*, that at 2.75*N* being the point of maximum swelling. By titration of the alkaline liquors after immersion of the fabric, the first two maxima were shown to correspond with the compounds of $(C_6H_{10}O_5)_4$,NaOH and $(C_6H_{10}O_5)_2$,NaOH, but no evidence of the compound corresponding with the third maximum, viz., $C_6H_{10}O_5$,NaOH (known to be formed by natural cellulose in concentrated alkali), was obtained. On the other hand, evidence of the transient formation of $(C_6H_{10}O_5)_6$,NaOH, not indicated by the swelling curve, was obtained in 0.5*N*-sodium hydroxide when the time of reaction was reduced.

Comparison of methods for the determination of the acetyl content of cellulose acetate favors the alkaline hydrolysis method of Torii as modified by Yarsley. Natural cellulose (cotton wool) does not react readily with acetic anhydride and decomposition becomes marked when heating is prolonged. Nevertheless, some triacetate is formed with acetic anhydride at 125°, the curve showing ill-defined points of inflection corresponding with $C_{24}H_{39}O_{20}Ac$ and $C_6H_9O_5Ac$; at the b. p. of the anhydride these intermediate stages are much better defined, but decomposition soon occurs. The end of the reaction at the

scopic differentiation of artificial filaments[1], acetyl silk shows very characteristic melting phenomena whereby the fibers lying one above the other blend at the point of junction. Aceto, Setilose and Celanese exhibit barrel-shaped formations arranged at practically regular intervals, blistery inclusions being observable on strongly heating or with fibers of coarser deniers. Determination of nitrogen and acetyl content of cellulose acetonitrate has been published[2].

Cotton linters may be acetylated so as to retain the

first stage when acetic acid at its b. p. is used is confirmed, as also the statement that pre-treatment of the cellulose with either 18% or 40% sodium hydroxide allows the reaction to proceed to the monoacetate stage. The effect of such pre-treatment when acetic anhydride is used as the acetylating agent is that the first stage disappears completely with the more dilute alkali, and the second also when the more concentrated alkali is used.

Viscose is slowly hydrolysed by heating with glacial acetic acid, becoming brittle and easily disintegrated, but this does not seem markedly to affect either the rate or the amount of acetylation. It reacts much more rapidly than does natural cellulose with the anhydride at 100°, and gives the triacetate, passing through the usual intermediate stages. Treatment with 2% and 10% sodium hydroxide solution increases the reactivity towards acetic anhydride to approximately the same extent as do the 18% and 40% alkaline solutions in the case of cotton; thus with the former the first, and with the latter the second, intermediate stage disappears completely. The action of acetic acid at 100° gave no maximum corresponding with the first intermediate, the reaction proceeding towards the limit of the monoacetate, this limit being unchanged by previous alkali treatment. In the presence of sufficient anhydride to combine with the water set free, esterification becomes very rapid and proceeds to the triacetate; in this case the intermediate stages are less marked, but are undoubtedly present.

The ordinary technical acetylating agents, such as mixtures of acetic acid and anhydride with zinc chloride or sulfuric acid, are unable to penetrate the viscose fiber; consequently superficial action appears to occur, and leads to the triacetate or lower esters. Further examples of the similarity of pyridine and other organic bases to sodium hydroxide in their action on cellulose are given. Technical cellulose acetate is rapidly and completely converted by acetic anhydride in pyridine solution into the triacetate. This effect is not due to the solubilising or dispersing action, since acetone is without effect.

1. Beutel & Grunsteidl, Kunst. 1930, **20**, 76; abst. Rayon Record, 1930, **4**, #9, 494.

2. W. Billing and J. Tinsley, Ind. Eng. Chem. (Anlyt. Edit.), 1930, **2**, 380; abst. C. A. 1930, **24**, 6005; J. S. C. I. 1931, **50**, 241-B; Cellulose, 1930, **1**, #11, 292.

fibrous structure[1] by means of a reaction mixture comprising acetic acid and anhydride, ethyl acetate and sulfur dioxide, the latter being allowed to evaporate during esterification whereby a cooling effect is induced. Maintenance of uniform temperature is assured by the application of reduced pressure. Acetic anhydride may be prepared by submitting acetic acid to pyrogenetic decomposition in the presence of a catalyst presenting an incomplete development of its surface, e.g., a gel or silicon or aluminum oxides. The porosity of the catalytic surface may be reduced by the action of ammonia or HCl, or by heating it to a temperature at which it begins to agglutinate[2]. Aliphatic anhydrides are also obtainable by a similar action of the corresponding fatty acids or their salts on *a-a'*-dichlordiethyl ether, acetic anhydride and propionic anhydride resulting using zinc chloride or stannous chloride as catalyst[3]. Fuming sulfuric acid (oleum) or sulfur trioxide may be employed[4]. C. Boyce[5] has described a method for finishing photographic prints mechanically. He employs a coating composition of acetylcellulose associated with gelatin.

H. Brandenburger has described the properties of various dyes and methods of applying them to acetylcellulose[6], with tables showing the dyeing constants and the absorption maxima of various classes of dyes, and a classification of various procedures for delustering viscose, cuprammonium and acetate filaments[7], including a determina-

1. C. Boehringer & Soehne, E. P. 312242. Belg. P. 371220.
2. *Ibid.* F. P. 696154; abst. C. A. 1931, **25**, 2739; Chem. Zentr. 1931, I, 2535. Belg. P. 371637. E. P. 362462.
3. *Ibid.* F. P. 696530; abst. C. A. 1931, **25**, 2739; Chem. Zentr. 1931, I, 2535. E. P. 352176; abst. J. S. C. I. 1931, **50**, 1040-B. Belg. P. 370835, 377006.
4. H. Bohme, A.-G., Belg. P. 376547. Ital. P. 262755.
5. U. S. P. 1725699. Re-issue 18192.
6. Jentgen's Rayon Review, 1930, **2**, #2, 78, 122, 186, 209, 251; abst. C. A. 1930, **24**, 5501; 1931, **25**, 209. Kunsteide, 1930, **12**, 140, 173, 223, 267, 305; abst. C. A. 1930, **24**, 5501; 1931, **25**, 209; 1931, **25**, 1677; J. S. C. I. 1931, **50**, 291-B. Chem. Zentr. 1930, II, 1777. Rayon and The Rayon Journal, 1930, **10**, #12, 10.
7. H. Brandenburger, Kunstseide, 1930, **12**, 102; Jentgen's Rayon Rev. 1930, **2**, 189; abst. C. A. 1930, **24**, 2504.

tion of causes of the streaky dyeing[1]. Acetic acid of high percentage is extracted directly from mixtures of acetylcellulose and acetic acid by neutralizing the sulfuric acid, heating the mixture, and pulverizing in a closed chamber, the acetic acid being removed by hot air or gas[2]. It has been stated that viscose is slightly more resistant to the effects of heat and sunlight than acetylcellulose silk[3].

Yarns, fabrics, threads and films of acetylcellulose[4] are saponifiable by combined treatment with ammonium or barium hydroxides in the presence of a swelling agent as methyl or ethyl alcohols, or saponifier and swelling agent may be combined by the use of sodium or potassium alcoholates. Low viscosity acetylcellulose which has all the desirable properties of the high-viscosity esters and in addition is compatible with natural or synthetic resins[5] are obtained by esterifying at not above 50-55°, and ripening the ester to a stage between solubility in hot chloroform and very slight plasticity therein, the mixture at the same time being soluble in a mixture of hot alcohol and benzene without addition of water.

Purified cellulose materials are more readily[6] esterified if they are treated (a) first with organic anhydrides (acetic anhydride), either alone or mixed with a liquid hydrocarbon, or in vapor form alone or mixed with an inert diluent, and then with an organic acid with or without anhydride (e.g., acetic acid and acetic anhydride), or (b) first with one or more organic acids (e.g., formic or acetic), alone or mixed with inert diluents, and then with one or

1. H. Brandenburger, Rayon and Rayon J., 1930, **11**, #4, 10.

2. K. Bratring and E. Roth-Schmidt, F. P. 689733; abst. C. A. 1931, **25**, 971; Chem. Zentr. 1931, I, 686. Belg. P. 367679.

3. B. Brechenridge, R. Edgar and K. Crance, J. Home Econ., 1930, **22**, 39; abst. C. A. 1930, **24**, 1987.

4. Brit. Celanese, Ltd., E. P. 313404. Cites E. P. 125153.

5. *Ibid.* E. P. 326515; abst. C. A. 1930, **24**, 4931; J. S. C. I. 1930, **49**, 858-B; Brit. Plastics, 1930, **2**, #17, 100. Cites E. P. 300140; abst. J. S. C. I. 1930, **49**, 655-B.

6. *Ibid.* E. P. 332607; abst. C. A. 1931, **25**, 414; J. S. C. I. 1930, **49**, 900-B.

more organic anhydrides, without or with organic acids, a condensing agent being present in each case, if desired.

Or[1], the cellulosic materials are first treated with one or more organic acids alone or mixed with inert diluents and then with one or more organic anhydrides with or without organic acids. The organic acids may be employed in liquids or vapor form either alone or mixed with inert substances, for example air or carbon dioxide in the case of employing the acid in vapor form, or benzene in the case of employing the organic acid in liquid form. After the pretreatment with organic acids the latter may be wholly or partly removed, for example by passing air or other inert gas through the material.

In treating knitted fabrics comprising cellulose acetate[2], a shrinking agent as nitric acid is applied to the fabric, and reduces tendency to develop such faults as laddering, running or splitting, while reducing to some extent the luster. Splinterless glass is producible by incorporating at least 40% by weight of dibutyl or diethyl tartrates with the acetylcellulose used to sandwich the sheets of glass together[3]. Ponsol blue to neutralize the yellow cast of the sheet is recommended. If a toluenesulfonamide-aldehyde condensate is further condensed with a toluenesulfonamide and an addition of 5-10% urea, the products of reaction are stated to be especially applicable for lacquer formation when added to acetylcellulose[4]. An aldehyde may be employed instead of urea[5].

In preparing acetic acid and methyl acetate[6], methyl alcohol, with phosphoric acid as catalyst, is subjected to

1. Brit. Celanese, Ltd., E. P. 332608; abst. C. A. 1931, **25**, 414; J. S. C. I. 1930, **49**, 900-B.
2. *Ibid.* E. P. 335139; abst. C. A. 1931, **25**, 1393; J. S. C. I. 1930, **49**, 1105-B.
3. *Ibid.* E. P. 335878; abst. C. A. 1931, **25**, 1963; Brit. Plastics, 1931, **3**, #26, 82. Compare E. P. 296675, 299065.
4. *Ibid.* E. P. 338002; abst. C. A. 1931, **25**, 2312.
5. *Ibid.* E. P. 338024, addn. to 338002; abst. C. A. 1931, **25**, 2313.
6. Brit. Celanese, Ltd., and W. Bader, E. P. 337053; abst. C. A. 1931, **25**, 1843; abst. Chem. Zentr. 1931, I, 685.

the action of CO at 200-450° at pressures up to 300 atm. Fabrics have been described containing both shrunk and unshrunk yarns of cellulose acetate[1], so that on treating them with nitric acid or other shrinking agent, crepe, semi-crepe, pebble or other ornamental effects may be produced while the fabric is capable of being dyed a level shade. In the preparation of threads and ribbons[2], uniform saponification of the cellulose acetate is effected by carrying out the treatment continuously with the formation of the threads by coagulation in 50-55% aqueous diacetone alcohol and then passing directly into 2.5% caustic alkali, the saponification being only partial. The acetylcellulose solution is preferably spun from a nozzle comprising a line of extrusion orifices, while a collector device, having a shape appropriate to that of the spinning nozzle substantially constrains the whole of the evaporative medium to pass through the immediate vicinity of the orifices[3].

In coloration of union goods and mixed fabrics[4], the cellulosic content in fibers containing also cellulose acetate is mordanted with tannin and tartar emetic under such conditions as to leave the esters unmolested, the amount of mordant used being arranged so that basic colors are taken up equally by both constituents of the fabric. If the acetate silk is impregnated with amines followed by diazotization and development with a coupling agent[5], resist or discharge effects are obtained by local application of chlorates, chromates, sulfoxylates or hyposulfites which pre-

1. 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. Cf. E. P. 274584.

2. 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, 203092, 300998, 304674, 312203.

3. British Celanese, Ltd., H. Dreyfus, E. Kinsella, J. Bower and W. Taylor, E. P. 326232; abst. C. A. 1930, **24**, 4392; J. S. C. I. 1930, **49**, 456-B.

4. British Celanese, Ltd., and G. Ellis, E. P. 323180; abst. C. A. 1930, **24**, 3118; J. S. C. I. 1930, **49**, 370-B; Chem. Zentr. 1930, I, 3244.

5. 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.

vent diazotization of the fiber. For colored discharge effects a dye which resists the particular discharge color applied is added, e.g., for acetate silk, acetylated aminoanthraquinones. Examples, acetate silk is padded with 5-nitro-*o*-anisidine, printed with sodium chlorate, diazotized and coupled with 2.3-hydroxynaphthoic acid for a white pattern on a pink ground; or padded with anisidine, printed with Durinodone red Y, alkali, anthraquinone, hyposulfite, and Formosul, steamed, diazotized, and developed with 2.3-hydroxynaphthoic acid for a red pattern on a navy-blue ground. Oxidation catalysts such as salts of iron, copper or vanadium may be used instead of chlorates[1].

An excellent wetting and dispersive agent for use in dyeing acetate silk with insoluble dyes[2] is obtained with naphthalene condensed with a natural resin and sulfonated. Acetic acid is formed from a mixture of CO and the vapor of methyl alcohol, by passing through a heat exchanger into a reaction chamber containing phosphoric acid as catalyst[3], or when formaldehyde or its condensation products with aliphatic alcohols, as formal[4], together with CO is heated to 200-450° under 100 atm. or more pressure, the reaction being facilitated by the presence of water and a suitable catalyst. Crude 2.4.6-tribromaniline is sublimed at 160-165° and then diacetylated to give colorless, noninflammable products with acetylcellulose[5], and when employed in amounts up to 10% produces practically no discoloration, and shows no indication of freezing out at temperatures below 0°.

1. Brit. Celanese, Ltd., G. Ellis and W. Miller, E. P. 324683; abst. C. A. 1930, **24**, 3910; J. S. C. I. 1930, **49**, 458-B; Chem. Zentr. 1930, I, 3727.
2. British Celanese, Ltd., G. Ellis, H. Olpin and E. Kirk, E. P. 323788; abst. C. A. 1930, **24**, 3332; J. S. C. I. 1930, **49**, 362-B; Chem. Zentr. 1930, I, 2634.
3. British Celanese, Ltd., S. Green and R. Handley, E. P. 334189; abst. C. A. 1931, **25**, 971; Chem. Zentr. 1930, II, 3461. Cites E. P. 283989.
4. *Ibid.* E. P. 334207; abst. C. A. 1931, **25**, 970; J. S. C. I. 1930, **49**, 1058-B; Chem. Zentr. 1930, II, 3461.
5. British Celanese, Ltd., and B. Miller, E. P. 334217; abst. C. A. 1931, **25**, 973; J. S. C. I. 1930, **49**, 1058-B.

A process has been described for the simulation of wool in appearance with acetylcellulose[1], by subjecting filaments of the latter to a blast of air to produce a fibrous mass which is teased or combed to render the filaments unidirectional, torn or cut to staple lengths and then spun in a manner similar to wool or cotton. If it is desired to produce flattened or ribbon-like products[2], a solvent or softening agent is applied to acetate filaments to render them sticky, then subjecting to pressure. The treatment of acetate filaments, yarns and threads in a continous manner by means of suitable rotary, oscillatory or reciprocatory devices has been patented[3], and a vacuum treatment process for removing residual solvent from freshly spun acetylcellulose filaments[4].

In order to reduce the luster of articles such as stockings made of cellulose acetate[5], abrasive material is rubbed over their surface. Pattern effects may be produced by localized application of the abrasive material. Kieselguhr, pumice, powdered glass, corundum or emery are suitable. An insulation for electric wires and cables has been described[6] formed of layers of acetylcellulose applied under approximately atmospheric pressure with textile supporting layers, the latter being impregnated by the application of sufficient heat to soften the acetate; or[7], a wrapping of esterified cellulose containing a plastifier enclosed in tape or lead sheath, is heated at about 100°, so that the layers of wrapping unite to form a homogeneous coating. A suit-

1. British Celanese, Ltd., and W. Taylor, E. P. 323209; abst. C. A. 1930, **24**, 3120; J. S. C. I. 1930, **49**, 236-B.
2. *Ibid.* E. P. 328312; abst. C. A. 1930, **24**, 5497; J. S. C. I. 1930, **49**, 554-B.
3. *Ibid.* E. P. 332290; abst. C. A. 1931, **25**, 216; J. S. C. I. 1930, **49**, 1025-B. Cites E. P. 325823.
4. *Ibid.* E. P. 332527; abst. C. A. 1931, **25**, 421; Chem. Zentr. 1931, I, 1700.
5. British Celanese, Ltd., W. Taylor and C. Dreyfus, E. P. 335204; abst. C. A. 1931, **25**, 1393. Compare E. P. 328247.
6. British Insulated Cables, Ltd., and F. Brislee, E. P. 330552; abst. C. A. 1930, **24**, 5899; J. S. C. I. 1930, **49**, 775-B.
7. *Ibid.* E. P. 337052; abst. J. S. C. I. 1931, **50**, 70-B; Brit. Plastics, 1931, **2**, #21, 432.

able composition is cellulose acetate 10, ethyltoluenesulfonamide 5, toluenesulfonanilide 3 and tolyl phosphate 3.

An account of osmotic pressure measurements of acetylcellulose in acetone, acetophenone and benzyl alcohol by the method of van Campen has been given[1], which depends on measuring the velocity with which the solvent diffuses through the semipermeable membrane against an applied pressure and extrapolating for zero velocity. Various samples which have different viscosities give the same value for the molecular weight, so that there is no connection between the latter and the viscosity. Ethylidene diacetate and vinyl acetate are formed when mercuric oxide dissolved in acetic acid is added to sulfur trioxide and excess of acetylene passed through[2]. In the concentration of acetic acid[3], the dilute acid in a ternary mixture with sulfuric acid and water where the composition at the boiling point in the vapor phase is greater than the concentration of the acetic acid-water component of the liquid phase is distilled by constantly supplying concentrated sulfuric acid and removing vapors of acetic acid. J. Calladine has given details of the preparation of acetate fabrics and their proper dyeing treatment[4].

The rate of the simultaneous hydrolysis and alcoholysis of acetic anhydride by binary mixtures of water with methyl and ethyl alcohols has been determined at 25%[5]. With increase in amount of alcohol, the unimolecular velocity coefficient of hydrolysis decreases continuously, but that of alcoholysis first rises and then falls, the maximum being attained with a solvent containing about 40% by volume of alcohol. In the casting of acetate films by flowing or

1. E. Buechner and P. Samwel, Proc. Akad. Wetensch. Amsterdam, 1930, **33**, 749; abst. J. S. C. I. 1931, **50**, 35-A.
2. Canadian Electro Products Co., Ltd., F. Skirrow and G. Morrison, E. P. 335223, addn. to 308169; abst. Chem. Zentr. 1931, I, 156. Compare E. P. 308170.
3. Canadian Industries, Ltd., Can. P. 305657.
4. Russa, 1930, **5**, 1871; abst. C. A. 1931, **25**, 1677.
5. J. Caudri, Rec. Trav. Chim., 1930, **49**, 1; abst. J. S. C. I. 1930, **49**, 300-A. See also Rec. Trav. Chim. 1929, **48**, 422; abst. J. S. C. I. 1929, **48**, 655-A.

extrusion[1], it is advocated to maintain the cellulose acetate at an elevated temperature, and in the preparation of solutions to employ *unpolymerized*[2] or but partially polymerized vinyl compounds[3].

Treatment of cellulose triacetate with boiling 5% methyl alcohol solution of HCl results in a dissolution of a portion of the material in the formation of *a*-methylglucoside[4]. Reacetylation of the insoluble fraction which has suffered considerable deacetylation yields a triacetate, indicating the insoluble portion has suffered progressive and far-reaching hydrolytic degradation. P. Chaumeton and V. Yarsley in a series of papers with copious bibliographic references[5] have discussed the function of sulfuric acid in cellulose acetation, the hydrolysis of ripening, the varying solubility of the product, precipitation of the acetate and British Engineering Association standards to which the products should conform.

The flexibility and strength of threads of artificial silk are increased by treatment with sulfuric acid compounds of oils, fats and fatty acids[6], being applied after spinning. Unmercerized cotton and other vegetable fibers may be superficially acetylated to modify the dyeing properties[7], acetylation being carried out at above 25° C. with a relatively small proportion of catalyst (zinc chloride). Or[8], the cotton may be modified by acetylating in a bath containing reduced proportions of acetic anhydride, even down to those theoretically necessary for producing mono- and di-acetate.

1. Celluloid Corp., Can. P. 300132.
2. *Ibid.* Can. P. 300775. 3. *Ibid.* Can. P. 300776.
4. J. Chalmers and J. Earl, J. Proc. Roy. Soc. N. S. Wales, 1930, **63**, 155; abst. C. A. 1930, **24**, 6002; J. S. C. I. 1930, **49**, 1415-A.
5. British Plastics, 1930, **1**, 316, 356, 445, 464; 1930, **2**, 38, 74, 128, 177, 271, 290.
6. Chemische Fabrik Stockhausen et Cie, E. P. 317951; abst. J. S. C. I. 1929, **48**, 893-B; Chem. Zentr. 1930, I, 3378. E. P. 293480, 293717.
7. Chemische Fabrik vorm. Sandoz, E. P. 323500; abst. C. A. 1930, **24**, 3119; J. S. C. I. 1930, **49**, 280-B; Chem. Zentr. 1930, II, 1165.
8. *Ibid.* E. P. 323515; abst. C. A. 1930, **24**, 3119; J. S. C. I. 1930, **49**, 280-B; Chem. Zentr. 1930, II, 1165. Mentions E. P. 280493.

Threads of a softer feel are thus produced than where larger amounts of anhydride are employed. The acetylating bath should be kept in motion to ensure uniform esterification. Or[1], the cotton may first be impregnated with acetic anhydride which considerably augments its esterification reactivity and then acetylated with a reduced amount of anhydride in presence of $ZnCl_2$.

Dyed effects threads, fast to cross-dyeing are obtained by subjecting cellulose to acetylating treatment as indicated in the foregoing paragraph[2], azo, polyazo, stilbene, sulfur or vat series of dyes which are fast to acids and insoluble in acetic acid being used. If the superficial acetylating of cellulose is carried to the point where the affinity of the fibers for substantive dyestuffs is completely removed but the fibrous structure of the cellulose apparently has been unaltered[3], differential dyeings are possible in weaving such fibers without those of acetylcellulose prepared in the usual manner.

S. Cherbov[4] has determined that the degree of association of acetic acid in solution depends both upon the nature of the other component and the temperature. E. Clayton has postulated a theory of dyeing acetate silk[5], finding that picramic acid dyes to a reddish-brown shade which may be oxidized to black by means of sodium dichromate or to brownish-black by diazotization and coupling with *m*-tolylenediamine. From the behavior of picramic acid, picric acid, and 2-aminoanthraquinone towards cellulose acetate silk it is concluded that the dyeing process is one of absorption (adsorption may play a small part) followed almost instantaneously by dissolution of the

1. Chemische Fabrik vorm. Sandoz, E. P. 323548; abst. C. A. 1930, **24**, 3119; J. S. C. I. 1930, **49**, 280-B; Chem. Zentr. 1930, II, 1165. E. P. 323500, 323515.
2. *Ibid.* E. P. 324680; addn. to 280493; abst. C. A. 1930, **24**, 3911; J. S. C. I. 1930, **49**, 458-B; Chem. Zentr. 1930, I, 3726. See also E. P. 314913, 323500.
3. *Ibid.* Can. P. 297070.
4. J. Russ. Phys. Chem. Soc. 1930, **62**, 1509; abst. C. A. 1931, **25**, 2630; J. S. C. I. 1931, **50**, 40-A.
5. E. Clayton, J. Soc. Dyers and Col., 1930, **46**, 367; abst. C. A. 1931, **25**, 1087; J. S. C. I. 1931, **50**, 155-B.

particles of the dye in the silk fiber. A true solution (in alcohol) of 2-aminoanthraquinone gives a shade on the silk which is 4-5 times as deep as that obtained with a suspension of equivalent concentration in the usual Turkey-red oil solution, but the dye may be removed by repeated extraction with alcohol or benzene in which the silk is not soluble. Dyed cellulose acetate is not an adsorption complex, since if a hot solution of cellulose acetate in acetone is colored (dyed) with 2-aminoanthraquinone and then poured into excess of water the dye does not separate from the precipitated cellulose, whereas if poured into benzene (a solvent which precipitates cellulose acetate) a considerable proportion of the dye passes into the benzene. Any advances in the efficiency of dyeing methods applicable to cellulose acetate silk will probably depend on the ability to produce dyes which besides being soluble in cellulose acetate are either soluble in water or easily dispersed in an aqueous medium to give exceedingly fine suspensions.

As a material for window glazing and other similar purposes[1], there has been patented a cellulose acetate sheet interposed between sheets of "Vita" glass, the whole being permeable to ultra-violet rays. In separating acetic and butyric acids from mixed aqueous solution[2], the acids are converted into salts, evaporated to dryness, and distilled with concentrated sulfuric acid to obtain the respective acids in substantially anhydrous condition. Formic, acetic, oxalic and succinic acids obtained by the alkali fustion of cellulose (sawdust)[3] are recovered by extracting the fusion products with approximately 75% by weight of aqueous methyl alcohol, and separating the components by methods given in the original patent. Acetic and butyric acids may also be separated in a similar manner[4].

1. M. Colefax, E. P. 323671; abst. C. A. 1930, **24**, 3095; J. S. C. I. 1930, **49**, 240-B; Brit. Plastics, 1930, **1**, #11, 498.

2. Commercial Solvents Corp., Can. P. 296404.

3. L. Swallen and Commercial Solvents Corp., Can. P. 302784; abst. C. A. 1930, **24**, 4522.

4. Commercial Solvents Corp., Can. P. 306960, 306961.

Phonograph records have been described[1] obtained by condensing resorcin and furfural, and combining this synthetic resin with acetylcellulose, wood flour being added. Anthraquinone derivatives which dye acetylcellulose are prepared by the reaction of aminohydroxyanthraquinone sulfonates (as diaminoanthrarufin, diaminochrysazine) with either an aldehyde or its substitutes in the presence of hypsoulfite compounds[2]. Thus, sodium diaminoanthrarufin-2.6-disulfonate is dissolved in water, benzene and sodium tetrathionate added, and the mixture heated. Cellulose acetate is dyed blue. R. Cottrell in 1930 reviewed the modern trends in scouring, bleaching, dyeing, delustering, weighting and iron-proofing of acetate yarn[3].

In the acetylation of cellulose[4], it is advised to add to the bath such substances as formic or oxalic acids which are capable of splitting up into CO_2 and water in the presence of sulfuric acid. Multi-ply glass sheets are formed by attaching one or more glass sheets coated with nitrocellulose enamel to a cellulose acetate film by means of diacetone alcohol, acetone oil or other harmonious solvent for both esters[5]. The J. Cumner phonograph record is formed by cementing top and bottom layers of acetylcellulose to an inner layer of pulp board by use of a composition containing amyl acetate and "overproof" methylated spirit[6]. Diethyleneglycol monoethyl ether has been advocated as

1. Compagnie Francaise pour l'Exploitation des Procedes Thomson-Houston, F. P. 680022; abst. Kunst. 1931, **21**, 18; Chem. Zentr. 1930, II, 1016.

2. Etablissements Kuhlmann, F. P. 692927; abst. C. A. 1931, **25**, 1679.

3. Textile World, 1930, **78**, 2247; abst. C. A. 1931, **25**, 598.

4. H. Courtois, F. P. 666342; abst. C. A. 1930, **24**, 1508; Chem. Zentr. 1930, II, 1167. Cellulose, 1930, **1**, #4, 126. D. R. P. 534366; abst. C. A. 1932, **26**, 843.

5. 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.

6. E. P. 324352: abst. C. A. 1930, **24**, 3333.

a useful cellulose ester plasticizer[1]. M. Deschiens[2] has explained determination of solubility of acetylcellulose in ternary mixtures graphically by means of triangular co-ordinates. As plasticizers for cellulose esters[3] have been described esters of partially hydrated naphthalene or hydronaphthols.

In the preparation of acetone-soluble acetylcellulose[4], it is claimed the introduction of sulfuric acid as catalyst in portions decreases the quantity of sulfuric acid in combination in the finished ester, thereby increasing its heat-resisting properties. Reactions conducted at slowly rising temperatures from 5° to not higher than 20° with 36 hrs. ripening at 22-23° produces an ester of 40-48 viscosity (according to Ostwald at 15°), while at 22-25° with a rise to 40° in the last 3-4 hrs. and the same ripening, produce viscosity of 5-8; viscosity of 2-4 being produced by a ripening temperature of 30-33°. The peptisation and coagulation of cellulose acetate and nitrate depend on the concentration, dispersing medium, temperature and the degree of ester depolymerization[5]. Acetylcellulose may be purified by fractional precipitation of their solutions[6], water being added to a solution of the ester in a mixture of methyl or ethyl alcohols and benzene.

The properties of cellulose acetate textiles may be enhanced by treating them with a dispersion of rubber latex and preferably in conjunction with a water-insoluble pigment as zinc oxide or graphite[7]. In order to increase receptivity for acetylation, it is advised to heat the cellulose

1. J. Davidson, U. S. P. 1770153; abst. Brit. Plastics, 1931, **3**, #25, 37. Cf. U. S. P. 1633927.
2. Rev. gen. mat. Plastiques, 1930, **6**, 387; abst. C. A. 1930, **24**, 6005.
3. Deutsche Hydrierwerke Akt-Ges., D. R. P. 513771; abst. Nitrocellulose, 1931, **2**, #10, 206.
4. G. Dmitrieva and N. Yasinskii, J. Chem. Ind. (Moscow), 1930, **7**, 375; abst. C. A. 1931, **25**, 4700; J. S. C. I. 1932, **51**, 16-B.
5. A. Dreiberg, J. Appl. Chem., Russia, 1930, **3**, 915; abst. J. S. C. I. 1931, **50**, 479-B.
6. C. Dreyfus, F. P. 689134; abst. C. A. 1931, **25**, 1081.
7. *Ibid.* F. P. 690406; abst. C. A. 1931, **25**, 1103; Chem. Zentr. 1931, I, 712.

with a lower fatty acid under high vacuum, before the esterizing components are brought in contact with the cellulose[1]. Or[2], the cellulose may be improved from an esterification viewpoint by treating with alkaline liquids at —10° (10% NaOH is specified), then acetating in the usual manner.

A series of nine patents was granted C. Dreyfus in Canada in 1930. Mixed fabric containing acetylcellulose is heated with an acid-containing material to the point of incipient carbonization in order to obtain differential dyeing effects after removal of the carbonized portion[3], or treating the fabric with a solution of basic metallic acetate then subjecting the fabric to printing[4]. In order to increase the homogeneity of plastic compositions, it is recommended to finely pulverize cellulose acetate[5], then adding plasticizer thereto at an elevated temperature.

In producing acetate yarns resistant to the delustering action of boiling water[6], the cellulose acetate is dissolved in a mixed solvent in such concentration that delustering action is nonexistent. A novel method of printing on acetate fabrics consists in treating the fabric with an excess of 50% aqueous acetone, and applying the fabric under pressure to a transfer sheet containing a design of a dye that is capable of coloring the ester[7], then evaporating the acetone therefrom to permanently fix the dye. The production of a cellulose acetate having a fusing point of about 260° has been described[8], from which plastic sheets may be fabricated by forming a plurality of layers of heavy acetylcellulose, and retarding the evaporation of solvent therefrom until complete coalescence has taken place[9].

1. C. Dreyfus and G. Schneider, U. S. P. 1783184; abst. C. A. 1931, **25**, 414; Plastics, 1931, **7**, #4, 233; Cellulose, 1930, **1**, #11, 294.
2. C. Dreyfus, Can. P. 296540. F. P. 694879; abst. C. A. 1931, **25**, 1993; Chem. Zentr. 1931, I, 1385.
3. *Ibid.* Can. P. 296741.
4. *Ibid.* Can. P. 297376.
5. *Ibid.* Can. P. 297377.
6. *Ibid.* Can. P. 297853.
7. *Ibid.* Can. P. 298341; abst. C. A. 1930, **24**, 2898.
8. *Ibid.* Can. P. 299650.
9. *Ibid.* Can. P. 300448. F. P. 695371; abst. C. A. 1931, **25**, 2862.

The solvents recommended are diacetin, triacetin, dibutyl tartrate or tritolyl phosphate. Best plastics are said to result[1] when the acetylcellulose has a viscosity above 200°.

In permanently pleating fabrics containing thermoplastic acetylcellulose[2], the fabric is treated with 25% aqueous acetone and submitted to a pleating operation, evaporating the solvent while mechanically protecting the pleats. Phenyl toluenesulfonate with triphenyl phosphate has been put forward as a desirable acetylcellulose plasticizer[3]. By combining a synthetic resin with cellulose acetate in small proportions, it is claimed the tensile strength of the cellulose acetate is considerably augmented[4].

A fabric containing cellulose acetate yarns may be partially saponified by immersion in a bath containing hydroxyl ions corresponding in concentration to that of an aqueous solution of about 0.5% NaOH at about 80°, the bath also containing a large amount of NaCl. Saponification is continued until not exceeding 11% of acetic acid has been removed[5]. In weighting acetyl cellulose[6], the material is first treated with a swelling solution and then with a metallic salt as a weighting agent, afterwards fixing the salt in an insoluble form. Novel effects are said to be obtained in cellulose filament formation by extruding the solution through the orifices in the form of a figure having indentations therein[7]. In the production of heavy filaments, such as artificial bristles or straw[8], a solution of acetyl cellulose in volatile solvents is extruded into a precipitating medium, the concentration of the solution being so heavy that it is relatively non-flowable.

In the formation of metallic screens[9], there is applied to wire a coating composition of acetyl cellulose containing

1. C. Dreyfus, Can. P. 300869. 2. *Ibid.* Can. P. 302423.
3. G. Schneider and C. Dreyfus, Can. P. 302648; abst. C. A. 1930, **24**, 4597.
4. C. Dreyfus, Can. P. 302650.
5. C. Dreyfus, Can. P. 302878; abst. C. A. 1930, **24**, 4631. H. Platt and C. Dreyfus, Can. P. 302879; abst. C. A. 1930, **24**, 4631.
6. C. Dreyfus, Can. P. 304293. 8. *Ibid.* Can. P. 306830.
7. *Ibid.* Can. P. 304450. 9. *Ibid.* Can. P. 307035.

a sufficiency of a phenol aldehyde resin to close the meshes thereof, and then applying the final coating composition of cellulose acetate. Wood surfaces may be filled and coated by first applying a primer of filler containing a non-drying oil at least partially compatible with cellulose acetate and then applying acetyl cellulose lacquers in one or more coats. Cocoanut oil is advocated as a suitable filler[1]. Adhesion is said to be increased by incorporating in the filler coating, an acetyl cellulose plastifier[2]. Cellulose acetate fiber may be fireproofed[3], by immersion in an aqueous solution containing approximately 100% orthophosphoric acid at 40° for 15 minutes.

A nearly theoretical yield of acetic anhydride is obtained by decomposing acetic acid at 350-700° in the presence of a catalyst deposited or spread on an asbestos support[4]; acetic acid being produced by admixing the vapor of formaldehyde with carbon dioxide or submitting the same to the action of heat to 100-200 kg. at a temperature of 300-400°, inorganic acids being the preferred catalyst[5]. Or[6], acetic anhydride may be produced by passing the vapor of aliphatic acids, particularly, acetic acid, in contact with the heated mass of copper. For the formation of ethyl alcohol[7], methyl alcohol vapor in the presence of a catalyst is combined with alkali or alkyl earth metals such as oxides, hydroxides and alcoholates of sodium, barium, potassium and calcium, preferably at a temperature range of 400-600°.

Aliphatic anhydrides as acetic anhydride are made by heating the vapor of the corresponding acid in contact with

1. C. Dreyfus, Can. P. 307036. 2. *Ibid.* Can. P. 307037.
3. H. Platt and C. Dreyfus, Can. P. 307239; abst. C. A. 1931, **25**, 830.
4. H. Dreyfus, F. P. 695969; abst. C. A. 1931, **25**, 2738. Ital. P. 270704. Can. P. 297693.
5. *Ibid.* F. P. 692735; abst. C. A. 1931, **25**, 1538.
6. *Ibid.* E. P. 334533; abst. C. A. 1931, **25**, 971; J. S. C. I. 1930, **49**, 1142-B. F. P. 692537; abst. C. A. 1931, **25**, p. 1538.
7. *Ibid.* E. P. 335631; abst. C. A. 1931, **25**, 1538.

a catalyst supported upon or mixed with asbestos[1], the acetic acid vapor being rapidly passed through a copper tube at 400-500° containing calcium tungstate, the anhydride formed being separated by fractional distillation. Instead of a tungstate, calcium, magnesium, sodium or potassium arsenates or antimoniates may be employed[2]. In the extraction of acetic acid from dilute solutions[3] by means of a solvent medium, a larger percentage of recovery is attained if the operation is conducted in two stages. In the first, 50-70% strength acetic acid is obtained, and in the second, glacial acid results.

If acetic acid in vapor form is subjected to a mixture of 1-10 parts CO relative to the acid employed, at a temperature of 250-700°, a nearly theoretical yield is obtained[4]. A range of 300-600° is preferred[5]. To produce methoxyacetic anhydride[6], Na. K. Ca. or Mg. methoxyacetates are brought into reaction with a compound of chlorine and sulfur, and subjecting the anhydride formed to purification from sulfur compounds. In acetic anhydride formation[7], acetic acid in the vapor phase is brought into contact with concentrated hydrochloric acid. Or[8], the acid may be transformed into anhydride in the presence of zinc or aluminum phosphates or tungstates in the presence of free carbon (lampblack, sugar charcoal), or granulated pumice, kieselguhr or carborundum[9]. Silica gel has also been recommended as a suitable catalyst[10], or the reaction may

1. H. Dreyfus, E. P. 336668; abst. C. A. 1931, **25**, 2156; J. S. C. I. 1931, **50**, 148-B. Can. P. 297861. Ital. P. 270613.
2. *Ibid.* E. P. 336960; abst. C. A. 1931, **25**, 1843; J. S. C. I. 1931, **50**, 148-B. F. P. 693483; abst. C. A. 1931, **25**, 1538; Chem. Zentr. 1931, I, 1008. Can. P. 297862; C. A. 1930, **24**, 1869. Ital. P. 270602. See also F. addn. 36811, 37087 to 634167. F. addn. 36747 to 656901.
3. *Ibid.* Ital. P. 271470. Can. P. 297866.
4. *Ibid.* Ital. P. 271751. Can. P. 305319.
5. *Ibid.* Ital. P. 277656. Can. P. 305318.
6. *Ibid.* Ital. P. 277906. Can. P. 305322.
7. *Ibid.* Ital. P. 278040. Can. P. 305323.
8. *Ibid.* Ital. P. 278041. Can. P. 305324.
9. *Ibid.* Ital. P. 278539. Can. P. 305539.
10. *Ibid.* F. P. 700569; abst. C. A. 1931, **25**, 3670. See F. P. 695969. Can. P. 305540.

be performed in presence of any of the following bases or salts: ammonia, alkylammonium bases, tetra-alkylammonium bases, pyridine, picoline, quinoline, piperidine, aniline, alkylaniline, cyclohexylamine, or the chloride, phosphate or sulfate of these bases[1].

H. Dreyfus extracts dilute acetic acid with ether[2], then adds benzene to the extract to remove water as a dilute acetic acid solution, the latter in concentrated condition being prepared by the action of CO on methyl alcohol in the presence of metallic catalysts of mol. wt. between 50-60 (i.e. Fe., Mn., V., Cr., Co. or Ni.)[3]. If the temperature is maintained between 280-320°, inappreciable amounts of ketones are formed[4].

The ripening of cellulose acetate may be carried out in an organic medium in which the primary acetate is insoluble[5], and in which the ripening agent, e.g. water, is soluble in sufficient quantity for ripening to satisfactorily take place. A suitable medium is ether, which may be used as a diluent in the acetylation process itself, except that its boiling point (35°) is too low for economical working. If the cellulose is pretreated with formic or acetic acids[6], followed by esterification in suspension in organic media containing a non-solvent for the cellulose ester (acetate, propionate, butyrate) but which is soluble in or miscible with water, as ether, methyl acetate, ethyl acetate or acetone, highly stable cellulose esters result. Or the cellulose may be pretreated with a tertiary base as methylpiperi-

1. H. Dreyfus, Can. P. 306858.

2. *Ibid.* F. P. 699828; abst. C. A. 1931, **25**, 3360. E. P. 338187; C. A. 1931, **25**, 2155; J. S. C. I. 1931, **50**, 237-B; Chem. Zentr. 1931, I, 1008.

3. *Ibid.* F. P. 699933; abst. C. A. 1931, **25**, 3360.

4. *Ibid.* F. P. 700568; abst. C. A. 1931, **25**, 3669.

5. *Ibid.* E. P. 325224; abst. C. A. 1930, **24**, 4156; J. S. C. I. 1930, **49**, 414-B; Rayon Record, 1930, **4**, #8, 441; Chem. Zentr. 1930, II, 2333. Ital. P. 276390. Compare E. P. 320842.

6. *Ibid.* E. P. 325231; abst. C. A. 1930, **24**, 4156; J. S. C. I. 1930, **49**, 414-B; Chem. Zentr. 1930, II, 2333. Ital. P. 276675.

dine or dimethyl-*n*-hexylamine[1], and then esterified in the usual manner.

In producing threads and films from acetylcellulose solutions[2], it is advised to carry out the coagulation under such conditions that the product emerges from the precipitating bath in a plastic state, which is effected by setting in a bath of acetylcellulose swelling agent of high concentration. If it is desired to introduce a wetting agent as Turkey red oil in the acetylcellulose, the former is made a component of the setting bath[3]. The filament or film may be toughened by following the usual coagulating bath with one containing 30-50% sulfuric acid[4], sulfoacetic acid[5], or methyl- or ethyl-sulfonic acids[6].

Oxygenated organic compounds as acetaldehyde, acetic acid and ethyl alcohol[7] are produced by contacting methane with steam at 200-500° and up to 500 atm. pressure. As catalysts, Zn., Mg., Ca., Al., Cr., Mn., V., W., Ti., Fe., Co. or Ni. phosphates, borates or silicates are recommended. Cellulose is rendered more easily esterified by treating with HCl, HBr or HI or by their ferric, stannic, manganese, nickel or cobalt salts, the amount of acid added being less than 30% of the weight of the cellulose[8].

Ribbons and artificial straw of flat cross section are made by submitting a series of acetylcellulose filaments in

1. H. Dreyfus, E. P. 325822; abst. C.A. 1930, **24**, 4156; J.S.C.I. 1930, **49**, 504-B. Ital. P. 271862, 273955, 278348. Belg. P. 371218.
2. *Ibid.* F. P. 683463; abst. C. A. 1930, **24**, 4632. F. Addn. 37857 to 683463; abst. C. A. 1931, **25**, 4707. F. Addn. 38175 to 683463; abst. C. A. 1931, **25**, 5559. See F. P. 694048, 694119.
3. *Ibid.* F. P. 688625; abst. C. A. 1931, **25**, 1084.
4. *Ibid.* F. P. 690772; abst. C. A. 1931, **25**, 1380. See F. P. 36751 Addn. to 531816.
5. *Ibid.* F. P. 692796; abst. C. A. 1931, **25**, 1686; Chem. Zentr. 1931, I, 2289.
6. *Ibid.* F. P. 693240; abst. C. A. 1931, **25**, 1686; Chem. Zentr. 1931, I, 2289. See F. P. 697896; abst. C. A. 1931, **25**, 3011.
7. *Ibid.* E. P. 337410; abst. C. A. 1931, **25**, 2152; Chem. Zentr. 1931, I, 1357. F. P. 698094; abst. C. A. 1931, **25**, 3011. Compare E. P. 337014, 337409.
8. *Ibid.* F. P. 699888; abst. C. A. 1931, **25**, 3481. See also F. P. 660623 and Addn. 36175; 664674, F. Addn. of July 26, 1930; 666896.

a thermoplastic condition to the action of sufficient heat and pressure to provoke union by incipient fusion[1], a ureoid base as alkyl urea being added as antacid and stabilizer[2]. If it is desired to form twisted threads[3], especially crepe threads, acetylcellulose yarn is drawn off from a rotating yarn package, the yarn in leaving the package passing in a balloon-shaped path to a light floating member surrounding the driving spindle of the yarn package, and permitting the yarn to rotate about the axis of the spindle.

In the weighting and mordanting of acetylcellulose[4], absorption of the metallic radicle is improved by simultaneously treating with zinc chloride, and to produce shades fast to light and washing[5], the acetate silk may be treated with *b*-oxynaphthoic arylide in the free state in form of a dispersion and then diazotized in the usual manner. As a plasticizing component[6], the application of an aqueous solution of a ureoid base has received patent protection.

In inducing differential effects on a pile fabric wherein the pile filaments are acetylcellulose and the back of other material[7], there is applied a softening and weakening agent in selected areas, the weakened pile filaments being afterwards mechanically removed. Acetic acid results from subjecting acetaldehyde vapor to temperatures of 250-700°, preferably at a temperature between 250-550, and fractionating off the acid[8]. Or[9], by submitting methyl alcohol to the action of CO in the presence of a copper salt as catalyst. Acetylcellulose may be simultaneously weighted and softened[10], by mordanting the ester with a metallic radicle and subquently converting into a metallic soap (aluminum palmitate or oleate). The acetylcellulose

1. H. Dreyfus, F. P. 701269; abst. C. A. 1931, **25**, 3833.
2. *Ibid.* Can. P. 296775.
3. *Ibid.* Can. P. 297858.
4. *Ibid.* Can. P. 297863.
5. *Ibid.* Can. P. 297864.
6. *Ibid.* Can. P. 301998.
7. *Ibid.* Can. P. 303274.
8. *Ibid.* Can. P. 305317. See Can. P. 305536, 305537.
9. *Ibid.* Can. P. 305541.
10. *Ibid.* Can. P. 305544, 306857, 307038, 307040.

may be dyed by applying thereto a 2-nitro-4-chlor (or brom)-methyl (or ethoxy or methoxy or acetylamino)-diphenylamine[1].

It is claimed that the peptization and coagulation of nitro- and acetyl-cellulose depends on concentration, dispersing medium, degree of depolymerization and temperature of the cellulose ester[2]. G. Druce[3] reviewed our knowledge in 1930 of cellulose palmitate, stearate, oleate, laurate, oxalate, benzoate, nitro- and amino-benzoate and L. Dufay the same year[4] described a mosaic screen for color photography comprising an apparatus for treating a long strip of dyed acetylcellulose sheet, having a resist pattern printed thereon for the production of two-color screens. An apparatus has been evolved for the continuous acetylation of cellulose[5], in which the latter is progressively passed through a narrow circular apparatus with temperature regulating means and of stirring members, the tube being vertical and fixed. Both acetaldehyde and acetic anhydride may be formed by submitting ethylidene diacetate in the presence of a halogen compound, bringing the vapors into contact with a compound which reacts with the halogen to remove the same[6].

A dressing for leather is formed of high viscosity cellulose acetate 1.7, dibutyl phthalate 0.8, carnauba wax 1.7, titanium dioxide 3.3, ethyl acetate 15.5, butyl acetate 10.3, and alcohol 66.7, so heavily flowable as to preferably spread by means of a spatula or doctor blade[7]. If it is desired to partially or wholly discharge dyed spun or woven acetylcellulose threads[8], treatment with a substance in heated condition having high adsorbing properties as charcoal,

1. H. Dreyfus, Can. P. 307039.
2. A. Drinberg, Zhur. Prikladnoi Khim, 1930, **3**, 915; abst. C. A. 1931, **25**, 1376; Chem. Zentr. 1931, I, 1696.
3. Rayon Record, 1930, **4**, #16, 841.
4. U. S. P. 1760048. E. P. 322454. F. P. 667412.
5. E. I. du Pont de Nemours and Co., Can. P. 296663.
6. *Ibid.* Can. P. 302999.
7. *Ibid.* F. P. 696523; abst. C. A. 1931, **25**, 2875; Chem. Zentr. 1931, I, 2153.
8. Du Pont Rayon Co., Can. P. 303000.

has received patent recognizance. If the product is dull in appearance[1], the luster may be restored by wetting the material and hot calendering at 125-170° at 0.1-0.5 kgm. per sq. cm. for 1.3 seconds. The threads may be preferably sized by submission to the combined action of a swelling agent and swelling material to obtain optimum penetration[2]. A solution of gelatin in acetic acid is specified.

In the decoration of toilet articles[3], one side of a diaphanous acetylcellulose sheet is decorated and then united to a second sheet so that the decoration is imprisoned between the two sheets, a relatively small amount of high boiler plasticizer being used as a cementing material. If the film is intended for wrapping purposes in the wetted condition to take advantage of a high contractility[4], as for encasing bottle stoppers, swelling agents are used in the absence of plastifying bodies. A. Eichengruen[5] has described a patented method by which acetylcellulose powder is compacted by high pressure and heat, the process being modified by prior swelling of the fibers, in which state they readily absorb plasticizers. No formulas given. An apparatus has been described for decomposing sawdust in an aqueous pulp to form acetic acid[6], in which the pulp is maintained in circulation under superatmospheric pressure (50-100 atm.) for 2 hrs. at about 300°, decomposition resulting in the formation of acetic acid, methyl alcohol, acetone and tarry products.

A process for acetate silk manufacture was described in 1930 wherein boron compounds as boric acid or borax are added to the spinning solution in combination with fats,

1. Du Pont Rayon Co., Can. P. 304199.
2. *Ibid.* Can. P. 304200; abst. C. A. 1930, **24**, 5511.
3. Du Pont Viscoloid Co., E. P. 323473; abst. Brit. Plastics, 1930, **1**, #11, 498.
4. J. Eggert, J. Soc. Dyers Col., 1930, **46**, 92.
5. Zeits. ang. Chem. 1930, **43**, 236; Cellulose, 1930, **1**, #9, 231; abst. C. A. 1930, **24**, 3641.
6. E. Erlenbach, U. S. P. 1764249; abst. C. A. 1930, **24**, 3898. D. R. P. 490401; abst. Chem. Zentr. 1930, I, 2200.

free fatty acids, alcohols or glucose[1], it being claimed that the desirable physical constants in the finished filament are thereby considerably augmented. W. Fermazin[2] has detailed carefully worked out methods for evaluating cellulose acetate, including the acetyl content, water absorption, viscosity, and solubility. The water absorption, which is dependent upon the acetyl content, is approximately inversely proportional to the wet strength, and the viscosity directly proportional to the tearing strength. G. von Frank and W. Caro have described various cellulose oxalic esters[3], and cellulose cinnamates[4].

1. Fabrique de Soie Artificielle de Tomaszow, F. P. 690795; abst. C. A. 1931, **25**, 1380; Chem. Zentr. 1931, I, 1699.

2. Chem. Ztg., 1930, **54**, 605; abst. C. A. 1930, **24**, 6005; J. S. C. I. 1930, **49**, 943-B; Rayon Record, 1930, **4**, #19, 1011; J. Soc. Dyers &Col., 1930, **46**, 389; Brit. Plastics, 1930, **2**, #18, 118 .

3. Ber. 1930, **63B**, 1532; abst. C. A. 1930, **24**, 4270; British Plastics, 1930, **2**, #17, 229. Cellulose is esterified by oxalic ester chlorides in pyridine with ease (in certain cases at little above room temperature), to soluble products which, from their method of preparation and composition are mixed cellulose alcohol oxalates corresponding, in the case of the triesters, to the general formula $C_6H_7O_5(COCO_2R)_3$. In this manner were obtained from ethyl, allyl, *iso*-amyl, cyclohexyl, menthyl and cetyl chlorides, products which are all easily soluble, but little degraded, and intermediate between a di- and triester. Comparison of their properties showed that their density increases with increasing molecular weight of the alcohol radical R, their solubility increases in non-polar and decreases in polar solvents, their softening point decreases, the plasticity of the film increases and its tearing strength increases. Viscosity determinations did not give definite results. Attempts to prepare free cellulose-oxalic acids by cautious saponification of these esters resulted in simultaneous splitting off of the cellulose residue. Cyclohexyl-, octyl-, menthyl-, cetyl- and *p*-nitrobenzyl-oxalyl chlorides were prepared and their properties described, and ethyl-, allyl-, *iso*-amyl, cyclohexyl-, menthyl- and cetyl-cellulose oxalates detailed. The *iso*-amyl compound is most readily prepared and shows the widest solubilities, but is difficult to purify. The solubilities, especially in mixed solvents, agree with the Highfield rules for the solubility of nitrocellulose. Except for the ethyl compound, they are all stable towards boiling water and hot 1.5% acetic acid, but rapidly hydrolyzed by hot sodium carbonate or soap solutions. After saponification, stretched films of the *iso*-amyl compound showed the Roentgen diagram of mercerized cellulose, but cellulose regenerated from oxalic esters which, unlike the *iso*-amyl compound, maintained the fiber structure during esterification, showed only a partial mercerization effect.

4. G. v. Frank and H. Mendrzyk, Ber. 1930, **63B**, 875; abst. C. A. 1930, **24**, 3763; J. S. C. I. 1930, **49**, 750-A. Cellulose tricinnamate obtained in 90% yield from 1 mol. nitrated paper heated 7 hrs.

In a resume of the uses of ethylene dichloride in lacquer formation[1], determinations of the solubility of nitrocellulose and cellulose acetate in various three-component solvent mixtures (one component being ethylene dichloride), show that a mixture of the dichloride (70-80%) and alcohol (30-20%) has the highest solvent power for the latter ester, the dichloride being exceptionally stable in lacquers, showing no tendency toward hydrolysis. Metallized films have been described in which a film-forming surface prepared by coating a metal drum or band with an acetylcellulose plastic composition[2], has applied over it by spraying, finely divided metal powder. Various suitable compositions are given. In the preparation of films for wrapping purposes[3], a metal film is formed or placed between layers of acetylcellulose or similar dielectric material and compacted by heat and pressure. A review of the manufacture and properties of cellulose acetate varnishes was published[4] in 1930.

In the production of acetated cellulose[5], after esterification in the usual way, the reaction mixture is poured into ethyl ether and the precipitated ester and acetylation mixture recovered by fractional distillation of the mother liquor. Cellulose acetonitrates containing 9.6-4.8% N and 20.6-41.2% acetyl[6] are obtained by acetylating nitrocel-

at 100-120° with 6 mols. pyridine and 8 mols. cinnamyl chloride in nitrobenzene, has the appearance of paper, is slightly yellowish, is wetted by boiling water only on addition of alcohol, sinters at 180°, and becomes transparent at 200°, does not decompose at 270°, swells in carbon tetrachloride, forms brittle films when a pyridine solution is evaporated. Gives with bromine in chloroform, cellulose tris(dibromhydro)cinnamate. A cellulose dicinnamate has been prepared.

1. R. Frazier and E. Reid, Ind. Eng. Chem., 1930, **22**, 604; abst. J. S. C. I. 1930, **49**, 726-B.
2. G. Frenkel, E. P. 332254; abst. C. A. 1931, **25**, 178; Chem. Zentr. 1930, II, 2721.
3. *Ibid.* E. P. 332256; abst. C. A. 1931, **25**, 178; Chem. Zentr. 1930, II, 2721.
4. J. Frydlender, Rev. prod. chim. 1930, **33**, 225, 257, 289, 321; abst. C. A. 1930, **24**, 6038; Chem. Zentr. 1930, II, 1145.
5. H. Gardner, U. S. P. 1764204; abst. C. A. 1930, **24**, 3901; J. S. C. I. 1930, **49**, 1146-B.
6. H. Gardner and C. Knauss, U. S. P. 1786989; abst. C. A. 1931, **25**, 812; J. S. C. I. 1931, **50**, 877-B; Plastics, 1931, **7**, #4, 236.

lulose containing one or more unsubstituted OH groups and about 11% N. The acetylated product is then precipitated with dichlorethane and excess acetic acid recovered by distillation. Cellulose acetonitrates thus obtained are soluble in acetone and most of the usual solvents, give solutions of low viscosity and excellent film forming properties and are of low flammability. A discussion of the composition, properties and durability of pigmented and non-pigmented cellulose ester airplane varnishes was published by H. Gardner[1], while C. Glaser[2] described metallized film formation involving the employment of acetylcellulose in conjunction with synthetic resins.

In the preparation of "proofed cloth" for use as printer's blankets[3], a woolen cloth or moleskin is impregnated with an acetylcellulose solution admixed with plasticizer and castor oil with a pigment as carbon black or iron oxide, each coat being partially dried by being passed through steam heated friction rollers before the next coat is applied. In forming multicolor screens upon an acetylcellulose support[4], a greasy resist containing a dye is applied as by printing, to the surface of the film in a series of parallel lines or in a geometrical pattern, the dye migrating from the resist into the surface of the film so that after removal of the resist by a solvent, a pattern remains on the film. The manufacture and properties of acetylcellulose Crepe de Chines have been detailed by F. Grove-Palmer[5], and the

1. Proc. Am. Soc. Testing Materials, 1930, Reprint No. 33, 37; abst. C. A. 1931, **25**, 1690; J. S. C. I. 1930, **49**, 779-B; Brit. Plastics, 1930, **2**, #17, 101.

2. C. Glaser, F. P. Addn. 37009 to 628734; abst. Chem. Zentr. 1931, II, 2950. F. P. 628734; abst. Chem. Zentr. 1928, I, 609.

3. C. Goddard, E. P. 325034; abst. C. A. 1930, **24**, 3912; J. S. C. I. 1930, **49**, 370-B; Chem. Zentr. 1930, II, 3876.

4. J. Goldsmith and Spicers, Ltd., E. P., 334243; abst, C. A. 1931, **25**, 886; Chem. Zentr. 1930, II, 3891.

5. Rayon and Rayon Journal, 1930, **10**, #10, 55, #11, 16, 1930, **11**, #3, 18; abst. C. A. 1930, **24**, 5504. Silk J. and Rayon World, 1930, **6**, #67, 61; **6**, #68, 47; abst. C. A. 1930, **24**, 2607.

laundry care in dyeing acetate fabrics[1], especially with light-fast colors[2].

Acetaldehyde may be prepared by passing methane and CO through an electric field produced by electric currents of high frequency and tension[3], contact substances being placed in the field. Rayons (regenerated cellulose) may be differentiated from acetate silk by means of National Erie Black GXOO, which dyes the former black and the latter yellow or orange[4]. It is claimed[5] that the rigidity, creasability, luster and dyeing properties of acetylcellulose and viscose fibers are correlated with the parallelism of their micelle chains and the effect on these of stretching. Resistance to creasing with acetylcellulose rapidly decreases with increased stretching, while rigidity increases. Curves show that acetyl fibers gradually lose their power of recovering to the original length as the degree of stretching increases, while retention of luster when immersed in a stretched condition in boiling water is ascribed to the effect of the stretching in maintaining the cellulose acetate micelle chains parallel. Greater parallelism of micelle chains confers increased rigidity and creasability.

The effects of progressive saponification (with barium hydroxide)[6] on the properties of cellulose acetate, saponification to the extent of removal of 4-10% acetyl raises the fusing point from 200-201° to 222-230°, a 4% saponification preventing acetate yarn from becoming woolly when immersed in boiling liquors, but it is only by saponifying to the extent of 68% that the fibers become neither woolly nor opaque, still retaining the original luster when immersed

1. Textile Colorist, 1930, **52**, 245; abst. C. A. 1930, **24**, 4935; Chem. Zentr. 1930, II, 816.
2. Silk. J. 1930, **23**, #1, 54; abst. C. A. 1931, **25**, 5772.
3. Gutehoffnungshutte Oberhauser Akt.-Ges., F. P. 694382; abst. C. A. 1931, **25**, 1844. E. P. 353455; abst. J. S. C. I. 1931, **50**, 1132-B.
4. A. Gyzander, Dyestuffs, 1930, **31**, 1; abst. C. A. 1931, **25**, 2854.
5. A. Hall, J. Soc. Dyers and Col., 1930, **46**, 257; abst. J. S. C. I. 1930, **49**, 1023-B. Compare J. Soc. Dyers and Col. ,1929, **54**, 98.
6. *Ibid.* Rayon Record, 1930, **4**, #7, 390.

for 15 minutes in boiling soap solution. About a 15% saponification with an accompanying 6% loss in weight is necessary to give cellulose acetate a satisfactory affinity for cotton dyes, the saponified acetate not appreciably suffering in respect to softness and retaining its original resistance to creasing. With progressive saponification the natural moisture content steadily increases up to about 10.5%, from which it appears that limited saponification does not diminish the normal valuable properties of acetylcellulose[1]. A. Hall[2] has pointed out the defects and remedies for laundering and ironing cellulose acetate fabrics, due to the fact that the normal fusing point of acetylcellulose is about 200°. He also describes methods for aniline-black dyeing[3].

In coating electrical conductors with fibrous materials according to the E. Hall process[4], the material is subjected to the action of an acetylcellulose varnish and a liquid as water which is a non-solvent for the coating substance but is readily absorbed by the fibrous material being treated so as to form a superficial coating on the material. An apparatus has been described[5] for carrying the process into effect. Tentative standards of the American Association of Testing Materials were set in 1926 at 6.5% regain for cellulose acetate[6], work in 1930 at the Mass. Institute of Technology giving the figure, 6.4%.

Wire gauze or netting (see p. 678, n. 5) may be coated or filled with acetylcellulose containing 1-2% of rubber, paraffin or paraffin oil[7], an outer coating of an air- and

1. A. Hall, Rayon Record, 1930, **4**, #13, 703, 801; abst. C. A. 1930, **24**, 4936.
2. *Ibid.* Rayon Record, 1930, **4**, #25, 1299. Compare E. P. 304596, 313404, 317936.
3. *Ibid.* Silk J., 1930, **7**, #77, 37, #78, 33; abst. C. A. 1931, **25**, 1677. See also A. Hall, Silk J., 1930, **7**, #76, 39.
4. U. S. P. 1764624; abst. C. A. 1930, **24**, 4175. Cites U. S. P. 1615416.
5. E. Hall, U. S. P. 1764625; abst. C. A. 1930, **24**, 4175. Cites U. S. P. 1615416.
6. G. Haven, Rayon, 1930, **10**, #12, 24; abst. C. A. 1930, **24**, 6027.
7. E. Haver, E. P. 335775; abst. C. A. 1931, **25**, 1692.

water-proof material as wax, fat or resin being applied dissolved in a volatile solvent having a softening action on the underlying coating. Formulas are given. In fireproofing cellulose esters[1], sodium or tin tungstates have been recommended. Cellulose butyrate may readily be prepared by first feebly formylating cellulose[2], then esterifying with butyric anhydride and zinc chloride, afterwards partially saponifying.

K. Hess[3] has determined freezing point curves for acetone-soluble acetylcellulose, glucose penta-acetate, amylose acetate, inulin acetate and biosan acetate, his results, especially in respect to the latter compound, being called in question[4]. It appears[5] that if either fibrous cellulose triacetate I or the crystalline triacetate II is dissolved in pyridine and the solution evaporated at different temperatures, the products give identical X-ray diagrams between approximately 35° and 75°. This behaviour is also observed with other solvents, but the temperatures vary. The transformation of triacetate I into triacetate II is therefore reversible and is characterised by an equilibrium which depends on temperature and solvent. By the acetylation of ramie fibers, whether mercerised or not, fibrous bundles of either triacetate, or mixtures of both can be obtained, the nature of the product depending on the temperature of acetylation, triacetate I preponderating at low temperatures and triacetate II at high. Since, by hydrolysis, triacetate I gives natural cellulose and triacetate II cellulose hydrate, the two celluloses can also be changed reversibly into one another through their acetates, the extent, under similar

1. A. Hay, Rayon Record, 1930, **4**, 431; abst. C. A. 1930, **24**, 3376.
2. R. Herzog and G. Frank, F. P. 700165; abst. C. A. 1931, **25**, 3481.
3. Ber. 1930, **63B**, 618; abst. C. A. 1930, **24**, 2360.
4. K. Freudenberg and E. Bruch, Ber. 1930, **63B**, 535.
5. K. Hess, C. Trogus, W. Ostwald and K. Dziengel, Z. physik. Chem., 1930, **7-B**, 1; abst. C. A. 1930, **24**, 2877; J. S. C. I. 1930, **49**, 750-A. C. Trogus, K. Hess and J. Katz, Z. physik. Chem., 1930, **7**, B, 17; abst. C. A. 1930, **24**, 2877. See also C. Trogus and K. Hess, Zts. phys. Chem. 1929, **4B**, 321; **5B**, 161; abst. J. S. C. I. 1929, **48**, 1222.

conditions of hydrolysis, depending on the position of equilibrium of the two acetates. The influence of variations in the conditions of hydrolysis on the composition of the product is unknown.

iso-Propylideneglyceryl acetate has been described[1] of possible value as a cellulose ester softener.

Acetic acid may be made by the continuous oxidation of acetaldehyde by means of oxygen[2], at a temperature of 60-75°, the 0 being kept considerably in excess of the amount theoretically necessary. In the manufacture of lacquers and plastic masses of acetylcellulose containing rubber (see p. 86, n. 5; 128, n. 5; 232, n. 2; 254, n. 6; 538, n. 5; 665, n. 5) use is made, as common solvents of acrylic acid esters, methyl oleate or butyl cinnamate[3]. In the pretreatment of cellulose[4], a water-miscible organic liquid (glacial acetic acid) is forced through a cake of moist cellulose; the acetic acid may then be expelled under pressure by means of a liquid as benzene, which is miscible with acetic acid but immiscible with water.

When a mixture of acetylene and steam is passed over a catalytic mass free from water of hydration comprising aluminum oxide activated by one or more dehydrogenating catalyst as cadmium or zinc oxide, sulfide, chromate, tungstate or molybdate, acetaldehyde in nearly theoretical yield is obtained if the temperature range[5] is kept at 150-200°. Zinc selenide or phosphide[6] are stated to be especially applicable as catalysts in the above process. Acetic acid vapor passed over boron phosphate as catalyst at temperature of 400-700°, especially in conjunction with an alkali metal

1. H. Hibbert and J. Morazain, Can. J. Research, 1930, **2**, #1, 35.
2. Holzverkohlungs-Ind. A.-G., F. P. 687789; abst. C. A. 1931, **25**, 714; Chem. Zentr. 1930, II, 3848.
3. A. Hügel & I. G. Farbenindustrie, D. R. P. 483002; abst. C. A. 1932, **26**, 1078.
4. E. Hubert, A. Roest-Grande and E. Correns, U. S. P. 1752596; abst. C. A. 1930, **24**, 2599; J. S. C. I. 1930, **49**, 900-B.
5. I. G. Farbenind. A.-G., E. P. 332635; abst. C. A. 1931, **25**, 304; J. S. C. I. 1930, **49**, 980-B; Chem. Zentr. 1930, II, 2572. Cf. E. P. 329867.
6. *Ibid.* E. P. 329867; abst. C. A. 1930, **24**, 5768; J. S. C. I. 1930, **49**, 807-B.

phosphate yields acetic anhydride. When a deposit of carbon forms, the catalyst is regenerated by ignition in air[1]. Glacial acetic acid results from the dilute acid[2] when the latter is preliminarily concentrated to the eutectic point by freezing, freeing the ice crystals from acid, and distilling.

Cellulose acetonitrates are formed by nitrating a partially acetylated cellulose[3] under such conditions that about a cellulose monoacetyl-dinitrate forms, which is the mixed ester of maximum stability coupled with minimum inflammability. The ester may be stabilized, as likewise acetylcellulose[4], by heating for 3 hrs. with 0.025% sulfuric acid at 85-90°. Methylene or ethylene chlorides may be used as solvent in the manufacture of cellulose aliphatic esters[5], 0.5% sulfuric acid being sufficient as catalyst. The alkylene chloride assists the concentration of the dilute acetic or other acid when wet precipitation is employed. For mixed esters, one acid and another anhydride may be used in the desired proportions, no excess of acid being needed for solvent purposes[6]. Or[7], the ester may be prepared by adding liquid sulfur dioxide to the esterizing bath. Acetylcellulose is also formed by introducing cellulose at a temperature range of 80-100° into a mixture containing an indifferent medium (chlorbenzene, pyridine, quinoline) and an addition of acetyl chloride and an organic base, then raising the temperature to 110-115°[8].

The acetylation of wood as beech, aspen, fir or pine[9] is effected with the corresponding anhydride in the absence

1. I. G. Farbenindustrie, A.-G., E. P. 330537; abst. C. A. 1930, **24**, 5768; J. S. C. I. 1930, **49**, 855-B; Chem. Zentr. 1930, I, 1770. F. P. 698907; abst. C. A. 1931, **25**, 3361. Belg. P. 371859.
2. *Ibid.* Can. P. 297468; Belg. P. 374228.
3. *Ibid.* Belg. P. 375245. 4. *Ibid.* Swiss P. 139515.
5. *Ibid.* E. P. 337366; abst. C. A. 1931, **25**, 2288; J. S. C. I. 1931, **50**, 197-B. Belg. P. 372104.
6. *Ibid.* Can. P. 305458; Belg. P. 371607.
7. *Ibid.* Can. P. 306973.
8. *Ibid.* Can. P. 306968. Belg. P. 370932. I. G. Farbenindustrie, Akt.-Ges, M. Hagedorn, P. Moeller, Can. P. 304219. In this connection, see Can. P. 306326.
9. *Ibid.* E. P. 336969; abst. C. A. 1931, **25**, 1996; Brit. Plastics, 1931, **2**, #23, 530. Can. P .298014.

of inorganic catalysts, the wood being either in fine powder or sheet form, and should previously be dewaxed and deresinified. The esterified wood gives but a faint color reaction with phloroglucinol and HCl, and may be converted into a plastic mass by pressure at 100°. If the wood be previously treated with 8-14% sulfuric, hydrochloric or phosphoric acids, the swollen mass no longer is fibrous, and the acetated wood passes into solution in the esterizing bath[1].

Cellulose acetobutyrate filaments stable to boiling, soaping and alkali result when 0.5 molecule of butyric acid with a small amount of acetic acid is added to the solution before spinning[2], and acetonitrates[3] by acetylating cellulose between 50-100° by means of acetic acid and anhydride in the presence of a small amount of sulfuric acid as catalyst together with a salt of nitric acid and urea nitrate. In producing cellulose acetobutyrate or butyropropionate or starch acetobutyrate[4], carbohydrates are esterified with the calculated amount of fatty anhydride to form the triacetyl compound in combination with a fatty acid different from that of the anhydride used, in the presence or not of catalysts and diluents. By using the chlorides of higher fatty acids, such as the chloride of cocoanut oil acid, stearyl or lauryl chlorides on the unaltered carbohydrates in the presence of tertiary bases as pyridine in amount less than equivalent to the amount of halide present (see p. 200, n. 6; 232, n. 8; 648, n. 6)[5], cellulose and starch laurates, stearates, myristates, palmitates and oleates result.

Mixed cellulose esters may also be formed by the action of saturated and unsaturated fatty acid chlorides on cellu-

1. I. G. Farbenindustrie, A.-G., E. P. 337791; abst. C. A. 1931, **25**, 2289; Chem. Zentr. 1931, I, 1994; J. S. C. I. 1931, **50**, 59-B; Brit. Plastics, 1931, **2**, #21, 433.
2. I. G. Farbenindustrie, Akt.-Ges., Can. P. 300573. F. P. 687627; abst. C. A. 1931, **25**, 813; Chem. Zentr. 1931, I, 2289.
3. *Ibid.* Can. P. 302804.
4. *Ibid.* F. P. 691031; abst. C. A. 1931, **25**, 1260. See F. P. 668686.
5. *Ibid.* F. P. 699217; abst. C. A. 1931, **25**, 3482. Compare F. P. 691031.

lose which has previously been partially esterified as with nitric or acetic acids[1]. The reaction preferably takes place in the presence of pyridine. Example, cellulose dinitrate in pyridine is treated with lauryl chloride, giving a 80-90% yield of cellulose laurodinitrate (laurodinitrocellulose). Cellulose palmitoacetate or palmitonitrate may be similarly formed. If it is desired to produce a cellulose ester soluble in benzene, toluene or xylene[2], a similar method of procedure permits the formation of such bodies as cellulose lauronaphthenate (see p. 200, n. 6). A desirable plastic is formed when cellulose laurate is incorporated with benzene and monochlorbenzene and resin as dammar[3], fillers as talc and lithopone being added if desired.

Acetate silk may be dyed by treatment in an aqueous medium with non-acidylated aminoanthraquinones[4], or their feebly basic substitution products, which do not dye natural fibers, as 1.4-diaminoanthraquinone (bluish-violet), 1.7-di- (red), 1.2.4-tri- (reddish-violet), and 1.4.5.8-tetraaminoanthraquinone (blue). Spools for textile fibers may be, with advantage[5], coated with cellulose oleate, stearate, palmitate or margarate. Hollow threads are made by dissolving acetyl cellulose in one or more solvents[6], adding nonsolvents, the boiling points of which are higher than the solvent portion, heating the spinning solution and spinning into a gaseous medium, the temperature of which is lower than the b. pt. of the nonsolvents. Acetone, benzene and toluene are suitable.

1. I. G. Farbenindustrie, A.-G., D. R. P. 483999; abst. C. A. 1930, **24**, 961; Chem. Zentr. 1930, I, 146.

2. I. G. Farbenindustrie Akt.-Ges., M. Hagedorn, G. Hingst, Can. P. 304212.

3. M. Hagedorn and I. G. Farbenindustrie, Akt-Ges., E. P. 326952; abst. C. A. 1930, **24**, 4932; J. S. C. I. 1930, **49**, 457-B; Chem. Zentr. 1931, I, 1859. Can. P. 304211.

4. I. G. Farbenindustrie, A.-G., K. Meyer, H. Hopff and A. Guenther, D. R. P. 489344; abst. C. A. 1930, **24**, 2309; Chem. Zentr., 1930, I, 2316.

5. I. G. Farbenindustrie, A.-G., D. R. P. 487011; abst. C. A. 1930, **24**, 1228.

6. *Ibid.* F. P. 697329; abst. C. A. 1931, **25**, 5168.

Mottled effects may be produced by dyeing acetyl silk with a dye that is decomposed by chlorates[1], then printing with a composition containing a chlorate and a dye stable to chlorates. The oxazin dyestuffs are suitable. Acetate silk articles are shaped by treatment with swelling agents as formic or acetic acids or ethyl acetate, and then drying in the desired shape[2]. If it is desired to produce surface designs[3], there is incorporated in the surface of the acetylcellulose products which are capable of changing under the influence of light, the physical or chemical properties of the ester, exposing the layers to light under a negative, and rendering the image visible by appropriate treatment. Emollients and gelatinizers for acetylcellulose have been patented[4] comprising trialkyl phosphates, the alkyl groups of which are different.

Electric insulating materials have been patented comprising mixed cellulose esters of fatty acids of low molecular weight (cellulose aceto-butyrate, monoaceto-dipropionate), readily soluble in acetone[5]. Plastics of acetylcellulose may also be produced by combining the ester with a plastifying agent composed of the monoalkyl or monoaryl esters of phosphoric acid[6], as dimethyl-(or ethyl or propyl) glycolbutylglycol phosphate. Shaped articles of cellulose esters of the higher fatty acids are best formed by subjecting them to a rolling operation before the shaping treatment[7], or dissolving in an alkylene oxide as a swelling agent[8], then adding a solvent and shaping. Monosod-

1. I. G. Farbenindustrie, A.-G., and A. Fischesser, D. R. P. 485266; abst. C. A. 1930, **24**, 974; Chem. Zentr. 1930, I, 897.
2. I. G. Farbenindustrie, A.-G., F. P. 699256; abst. C. A .1931, **25**, 3498.
3. *Ibid.* F. P. 689007; abst. C. A. 1931, **25**, 887; Chem. Zentr. 1930, II, 3891.
4. *Ibid.* F. P. 700680; abst. C. A. 1931, **25**, 3832. See Can. P. 297081, 297082.
5. *Ibid.* F. P. 687702; abst. C. A. 1931, **25**, 754; Chem. Zentr. 1931, I, 1954. See Can. P. 297083.
6. *Ibid.* Belg. P. 369299. F. P. 693496; abst. C. A. 1931, **25**, 1672.
7. *Ibid.* Can. P. 301676. See Can. P. 305459.
8. I. G. Farbenindustrie, A.-G., and M. Hagedorn. Can. P. 304220.

ium sulfopalmitate has been patented as an acetylcellulose softener[1]. A method for the preparation of asymmetric dichlorethylene has been patented[2].

In dyeing acetate silk[3], the ester is colored blue or black by treatment with dyes of the type (4) $H_2NRN:NR'-NX_2(4)'$, where R is phenyl group, R' a phenyl or naphthyl group and X an aliphatic group, diazotizing and developing with 2-hydroxynaphthalene-3-carboxylic acid. Desulfonated aminonaphthaphenazine[4] may be used for dyeing acetylcellulose. If it is desired to both dye and print[5], diazo compounds are coupled with quinolines, both being free from sulfonic and carboxylic groups, e.g., with dyes formed from *m*-nitroaniline or *p*-aminodimethylaniline and *N*-methyl-4-hydroxy-2-quinoline, or from *p*-chloraniline and 6-chlor-*N*-ethyl-4-hydroxy-2-quinoline. Or acetyl silk may be dyed black with white or colored effects[6] by impregnating the fiber with aminodiphenylamine either before or during treatment with the resist. The diphenyl black may be developed by steaming. Thus, undyed fiber is treated with a white resist containing a thickener, sodium sulfoxylate-formaldehyde and sodium acetate. After printing and drying it is treated with aminodiphenylamine.

Dyes suitable for coloring acetylcellulose, wool or silk (depending upon the substituents present in the components)[7] are formed by coupling a base as *m*-aminobenzene-2-sulfonic acid methylphenyl amide or the *o*-tolylamide with a pyrazolone as 1-(4'-sulfophenyl)-3-methyl-5-pyrazolone.

1. I. G. Farbenindustrie, A.-G., Belg. P. 369053. E. P. 330904; abst. J. S. C. I. 1930, **49**, 895-B; Chem. Zentr. 1930, II, 2050.
2. *Ibid.* Belg. P. 373749.
3. *Ibid.* F. P. 696026; abst. C. A. 1931, **25**, 2859; Chem. Zentr. 1931, I, 2270.
4. *Ibid.* E. P. 328291; abst. J. S. C. I. 1930, **49**, 757-B; Chem. Zentr. 1930, II, 2311.
5. *Ibid.* E. P. 327394; abst. C. A. 1930, **24**, 5166; J. S. C. I. 1930, **49**, 610-B; Chem. Zentr. 1930, II, 2309.
6. I. G. Farbenind., A.-G., and A. Fischesser, D. R. P. 508562; abst. C. A. 1931, **25**, 826. Compare F. P. Addn. 36398 to 666507.
7. I. G. Farbenind., A.-G., E. P. 325229; abst. C. A. 1930, **24**, 4167. F. P. 660576; abst. Chem. Zentr. 1930, I, 133.

In order to produce acetate silk of high stability to boiling[1] an acetone-soluble secondary cellulose acetate of 54-56% acetic acid content is used, and which on heating with 70% alcohol does not dissolve or does so incompletely. In acetylating cellulose with the use of sulfuric acid and zinc chloride as catalysts[2] production of an ester giving turbid solutions is prevented by adding to the mixture a little HCl or a substance yielding it.

Difficultly soluble cellulose esters of the higher fatty acids are solubilized by treatment in a liquid medium at an elevated temperature not exceeding 200° with an organic acid, acid anhydride or acid salt. Thus[3], cellulose tristearate gives a clear solution when heated in tetrachlorethane to 145°, and the ester, isolated by pouring the solution into ethyl alcohol, is soluble in benzene, trichlorethylene or amyl acetate. Or[4], cellulose may be treated with chloracetic anhydride and higher homologues of acetic acid in the presence of a catalyst, the solubility properties of the esters being improved by after-hydrolysis.

Filaments and films may be made from condensation products of diolefines[5], either alone or in conjunction with cellulose derivatives, by treating the diolefine with a volatile sulfurizing agent at a temperature not exceeding 100°. Where paper is saturated with the higher fatty acid cel-

1. I. G. Farbenindustrie, A.-G., E. P. 319014; abst. Chem. Zentr. 1930, I, 3378. Can. P. 297084.

2. I. G. Farbenind., A.-G., and H. Hartlein, D. R. P. 513363, 1930; abst. C. A. 1931, **25**, 1379; Chem. Zentr. 1931, I, 1388. F. P. 700345; abst. C. A. 1931, **25**, 3832.

3. I. G. Farbenind., A.-G., M. Hagedorn and G. Hingst, D. R. P. 515107, 1930; abst. C. A. 1931, **25**, 1671; Chem. Zentr. 1931, I, 1544. E. P. 284298; abst. Chem. Zentr. 1928, I, 2146. See D. R. P. 513061; abst. C. A. 1931, **25**, 1379.

4. I. G. Farbenind., A.-G., A. Gundlach and T. Becker, D. R. P. 516250; abst. C. A. 1931, **25**, 1993; Chem. Zentr. 1931, I, 2141. Belg. P. 366979, 1930. See also D. R. P. 515106, 515107; abst. C. A. 1931, **25**, 1671.

5. I. G. Farbenind., A.-G., E. P. 327164. F. P. 676658; abst. Chem. Zentr. 1930, I, 2976.

lulose esters[1] in combination with synthetic resins, cigarette papers may be produced therefrom.

Vapors containing acetic anhydride, acetic acid and water are recoverable by passing over activated charcoal maintained at 140°, whereby the acid and anhydride are absorbed[2], and may be recovered as 96.5% acetic acid and a mixture of acetic acid and anhydride by raising the temperature and reducing the pressure. In the manufacture of azo dyes for acetate silk[3], a mono-oxamic acid of 4.4′-diaminodiphenyl sulfide (m. pt. 108°) or trisulfide (m. pt. 122°) is diazotized and coupled with a coupling component. Examples, the mono-oxamic acid of the monosulfide (4-*p*-aminophenylthiol-phenyloxamic acid) with phenyl-J-acid (bluish-red); *m*-toluylenediamine with 2.4-dinitroaniline (red-brown); the trisulfide oxamic acid (m. pt. 290°) with salicylic acid (yellow); and *m*-phenylenediamine with *p*-chloraniline (orange-brown)[4].

The opacity of cellulose acetate in acetone and other solvents has been nephelometrically investigated[5], the transparency decreasing linearly in acetone and acetone-benzene with the concentration. In acetone-benzene (up to 20% acetone) and in acetone-water (up to 10% acetone), there is no change in translucency although in the former case the viscosity increases. Acetone-ethyl alcohol solutions decrease in opacity with increasing alcohol incre-

1. I. G. Farbenind., A.-G., E. Richter, M. Hagedorn and W. Becker, D. R. P. 517451; abst. Chem. Zentr. 1931, II, 3419.

2. Imperial Chemical Industries, Ltd., H. Hepworth and F. Leicester, E. P. 334986; abst. C. A. 1931, **25**, 1264; J. S. C. I. 1930, **49**, 1142-B; Chem. Zentr. 1930, II, 3848. F. P. 696711; abst. C. A. 1931, **25**, 2739. Imperial Chemical Industries, Ltd., and F. Leicester, E. P. 332983; abst. C. A. 1931, **25**, 524; J. S. C. I. 1930, **49**, 1015-B; Chem. Zentr. 1930, II, 2830. Belg. P. 369591. F. P. 694016; abst. C. A. 1931, **25**, 1843.

3. Imperial Chemical Industries, Ltd., and R. Brightman, E. P. 329049; abst. J. S. C. I. 1930, **49**, 756-B; Chem. Zentr. 1930, II, 2836. U. S. P. 1805715. See also Imperial Chemical Industries, Ltd., Ital. P. 271566.

4. W. Jenkins and Imperial Chemical Industries, Ltd., E. P. 336615. See also E. P. 310062.

5. S. Iwasaki and S. Masuda, J. S. C. I. Japan, 1930, **33**, 43-B; abst. C. A. 1930, **24**, 3642; J. S. C. I. 1930, **49**, 540-A.

ment, viscosity simultaneously decreasing. E. Jaks[1] has described a method of lacquering and iridizing acetylcellulose and nitrocellulose masses in such a way that the optical properties of mother-of-pearl are simulated with fidelity. Splinterless glass sheets are fabricated with an acetylcellulose sheet encased with sheets of glass[2], air being exhausted from between the covers, after which the sheets are heated and caused to coalesce by the action of atmospheric pressure alone.

"Flexible" glass has been described[3] comprising iron or steel netting dipped into acetylcellulose solution with a synthetic resin, the screen then being immersed in a second solution of cellulose acetate which closes the wire meshes forming a flexible wire substitute for glass. A. Johnston[4] has described a method of producing alkyl abietates (ethyl, *n*-propyl, *iso*propyl, *n*-butyl, *iso*butyl, *iso*amyl and hexyl), by heating the halide (chloride, bromide) in the presence of sodium hydroxide with rosin.

Photographic films, particularly those sensitized by diazo compounds[5] may be protected against damp by coating them before use with a layer of acetylcellulose varnish. Viscosity determinations on acetylcellulose in solution[6], indicate that the minimum quantities by weight of reagents required for complete acetylation are acetic anhydride 3, acetic acid 3 and sulfuric acid 0.2 for 1 part cotton wadding, and 2.5, 2.5 and 0.2 part respectively for 1 part linters pulp. In the preparation of hollow artificial threads[7], high-boiling petroleum fractions or other hydrocarbons are incor-

1. D. R. P. 488151; abst. C. A. 1930, **24**, 2250.
2. J. Jeffray, E. P. 327949; abst. C. A. 1930, **24**, 5124; Chem. Zentr. 1930, II, 2940.
3. E. Johns, Brit. Plastics, 1930, **1**, 366.
4. U. S. P. 1749483; abst. Plastics, 1930, **6**, #9, 518; Chem. Zentr. 1931, I, 3610. F. P. 656821; abst. Chem. Zentr. 1929, II, 1219.
5. Kalle & Co., A.-G., F. P. 696100; abst. C. A. 1931, **25**, 2654; Chem. Zentr. 1931, I, 1402.
6. Y. Kami, M. Inubushi and K. Kitazawa, Cellulose Ind. (Tokyo), 1930, **6**. 11; German Abstract 5; abst. C. A. 1930, **24**, 5151; J. S. C. I. 1930, **49**, 278-B; British Plastics, 1930, **1**, #11, 498.
7. H. Karplus, U. S. P. 1770310; abst. C. A. 1930, **24**, 4633; J. S. C. I. 1931, **50**, 342-B.

porated with acetylcellulose spinning solutions, being afterwards removed by subjecting the spun filaments to heat and vacuum, thereby leaving void the spaces previously occupied by these non-solvents.

When acetylstarch (44.17 acetyl) is heated in glycerol solution at 200-220°, elimination of acetyl takes place[1], forming products containing 7-10% acetyl, soluble in water, dialyzing completely through a collodion membrane, and yielding maltose hepta-acetate on treatment with acetyl bromide, the changes taking place being hydrolytic. *iso*Trihexosan[2], dextrinosan[3], and dextrinose are also converted into maltose hepta-acetate by treatment with acetyl bromide. The A. Keller planographic printing surface is made by hydrolyzing the surface of a triacetylcellulose film by rapid immersion in hot NaOH solution[4], with subsequent sensitization with concentrated bichromate, and 15-25 minutes exposure under a negative to a 35 ampere arclight. Development with water requires 10-15 seconds.

W. Kemmerich[5] has discussed the uses of acetylcellulose as applied to coating metal fabrics to prevent tarnishing, cellulose acetate threads embodying metal bronze, cellulose acetate in printing damask effects on cotton (stated to be much improved by use of such solvents as monomethyl [or ethyl] ether of glycol and their acetates, methyl [and ethyl] lactate and oxybutyrate), and dyes suitable for mixing with acetylated cellulose. Economies of the cellulose acetate printing process and four practical printing formulas containing cellulose acetate are given, utilizing Malachite green, Rhodamine B, Supramin Yellow R, Alizarine Rubinole B, Fanal Blue B, and Helio Fast Red RL.

1. P. Karrer and E. von Krauss, Helv. Chim. Acta, 1930, **13**, 1071; abst. J. S. C. I. 1930, **49**, 1415-A.

2. A. Pictet and H. Vogel, Helv. Chim. Acta, 1929, **12**, 700; abst. J. S. C. I. 1929, **48**, 914-A.

3. *Ibid.* Rec. trav. chim. 1929, **48**, 843; abst. J. S. C. I. 1929, **48**, 1167-A.

4. D. R. P. 509010.

5. Cellulose, 1930, **1**, #10, 263; abst. C. A. 1931, **25**, 4711.

In the formation of photographic films[1], a composition is used which comprises cellulose acetate, formate, nitrate or oxalate with 1-5% bone oil, whale oil, mutton fat, beeswax, fish oil, to which solvents and plasticizers are added. The absorption power of acetate silk for tannin is about 20% of the tannin in a given solution[2], the difference in percentage absorption between 1, 2 and 12 hours soaking being relatively slight. Tannin-mordanted acetylcellulose shows differences in action with basic dyes, Malachite green showing no difference. Rhodamine B and 6G give fluorescent shades on non-mordanted cellulose acetate, but no fluorescence on real silk.

Aqueous acetic acid may be concentrated by mixing with ethylene dichloride and distilling off an azeotropic mixture of water and ethylene dichloride[3] at a temperature below 100°. Double cellulose esters have been described[4] in which partly acetated cellulose is further esterified to produce cellulose aceto-lactate, -tartrate, -racemate, -malate, -glycollate, -glycerate and -mandelate. Or[5], partially nitrated cellulose may be further esterified as above to produce the above seven mixed esters (as cellulose nitro-lactate, etc.). The manufacture of cellulose acetate may be carried out by submitting cellulose to preliminary treatment (action of acetic acid), and distilling the mixture in the presence of a liquid which forms an azeotropic mixture with water as ethylene dichloride[6], then removing the water from the mixture and esterifying in the usual manner. Another series of mixed cellulose esters has been de-

1. P. King, E. P. 324911; abst. C. A. 1930, **24**, 3720; J. S. C. I. 1930, **49**, 321-B. Compare E. P. 925, 1904; 301017.
2. P. King and A. Sahasranam, J. Soc. Dyers Colourists, 1930, **46**, 118; abst. C. A. 1931, **25**, 212; J. S. C. I. 1930, **49**, 656-B. See Kodak, Ltd., E. P. 313408.
3. *Ibid.* E. P. 327444; abst. C. A. 1930, **24**, 5045; J. S. C. I. 1930, **49**, 602-B; Chem. Zentr. 1930, II, 306.
4. Kodak, Ltd., C. Webber, C. Staud, E. P. 336353. New Zealand P. 63303. F. P. 690115. E. P. 338201. Can. P. 312805.
5. Kodak-Pathe, F. P. 688601. E. P. 344151.
6. *Ibid.* F. P. 689200; abst. C. A. 1931, **25**, 1082.

scribed[1], prepared by digesting an incompletely acylated cellulose ester as the acetate with an acid containing a keto group, examples being cellulose aceto-pyruvate, -*a*-ketobutyrate, -*a*-ketovalerate, -*a*-ketocaproate and -levulinate, or, aceto-stearates.

Cellulose acetate may be made by treating cellulose with acetic anhydride vapor[2], following which the vapor of acetic acid liberated by the acetylation is maintained in contact with the material until esterified, air being removed from the reaction space at the commencement of the process. The ester retains the original fibrous structure of the cellulose and is soluble in chloroform. A suitable composition for casting films is produced by dissolving acetylcellulose 30 in amyl acetate 50, ethyl acetate 10-40, and acetone 40-10 parts[3]. A novel method of acetylcellulose manufacture has been disclosed[4], comprising treating cellulose with acetic anhydride and a catalyst in the presence of a mixture which dissolves the cellulose acetate produced and containing an amount of acetic acid insufficient by itself to dissolve the cellulose ester, together with an organic volatile liquid immiscible with water as dichlorethane. The cellulose acetate is precipitated in an aqueous bath at a temperature above the b. pt. of the volatile liquid, which is collected and condensed.

If cellulose is esterified in the presence of a nitrogen oxide, cellulose acetonitrates result[5] containing 38-42% acetyl and 0.3-3% N., which are soluble in acetone and excellent for film formation. Solutions, lacquers, films and artificial silk are prepared by treating cellulose acetobutyrate with mixtures of liquids which have no marked solvent

1. Kodak-Pathe, F. P. 690458; abst. C. A. 1931, **25**, 1082. Compare F. P. 687996; abst. C. A. 1931, **25**, 813.
2. *Ibid.* F. P. 692365; abst. C. A. 1931, **25**, 1379.
3. *Ibid.* F. P. 693131; abst. C. A. 1931, **25**, 1671.
4. *Ibid.* F. P. 693132; abst. C. A. 1931, **25**, 1671. F. P. 693133; abst. C. A. 1931, **25**, 1671. F. P. 693189; abst. C. A. 1931, **25**, 1671.
5. *Ibid.* F. P. 699807; abst. C. A. 1931, **25**, 3481.

properties for this ester[1], a mixture of equal amounts of ethyl alcohol and benzene being an appropriate combination. Cellulose stearate, palmitate and laurate have been advocated for drying benzine and other organic liquids containing water in suspension[2]. The ester must be insoluble in the organic liquid, and may be used in such form that the organic liquid can filter through it. D. Kruger[3] contributed an article on the solubility and "particle—size" of cellulose acetate, and[4] experiments in nitrating cellulose acetate, acetylating cellulose nitrate and simultaneously treating cellulose with nitric acid, acetic anhydride or sulfuric acid. It was found that mixed acetic anhydride, concentrated nitric acid and sulfuric acid contains diacetyl nitric acid which decomposes explosively, while the highly viscous mixture of acetic anhydride and concentrated sulfuric acid contains acetylsulfuric acid. In a considerable range of nitrating-bath composition with acetic anhydride and acetic acid variation, pure cellulose nitrates were obtained free from acetate and whose solubility in alcohol-ether were similar to ordinary nitrocellulose of the same nitrogen content.

In the range of pure nitrates there is a section where nitroacetates result which at first have the solubilities of the pure nitrates, but with decreasing nitrogen content these are soon lost. An acetyl nitrate of suitable degree of combustibility and solubility for practical purposes could not be obtained. In continued change of the acid mixtures no continuous or highly nitrated cellulose to pure highly acetylated cellulose acetate occurs; in this range where unstable products result and where excess of acidolysis and oxidation occur over esterification. Methods of determining the moisture and ash content, acetic copper and copper

1. Kodak-Pathe, F. P. 697471; abst. C. A. 1931, **25**, 3168; Chem. Zentr. 1931, I, 2416.
2. W. Koreska, Aust. P. 120875; abst. C. A. 1931, **25**, 2436; Chem. Zentr. 1931, I, 2149.
3. Cellulose, 1931, **1**, #11, 285.
4. D. Kruger, Cellulosechemie, 1930, **11**, 220; abst. C. A. 1931, **25**, 4121; J. S. C. I. 1931, **50**, 340-B. Kunstoffe, 1930, **20**, 73; abst. C. A. 1930, **24**, 4149; Chem. Zentr. 1930, II, 334.

number of acetyl cellulose[1] have been detailed, the methods proposed for these determinations being divided into two groups involving acid and alkaline hydrolysis[2]. D. Kruger[3] has discussed the preparation of cellulose acetate and its chemical and physical properties, the manufacture and properties of acetate rayon[4], the various methods for the detection and estimation of acetic acid[5] and identification of acetylated fibers[6].

In the manufacture of aliphatic acids and other products by the fermentation of cellulosic materials the acid is neutralized by means of ammonia[7], which addition liberates by decomposition the salts produced by a non-volatile base. A comparative study has been made of the relation existing between the chemical characters of organophilic colloids, as cellulose acetate[8], and certain alcoholic liquids in which these colloids swell and disperse. The results in general show that solvents or swelling agents for raw rubber are non-solvents or non-swelling agents for cellulose acetate and celluloid. This fact is related to the distribution of polar groups and the size of the hydrocarbon chain or residue of the organic liquid. Important and well-defined exceptions to the above rule were found. Methyl and ethyl benzoates are noteworthy, being solvents for both cellulose

1. D. Krueger, Farbe and Lack, 1930, #50, 584; abst. Chem. Zentr. 1931, I, 1992.
2. *Ibid.* Farben-Ztg., 1930, **35**, 2032; abst. Brit. Plastics, 1930, **2**, #17, 229; J. S. C. I. 1930, **49**, 812-B; Chem. Zentr. 1930, II, 3875.
3. Kunstseide, 1930, **12**, 262; abst. C. A. 1931, **25**, 1669; Chem. Zentr. 1930, II, 1163.
4. *Ibid.* Papier-Fabr., 1930, **28**, 1; abst. C. A. 1930, **24**, 3359; J. S. C. I. 1930, **24**, 137-B. Rayon and Synthetic Yarn Journal, 1930, **11**, #6, 14.
5. D. Krueger and E. Tschirch, Chem. Ztg., 1930, **54**, 42; abst. C. A. 1930, **24**, 1317; J. S. C. I. 1930, **49**, 357-A; Journ. Chem. Ed., 1930, **7**, #5, 1192. Pharm. Zentralhalle, 1930, **71**, 145; abst. C. A. 1930, **24**, 2083; J. S. C. I. 1930, **49**, 451-A.
6. *Ibid.* Textilber. 1930, **11**, 529; abst. Rayon Record, 1930, **4**, #16, 658; C. A. 1930, **24**, 6024.
7. H. Langwell, Can. P. 305584. F. P. 695724; abst. C. A. 1931, **25**, 2737.
8. W. Lee, J. S. C. I. 1930, **49**, 226-T; abst. C. A. 1930, **24**, 3842; Cellulose, 1930, I, #6, 175; India Rubber J. 1930, **79**, 14.

acetate and rubber, and strong swelling agents for celluloid. Among the 80 organic liquids used, a large number of apparently new solvents or swelling agents for important industrial organophilic colloids are reported[1]. A new triacetate silk from cellulose cyanoacetic esters has been recorded[2]. It has been found that mixed acetic and cyanoacetic cellulose esters rich in nitrogen may be prepared that spin like triacetate and may be mixed in all proportions in its acetic solution. The cellulose nitrate groups are transformed into CONH by treating at 40-50 with alkali and hydrogen under conditions in which the triacetate is not altered. The preparations with cellulose nitrate groups have a larger affinity for colors and principally for those with CONH groups. By hydrolysis further preparations are obtained with free carboxylic groups without saponifying the cellulose esters which retain the desirable physical properties of cellulose triacetate. In 1930 H. Levinstein[3] described the manufacture of cellulose acetate, and compared the various kinds of artificial silks. Acetol, of pos-

1. The solvent action on cellulose acetate and celluloid of nearly all of the following are tabulated: *n*-hexane, *n*-decane, trimethylethylene, *x*-cumene, *p*-cymene, tetrahydronaphthalene, pinene, ethyl acetate, ethyl acetoacetate, ethyl cyanoacetate, ethyl trichloracetate, amyl formate, amyl valerate, butyl stearate, ethyl orthoformate, ethyl oxalate, ethyl cinnamate, methyl benzoate, *iso*-amyl benzoate, methyl salicylate, butyl phthalate, phenyl butyrate, ethyl collidinedicarboxylate, vinyl acetate, citronellyl acetate, allyl bromide, acetic acid, thioacetic acid, *n*-hexoic acid, *n*-undecoic acid, undecoic acid, lactic acid, pyruvic acid, oleic acid, acetonitrile, diethylacetonitrile, phenylacetonitrile, chloroacetaldehyde, aldol, heptaldehyde, cinnamaldehyde, salicylaldehyde, citronellal, furfuraldehyde, furfuryl alcohol, cyclohexanol, *iso*-amyl alcohol, *tert.*-amyl alcohol, *by*-dibromopropyl alcohol, cineole, terpineol, cinnamyl alcohol, trimethylene glycol (commercial), diethylcarbinol, phenyldimethylcarbinol, dimethyl-*n*-butylcarbinol, diacetone alcohol, methyl tolyl sulphide, thiophen, pyrrole, pyridine, "methylpyridine," piperidine, *iso*-quinoline, xylidine, phenylhydrazine, diethylamine, benzylmethylamine, triethanolamine, methyl *p*-tolyl ketone, iodobenzene, benzylidene chloride, amylene dichloride, ethylene glycol monomethyl ether, and tetranitromethane.

2. G. Levi, Boll. assoc. ital. chim. ecol. 1930, **6**, 80; abst. C. A. 1930, **24**, 4387.

3. H. Levinstein, Chem. Trade J. **86**, 127; J. S. C. I. 1930, **49**, 55-T; abst. C. A. 1930, **24**, 1737; Journ. Chem. Ed. 1930, **7**, #8, 1951; Rayon Record, 1930, **4**, #3, 126.

sible value as a cellulose ester solvent[1], may be prepared by the action of KOH on dry methyl alcohol, ethyl formate and brom-methyl acetate. It readily polymerizes. Hollow filaments have been described by L. Lilienfeld[2].

As a suitable lacquer formula[3] has been recommended acetylcellulose 16, diethyleneglycol dibenzoate 8, acetone 50, cyclohexanone 20. Pentaethyleneglycol acetate has also been specified. A gas-tight material for balloons is prepared from fabric by treating it on one or both sides with acetylcellulose and with a gas-sealing agent as gelatin or casein with glycerol[4], thus rendering unnecessary the use of animal skins. The catalytic decomposition of pentachlorethane has been detailed[5].

H. Mark[6] has reviewed the development of X-ray analysis, giving diagrams for acetylcellulose fibers, discussing the subject under the three headings: analytical differentiation of various types of fibers, determination of fiber properties and structure analysis. In preparing solutions suitable for use as lacquers[7], acetyl- or nitro-cellulose is brought into intimate contact with uncombined methylamine, dimethylamine, trimethylamine or ethylamines (mono- or di-) in a quantity of about 0.1-5% that of the cellulose ester, which facilitates solution or gelatinization with the usual solvents. The intensity of fluorescence of cellulose acetate or nitrate films depends on the wave length of the exciting radiation, the chemical composition and the

1. P. Levene and A. Walti, Organic Syntheses, 1930, **10**, 1; abst. C. A. 1930, **24**, 1844; J. S. C. I. 1930, **49**, 746-A; Chem. Zentr. 1931, I, 3226.
2. L. Lilienfeld, Swed. P. 69983.
3. O. Loehr and I. G. Farbenindustrie, A.-G., U. S. P. 1783176; abst. C. A. 1931, **25**, 414; Plastics, 1931, **7**, #3, 177.
4. Luftschiffbau Zeppelin G. m. b. H. and H. Strobl, D. R. P. 483484; abst. C. A. 1930, **24**, 512. U. S. P. 1827213.
5. A. Mailhe and Sabrou, Bull. soc. chim. 1930, (4), **47**, 349; abst. C. A. 1930, **24**, 3984; Chem. Zentr. 1930, II, 225. See also A. Mailhe, Bull. soc. chim. 1921, **29**, 535; Compt. rend. 1921, **172**, 1582.
6. H. Mark, Kunstseide, 1930, **12**, 214; Jentgen's Rayon Rev. 1930, **2**, 196; abst. C. A. 1931, **25**, 211; Chem. Zentr. 1930, II, 1163. See C. Malm and A. Andersen, New Zealand P. 65256.
7. A. McDaniel, U. S. P. 1759489; abst. C. A. 1930, **24**, 3646.

micellar structure of the film[1]. The intensity for acetone solutions of acetylcellulose is independent of the colloidal properties of the solution.

A study of double refraction in cellulose acetate and nitrate films has been made[2], and a suitable instrument devised for determining the direction of orientation of micelles in transparent colloidal films. Uniaxial, biaxial, or isotropic films can be prepared from a given sample of cellulose acetate or nitrate by varying the tension on the film during drying. Films prepared by pouring a 2% solution of the ester on to a clean mercury surface and allowing to dry slowly are completely isotropic. The uses of acetylcellulose have been pointed out by J. Mercadel[3], and of degumming mixed silk-acetylcellulose fabrics with "superbatinase," a commercial enzyme of bacterial origin[4].

K. Meyer and H. Hopff[5] have investigated the more complex intermediate products of the acetolysis of cellulose, and report that the product m. pt. 261-262° obtained by K. Hess and H. Friese[6] is not homogeneous since it can be separated by fractional precipitation from acetone into four fractions melting between 229-275°, molecular weight determinations in freezing glacial acid giving values of about 600, or about 1000 if traces of water are rigidly excluded. In the boiling solvent, slight depressions were observed due to the production of an azeotropic mixture with minute amounts of water. In freezing bromoform, constant values of about 3000 were obtained, and it is shown that cellobiose formation is independent of the degree of association

1. J. McNally and W. Vanselow, J. Am. Chem. Soc. 1930, **52**, 3846; abst. C. A. 1931, **25**, 33; J. S. C. I. 1930, **49**, 1500-A.
2. J. McNally and S. Sheppard, J. Physical Chem. 1930, **34**, 165; abst. C. A. 1930, **24**, 1972; J. S. C. I. 1930, **49**, 287-A; Rayon Record 1930, **4**, #6, 338.
3. Quim. e ind. 1930, **7**, 30; abst. C. A. 1930, **24**, 2287; Chem. Zentr. 1930, I, 2825.
4. L. Meunier and J. Vallette, Russa, 1930, **4**, 1513; abst. C. A. 1930, **24**, 4163.
5. Ber. 1930, **63-B**, 790; abst. C. A. 1930, **24**, 3641; J. S. C. I. 1930, **49**, 750-A. K. Hess and H. Friese, Annalen, 1926, **450**, 40; abst. J. S. C. I. 1927, **46**, 44-A.
6. Ann. 1926, **450**, 40; abst. J. S. C. I. 1927, **46**, 44-A.

of cellulose or cellulose acetates. Hexa-acetyl- and hexa-methyl-biosans do not exhibit the tendency to association shown by cellulose acetates[1].

A composition of acetyl cellulose film has been described for tipping cigarets (see p. 296, n. 5; 367, n. 2; 384, n. 1; 425, n. 6; 514, n. 5)[2] in which the non-transparent film in very thin layer containing pigment or bronze powder in such limited amount as not to destroy the waterproofing character of the films has superposed on it another very thin film containing finely divided pigment, so as to produce a mat surface. A method of cellulose acetylation has been described in which the relatively expensive acetic anhydride is dispensed with[3], comprising treating cellulose with a mixture of acetic acid and ortho- or meta-phosphoric acid as a preliminary cellulose treatment, then acetylating with the same combination in the presence of sulfuric acid as catalyst.

In producing moire scratch patterns in fabrics made from acetylcellulose fibers[4], the fabric is moistened while in a folded condition, a pattern scratched thereon while folded, and then subjected to heat and pressure. J. Monypenny[5] has given the composition and properties of corrosion-resisting steels especially applicable for withstanding acetylation mixtures as used in the acetylcellulose industry, and Justin-Mueller[6] the characteristics of the amyloid obtained by treating cellulose with sulfuric acid 1.58 sp. gr., and diluting the solution.

1. K. Meyer, H. Hopff and H. Mark, Ber. 1930, **63-B**, 1531; abst. J. S. C. I. 1930, **49**, 1025-A; Chem. Zentr. 1930, II, 547.
2. C. Muench, E. P. 334271; abst. C. A. 1931, **25**, 1082; Chem. Zentr. 1931, I, 2290.
3. G. Miles and C. Dreyfus, U. S. P. 1742611; abst. C. A. 1930, **24**, 1217; J. S. C. I. 1930, **49**, 760-B; Brit. Plastics, 1930, **2**, #17, 100; Plastics, 1930, **6**, #6, 338.
4. A. Milhomme, U. S. P. 1781296; abst. C. A. 1931, **25**, 218; Chem. Zentr. 1931, I, 2286. E. P. 346561.
5. Rayon Record, 1930, **4**, #10, 521; abst. C. A. 1930, **24**, 4150; Chem. Zentr. 1930, II, 798.
6. Bull. Soc. Chim. 1930, **47**, 1400; abst. C. A. 1931, **25**, 3162; Chem. Zentr. 1931, I, 1438.

C. Mullin has reviewed recent methods in dyeing and finishing of rayons[1], the dyeing, printing and processing of acetate silks[2], the manufacture of acetic acid by hardwood distillation[3], and statistics on the production of acetate filaments[4]. A photosensitive material may be formed by impregnating paper or fabric with acetylcellulose, the surface made water permeable by superficial de-esterification, which is then impregnated with a light-sensitive salt as a silver, iron or chromium or diazo compound[5]. M. Nakano[6] has published photomicrographs of swollen acetylcellulose fibers with studies on their structure, and A. Nathansohn a method for waterproofing textiles[7] by incorporating them with the higher acids and anhydrides (stearyl chloride in benzene) and then esterifying. In other words, apparently a process for superficial esterification of cellulose into the corresponding stearate.

In order to increase the chemical reactivity, a process has been patented for drying cellulose by means of liquid sulfur dioxide which is then evaporated by reducing the pressure, the dried cellulose being particularly suitable for acetylation[8]. Laminated glass sheets made by imprisoning an acetylcelluloid or celluloid sheets between glass panes are pressed together at a temperature of 150-200°F., the sheet, after removal from the press being maintained at

1. C. Mullin, Rayon, 1930, **10**, #1, 16; abst. C. A. 1930, **24**, 1221. C. Mullin and A. Macormac, Manual of the Textile Industry of Canada, 1930, 175; abst. C. A. 1930, **24**, 5499; Chem. Zentr. 1931, I, 1014.
2. *Ibid.* Textile World, 1930, **78**, 1519; abst. C. A. 1931, **25**, 3173; Chem. Zentr. 1930, II, 3351.
3. C. Mullin and H. Hunter, Cellulose, 1930, **1**, #5, 138; #6, 170; #7, 183; #8, 215; #9, 235; abst. C. A. 1931, **25**, 4524; Cellulose, 1930, **1**, #10, 258; #11, 287.
4. C. Mullin, Ind. Eng. Chem. 1930, **22**, 461; abst. C. A. 1930, **24**, 3111; J. S. C. I. 1930, **49**, 653-B. Textile Colorist, 1930, **52**, 17; abst. C. A. 1931, **25**, 138.
5. H. Murray, D. Spencer and Colour Photographs (Brit. & Foreign), Ltd., E. P. 337868; abst. C. A. 1931, **25**, 2065.
6. J. Cell. Inst. (Tokyo), 1930, **6**, #8, 36.
7. F. P. 693803; abst. C. A. 1931, **25**, 1686; Chem. Zentr. 1931, I, 1385. E. P. 355256; abst. J. S. C. I. 1931, **50**, 1047-B.
8. G. Neumann, F. P. 693014; abst. C. A. 1931, **25**, 1670; Chem. Zentr. 1931, I, 2288.

80-90°F. for 24-48 hrs., and then placed in a freezing chamber to complete the process[1]. The following new acetals have been prepared, of possible value as cellulose ester solvents[2]; methylethylpinacol, glycolbutyl ether, diethyleneglycol, diethyleneglycol ethyl ether, glycerol methyl (or ethyl or phenyl) ether, dimethyl (or ethyl) tartrate or malate, dimethyl citrate.

It is claimed[3] that the Debye-Scherrer method alone is suitable for the X-ray examination of the microcrystalline cellulose dilaurate and distearate, and shows that the internal structure of the cellulose is completely destroyed by fixation of the long aliphatic chains. Dextrose α- pentaacetate, -laurate and -palmitate have been studied, the first by the rotating crystal method, and the last two after crystallization in fibrous form from chloroform-alcohol. It is shown that the long aliphatic chains are always approximately perpendicular to the axis of the fiber, and the molecules always orientated in the same direction, corresponding with a cell unit of side 5.28-5.39Å. A. Nuckolls has published data on the temperature of ignition of acetyl- and nitro-cellulose films, type of decomposition, and products of combustion for each type of film.

Acetic anhydride may be produced from acetic acid and acetone by submission of the mixture to a temperature above 600°, with or without a catalyst[5]. Acetylcellulose threads may be given a dull luster[6] by treatment with a solution of silicon fluoride under such conditions that silicic

1. J. Newton, F. P. 693919; abst. C. A. 1931, **25**, 1962. E. P. 333242; abst. Kunst. 1931, **21**, 93; Chem. Zentr. 1930, II, 2817.
2. J. Nieuwland, R. Vogt. and W. Foohey, J. Am. Chem. Soc. 1930, **52**, 1018; abst. C. A. 1930, **24**, 1841.
3. A. Nowakowski, Compt. rend. 1930, **191**, 411; abst. J. S. C. I. 1930, **49**, 1352-A. K. Meyer and H. Mark, Ber. 1928, **61**-B, 593; abst. J. S. C. I. 1928, **47**, 621-A.
4. A. Nuckolls, Projection Eng. 1930, **2**, 24; abst. C. A. 1930, **24**, 5649. Quarterly Nat. Fire Protection Assoc. 1930, **23**, 236; abst. C. A. 1930, **24**, 1972.
5. N. V. de Bataafsche Petroleum Maatschappij, F. P. 701145; abst. C. A. 1931, **25**, 3670; Chem. Zentr. 1931, II, 122. Belg. P. 372398.
6. Naamlooze Vennootschap J. A. Carp's Garen-Fabrieken, E. P. 337418; abst. C. A. 1931, **25**, 2289; Chem. Zentr. 1931, I, 871.

acid is produced by hydrolysis and partially incorporated in the material so that it is not removable by water, dilute acids or soap solutions. In preparing stable, primary acetate silk directly from the acetylating bath[1], sufficient water (1% excess) is added to the primary solution of cellulose-acetic anhydride-sulfuric acid to convert anhydride into acid and allow the sulfuric acid to be extracted from the fibers. Before spinning, sodium acetate is added to the solution to neutralize the free H_2SO_4. F. Ohl[2] has reviewed the industry of acetylcellulose silk manufacture, especially wet-spinning methods[3], and described experiments on the manufacture of cellulose acetate from wood pulp[4], and the spinning of filaments therefrom. The yield and quality of ester produced from sulfite-cellulose are improved by acid or alkaline pretreatment[5].

A study of the fractional precipitation of cellulose acetate has been made[6], the ester being fractionally precipitated in three portions from an acetone solution by the addition of distilled water. Fraction I gave a highly viscous solution that contained in addition to the ester, a large portion of the organic and inorganic impurities present in the original product. II consisted of very pure acetate, III giving a solution of very low viscosity, consisting on the one hand of impure cellulose acetate, and on the other of decomposition and intermediate products formed in the cel-

1. Naamlooze Vennootschap 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. Holl. P. 20680; abst. C. A. 1930, **24**, 4633; Chem. Zentr. 1931, I, 2142. Holl. P. 20725; abst. C. A. 1930, **24**, 4633; Chem. Zentr. 1931, I, 2291.

2. Chem. Ztg. 1930, **54**, 202; abst. C. A. 1930, **24**, 2598; J. S. C. I. 1930, **49**, 552-B; Chem. Zentr. 1930, II, 165.

3. F. Ohl, Jentgen's Rayon Review, 1930, II, #2, 72; abst. C. A. 1930, **24**, 5483.

4. *Ibid.* Kunstseide, 1930, **23**, 189; Jentgen's Rayon Review, 1930, **2**, #5, 224; #6, 245. Kunstoffe, 1930, **20**, 122; Rayon Record, 1930, **4**, #15, 811. Kunstseide 1930, **12**, 279; Jentgen's Rayon Review, 1930, **2**, 245; abst. C. A. 1931, **25**, 1669.

5. *Ibid.* Kunstoffe, 1930, **20**, 217; abst. J. S. C. I. 1931, **50**, 1134-B; Chem. Zentr. 1931, I, 2700.

6. *Ibid.* Kunstseide, 1930, **12**, 468; abst. C. A. 1931, **25**, 4121.

lulose acetylation. Filaments prepared from II showed the highest strength, that from III, the lowest, increased tensile strength being obtained by mixing II and III in certain proportions. No relation existed between the viscosity of solutions and the strength of resulting filaments.

In a study of the gases produced by the decomposition of nitro- and acetyl-cellulose films[1], both uncoated and emulsion coated, were decomposed by heat in air and nitrogen, the nitrogen oxides evolved on decomposition of the former being the most highly toxic gases formed. The quantity of CO produced is no higher than the amount given off by newsprint or other cellulose material. The hydrocyanic acid formed by decomposition of emulsion coated film is less than that evolved in the thermal decomposition of wool. Analyses of the gases evolved from each type of material are tabulated. The origin and formation of acetic acid of pyroligneous liquor has been studied[2]; a method for extracting formic acid from the waste liquors from the purification of cellulose patented[3], while H. Pratt[4] has shown methods for dyeing and finishing Celanese fabrics.

W. Plinatus[5] has disclosed a process for producing acetylcellulose plastic masses, comprising converting moist, low-viscosity esters into solid solutions by means of high-boiling gelatinizers accompanied by mechanical energy and heat. J. Preston has pointed out the advisability of using a microscopical mountant having the same *n* value as the

1. J. Olsen, A. Brunjes and V. Sabetta, Ind. Eng. Chem. 1930, **22**, 860; abst. C. A. 1930, **24**, 4397; J. S. C. I. 1930, **49**, 1047-B.
2. C. Padovani and A. Mariotti, Annali Chim. Appl. 1930, **20**, 205; abst. J. S. C. I. 1930, **49**, 750-B. Compare H. Pringsheim and H. Magnus, Zeitsch. physiol. Chem. 1919, **105**, 179; abst. J. C. S. 1919, **116**, i, 473.
3. Papeteries Navarre, Belg. P. 366337; abst. C. A. 1930, **24**, 4631. E. P. 342119; abst. J. S. C. I. 1931, **50**, 344-B. Can. P. 308394.
4. Proc. Am. Assoc. Textile Chem. Colorists, 1930, 15; Am. Dyestuff Rept. **19**, 19; Dyer, Calico Printer, 1930, **63**, 225; abst. C. A. 1931, **25**, 1087; Chem. Zentr. 1930, I, 2013.
5. Can. P. 300012.

section[1] when examining acetylcellulose fibers, water being unsuitable on account of its swelling action on the cellulose ester, although no mountant is available that does not cause some swelling. The most suitable for acetylcellulose fiber sections are glycerol jelly of *n* 1.37 for contrast, and Euparal of *n* 1.50 for rendering invisible. He has also[2] pointed out the uses and methods of application of partially hydrolyzed acetylcellulose with respect to printing, or to confer a modified "handle." A new degradation product of cellulose has been described[3], obtained by treating dissolved acetylcellulose with 0.25-1.% benzenesulfonic acid.

In the preparation of collapsible tubes from cellulose acetate foil (see p. 254, n. 5; 439, n. 8; 449, n. 5; 530, n. 2; 618, n. 10)[4], the latter is wound in tubular form, waterproofed with cellulose nitrate, and cemented with varnish, the solvents in which are compatible with acetylcellulose. According to H. Reedy[5], in the usual acetylation of cellulose, acetylsulfuric acid is considered to be first formed, and from it, sulfoacetic acid. The formation of sulfacetates is unlikely to be prevented by acetylation with acetylsulfuric acid, in which free sulfuric acid and sulfoacetic acid are in equilibrium. As softener for the cellulose esters has been patented mixed alkyl *cyclo*hexyl esters of phthalic acid, as *cyclo*hexyl phthalate, *cyclo*hexyl-*iso*propyl, -*n*-butyl, -amyl, -benzyl, -phenyl and -xylyl phthalates[6]. Acetamide has been brought forward as a polysaccharide solvent[7].

A process has been patented for preparing cellulose

1. J. Soc. Dyers and Col. 1930, **46**, 295; abst. J. S. C. I. 1931, **50**, 670-B; Chem. Zentr. 1930, II, 3103.
2. Rayon Record, 1930, **4**, #12, 651.
3. H. Pringsheim, G. Otto and J. Katz, Cellulosechemie 1930, **11**, 137; abst. C. A. 1931, **25**, 4120. H. Pringsheim, E. Kasten and E. Schapiro, Ber. 1928, **61-B**, 2019; abst. C. A. 1930, **24**, 1501.
4. L. Rado, E. P. 327212; abst. C. A. 1930, **24**, 5157.
5. Kunstseide, 1930, **12**, 420; abst. J. S. C. I. 1931, **50**, 581-B.
6. E. Reid and G. Schwartz, U. S. P. 1778567; abst. C. A. 1930, **24**, 6014; J. S. C. I. 1931, **50**, 597-B.
7. J. Reilly, R. Wolter and P. Donovan, Sci. Proc. Roy. Dublin Soc. 1930, **19**, 467; abst. J. S. C. I. 1930, **49**, 1561-A.

surfaces for the reception of cellulose ester lacquers[1], by applying to the surface an intermediate coating of a solution of cellulose ester in which at least one OH is esterified by a higher fatty acid, cellulose dilaurate or *mono*acetate-distearate are examples. Guttapercha may be incorporated with the ester. E. Robertson[2] has developed a modification of the "solution" theory of dyeing acetylcellulose with dispersed substances and of the "unimolecular layer" theory with basic dyestuffs, and described methods of forming "passive cotton," formed by treating cellulose with a mixture of acetic anhydride, acetic chloride and zinc oxide, the product, in properties, being similar to those of acetylcellulose, immunized and amidated cotton[3].

In the fractional precipitation of acetone-soluble acetylcellulose (see p. 896, n. 6), the ester was separated into the three fractions A, B and C, the former giving a highly viscous solution in acetone and consisting of the ester with a relatively high content of inorganic impurities and some coloring matter. The C-fraction is chemically pure cellulose acetate, precipitated in crystalline form, and the B-fraction characterized by low viscosity. The tensile strength of cellulose acetate films is proportional to the viscosity of the solution from which the film is prepared, the B-fractions yielding poorest films. The viscosity is not additive when two fractions are combined, but, in general, is reduced. Tensile strength of acetylcellulose films containing particles of large size may be increased to an optimum value by adding a small amount of a fraction containing small particles[4].

The bleaching of films and threads of acetyl- and nitrocellulose may be effected by treating the material with

1. E. Richter, K. Bitterfeld and W. Becker, U. S. P. 1778813; abst. Chem. Zentr. 1931, I, 369.
2. Rayon Record, 1930, **4**, 479; abst. C. A. 1930, **24**, 4161; Chem. Zentr. 1930, II, 140.
3. F. Robinson, Wool Record and Textile World, 1930, **37**, 1027; abst. C. A. 1930, **24**, 3375.
4. H. Rocha, Kolloidchem. Beih. 1930, **30**, 230; abst. C. A. 1930, **24**, 2597; J. S. C. I. 1930, **49**, 367-B.

10-20 times the quantity of 1-20% acetic acid solution, or 0.5-2% NaOH solution to effect slight preliminary swelling, and then treating with a chlorine compound in the usual manner[1]. K. Roos and H. Friese[2] have discussed the solubility characteristics of cellulose derivatives, especially acetated cellulose, influence of degradation products on solubility, methods of analysis and factors influencing development of the art. A paper containing rubber has been patented in France[3], in which a protective colloid as starch acetate (feculoid or feculose) or a protein is mixed with paper pulp. The mixture is rendered alkaline and a dispersion of rubber added. The pulp is then treated in the usual manner for making paper. A method of determining the purity of acetic anhydride has been worked out[4], based on the decomposition of anhydrous oxalic acid by acetic anhydride, with pyridine as catalyst, and the subsequent determination of excess oxalic acid by potassium permanganate. The method is said to be simple, rapid and accurate to 0.1%. J. Rossman[5] has given a list of United States acetylcellulose plastic patent abstracts, with explanatory notes. A. Rott evaluates acetic anhydride[6] by boiling a known weight with a definite weight of water, and deducing the water content of the resulting mixture by determination of the freezing point.

G. Rudolph[7] has discussed the dyeing properties for acetylcellulose of the Celliton colors, and H. Rudy[8] the

1. K. Roos, E. P. 326471; abst. C. A. 1930, **24**, 4931; J. S. C. I. 1930, **49**, 457-B; Chem. Zentr. 1930, II, 989.
2. Kunstseide, 1930, **23**, 11; abst. C. A. 1930, **24**, 5151.
3. R. Rose, H. Cude and General Rubber Co., F. P. 697683; abst. C. A. 1931, **25**, 3169. U. S. P. 1756035; abst. J. S. C. I. 1930, **49**, 1080-B; Chem. Zentr. 1930, II, 829. U. S. P. 1773201; abst. C. A. 1930, **24**, 5159.
4. C. Rosenbaum and J. Walton, J. Am. Chem. Soc. 1930, **52**, 3366; abst. C. A. 1930, **24**, 4760; Chem. Zentr. 1930, II, 2550.
5. J. Rossman, Plastics, 1930, **6**, #1, 21; #2, 74; #3, 150; #4, 211; #5, 270. See E. Roth-Schmidt, Belg. P. 368166.
6. Chem. Ztg. 1930, **54**, 954; abst. C. A. 1931, **25**, 666; J. S. C. I. 1931, **50**, 104-B.
7. Kunstseide, 1930, **12**, 198; Jentgen's Rayon Review, 1930, **2**, 216; abst. C. A. 1931, **25**, 208.
8. Kunstseide, 1930, **12**, 420; abst. C. A. 1931, **25**, 3827.

chemical reactions of sulfuric acid on acetic anhydride in acetylcellulose of the Celliton colors, and H. Rudy[8] the acetic acid, anhydride and sulfuric acid in the usual manner, except a pressure of 50-75 lb. per square inch and a hydration mixture as water and sulfuric acid is added and the pressure raised to about 100-200 lb., while maintaining the temperature about 40°[1]. Cellulose fibers may be softened prior to acetylation by first introducing chlorine or bromine gas into the dry fibers, then vaporizing acetic acid through the mass[2], the temperature being kept below 65°. An entirely homogeneous cellulose acetate is said to result when cotton is subjected to a preliminary treatment with hot acetic acid vapors so as to soften the cellulose[3], then adding the esterizing agent in successive and suitably selected portions, such additions being made only after the state of equilibrium, corresponding to the degree of concentration brought about by the addition which has modified the concentration has been established, and continuing until the desired acetyl content has been introduced into the cellulose.

It is claimed as advantageous in operating under the above process to effect saponification in two phases[4], the first consisting in destroying excess of acetic anhydride and restoration to a temperature bordering on that which existed prior to the commencement of the operation, while the second phase consists in adding a bath of water, acetic and hydrochloric acids. Or[5], the cellulose may first be pretreated with a halogen, and then to a series of successive partial esterifications, while preventing increase of temperature 6° during at least the first two partial acetyllations. Preliminary to treatment of cellulose with chlorine[6], a bath of hydrogen dioxide and a soap is said to

1. A. Russell and J. Hegeman, U. S. P. 1752853; abst. C. A. 1930, **24**, 2600; J. S. C. I. 1930, **49**, 900-B; Brit. Plastics, 1930, **2**, #17, 230; Plastics, 1930, **6**, #7, 394; Rayon and Rayon Journal, 1930, **10**, #10, 8.
2. Ruth-Aldo Co., Inc., Can. P. 301734.
3. *Ibid.* Can. P. 301932.
4. *Ibid.* Can. P. 301933.
5. *Ibid.* Can. P. 301934.
6. *Ibid.* Can. P. 301935.

open up the fibers and result in a more uniform acetylcellulose being produced.

Color screens have been described[1] formed of particles of dyed and hardened gelatin held with a cellulose acetate solution. These particles, dyed red, blue and green, are hardened with formaldehyde, dried and reduced to powder, the grains being then mixed in desired proportion with acetylcellulose lacquer and poured on the surface of the emulsion or backing, and traversed by a scraper to produce a layer of thickness of an individual particle. Or[2], particles of dyed cellulose ester may be used. If acetylcellulose is to be dyed with phenolic ethereal salts of vat colors[3], the ester is impregnated with the ethereal salt at an elevated temperature (50-80°), preferably with addition of salt, and after ½-1 hour the vat dye is developed. Or[4], the ester may be padded with the ethereal salts of vat dyes at a raised temperature, and the dyeings developed after drying without steaming.

Anthraquinone monosulfonates are prepared by way of mixed 9.10-esters[5], 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, acylating, and partially hydrolyzing the resulting mixed 9.10-diester to split off the acyl group. Products are obtained excellent for dyeing acetyl silk. Dry powders of anthraquinone (acetylcellulose silk dyes as Duranol Blue CB, Duranol Orange G, or Duranol Red 2B) are prepared by mixing aqueous pastes of the dyes with alkali soaps of higher fatty acids[6],

1. C. Ruzicka, E. P. 326764; abst. Chem. Zentr. 1930, II, 3691.
2. *Ibid.* E. P. 326779, 326780, 326781; abst. C. A. 1930, **24**, 4721; Chem. Zentr. 1930, II, 3691. Ital. P. 270336.
3. J. Wilson, J. Thomas and Scottish Dyes, Ltd., E. P. 330216; abst. C. A. 1930, **24**, 6033; J. S. C. I. 1930, **49**, 859-B.
4. *Ibid.* E. P. 330253; abst. C. A. 1930, **24**, 6033; J. S. C. I. 1930, **49**, 859-B.
5. D. Fairweather, J. Thomas and Scottish Dyes, Ltd., E. P. 332907; abst. C. A. 1931, **25**, 604; Chem. Zentr. 1931, I, 3399.
6. J. Wilson, F. Beckett, J. Thomas and Scottish Dyes, Ltd., E. P. 333236; abst. C. A. 1931, **25**, 602; Chem. Zentr. 1930, II, 3338.

and subsequently drying below 50°. Other solubilizing or dispersing agents may be conjointly used, as saponin, cellulose waste liquor, formaldehyde-naphthalenesulfonic acid condensate, or condensation products of naphthalene sulfonic acids.

Cellon and Cellophane may be easily differentiated by the fact that acetone dissolves the former, but not the latter, but A. Segitz[1] prefers to use ultraviolet light, wherein the former does not absorb the violet fluorescing component of spruce bark extract, while Cellophane does. The cellulose nitrobenzoates have been critically studied[2], and the monobenzoate, mononitrobenzoate and mononitrate prepared. The explosive properties of the nitrobenzoates are similar to normal cellulose nitrates, but, compared with equally nitrated normal cellulose, these mixed esters are more stable, less hygroscopic, and less soluble in ether-alcohol, and burn at a slower rate.

The increasing percentage of rayon and acetylcellulose in rags used for paper making[3] has caused a pulping study to be made. The samples were digested with NaOH and calcium hydroxide with a loss of 4-12% of fiber, the strength of the rayon pulps being insufficient to allow the preparation of test sheets. The addition of these pulps to sulfite greatly decreased the strength of test sheets made from the mixture. E. Shilov[4] has discussed the thermodynamic problems in the preparation of acetic acid from methyl alcohol and carbon dioxide, and N. Sidgwick and L. Woodward[5], the spectrometric determinations of the effect of a neutral salt on the dissociation of acetic acid. Acoustic

1. A. Segitz, Papier-Fabr. 1930, **28**, 206; abst. C. A. 1930, **24**, 3642; Chem. Zentr. 1930, II, 840.
2. M. Sendo and J. Kondo, Cellulose Ind. (Tokyo) 1930, **6**, 150; abst. C. A. 1931, **25**, 1668; J. S. C. I. 1930, **49**, 812-B; Chem. Zentr. 1930, II, 1214.
3. M. Shaw and G. Bicking, Bur. Standards J. Research, 1930, **4**, 203; abst. C. A. 1930, **24**, 3365.
4. J. Chem. Ind. (Moscow) 1930, **7**, 110; abst. C. A. 1931, **25**, 4524; J. S. C. I. 1932, **51**, 12-B; Chem. Zentr. 1930, II, 463.
5. Proc. Roy. Soc. 1930, A, **130**, 1; abst. J. S. C. I. 1931, **50**, 168-A.

diaphragms, as those of telephone transmitters[1] (see p. 543, n. 7) may be made of cellulose acetate, various structural details being described in the original patent.

Acetic acid may be recovered from an acetylation mixture by adding an amount of water greater than that necessary to destroy all the anhydride remaining (e.g. 6-8% water)[2], the mixture being allowed to stand at 30-35° until the acetylcellulose has become soluble in acetone, then transferred to a digester and intimately mixed with finely ground sodium acetate, and the acetic acid distilled off. In the dyeing of aniline black on cellulose acetate[3], fibers or fabrics are treated with a mixture containing aniline and at least one organic amine serving as an oxidation catalyst, as *p*-aminodiphenylamine, *p*-phenylenediamine, *p*-aminophenol or nitrosodimethylaniline, followed by oxidation in a hot, acidified bichromate solution nearly saturated with salt. Other amines may be used, as *o*- and *p*-toluidines, *m*-phenylenediamine or *α*-naphthylamine. P. Sisley in 1930 reviewed the various[4] types of dyeing acetylcellulose, pointing out the dyes still needed in the industry.

In cellulose formate manufacture[5], completely dried cellulose is treated with substantially absolute formic acid in the presence of sulfuric, hydrochloric, sulfurous, benzenesulfonic or toluenesulfonic acids, zinc, calcium, or iron chlorides or bisulfates, and the formyl esters obtained hydrolyzed directly in a sufficiently concentrated formic medium by the progressive addition of a small quantity of water while assisting the reaction by stirring. Wood may be formylated into the ester, and formic acid in the vapor form used[6]. Acetic acid may be obtained from pyrolig-

1. Siemens Bros. & Co., Ltd., and W. Goodwin, E. P. 329429; abst. C. A. 1930, **24**, 5445.
2. O. Silberrad and H. Bleasdale, F. P. 693568; abst. C. A. 1931, **25**, 1671. See F. P. 693569.
3. Silver Springs Bleach. & Dye. Co. and A. Hall, E. P. 337746.
4. Tiba, 1930, **8**, 1043; abst. C. A. 1931, **25**, 208.
5. Soc. Anon. Distilleries des Deux-Sevres, E. P. 311695; abst. C. A. 1930, **24**, 959; Chem. Zentr. 1929, II, 1601. Can. P. 301020.
6. *Ibid.* E. P. 323693, Addn. to 311695; abst. J. S. C. I. 1930, **49**, 236-B; Chem. Zentr. 1930, I, 3366.

neous acid[1], by extracting with such solvents as mesityl oxide, butyrone, cyclohexanone, or mixtures of these, including amyl acetate. Acetic acid may be produced from lactic acid by neutralizing a suitable fermentation wort[2], clarifying and concentrating, then extracting with a solvent as above outlined. Acetic acid may be concentrated in aqueous solution by using two solvents[3]. The first solvent (benzene, xylene, carbon tetrachloride, chloroform) permits extraction of acetic acid from water in which it is but slightly soluble, and the other solvent (sulfuric acid, or phosphoric acid mixed with calcium chloride) being insoluble in the former, but can dissolve acetic acid contained in it. From the latter mixture, concentrated acetic acid may be distilled.

Cellulose butyrates and *iso*butyrates may be prepared by treating cellulose with butyric anhydride in the presence of sulfonic acids derived from aliphatic hydrocarbons as methane- or ethane-sulfonic acid, preferably in the presence of a solvent for the ester formed, as butyric acid, benzene or monochloracetic acid. Improved results are obtained by pretreatment of the cellulose with butyric acid, with or without a catalyst as methanesulfonic acid[4]. Cellulose butyrates soluble in methyl alcohol are obtained by subjecting cellulose tributyrate dissolved in a solvent containing water as butyric acid[5], to the saponification action of the water present, preferably in the presence of a saponification catalyst such as an inorganic acid, sulfonic acid, a bisulfate or zinc chloride.

1. Soc. Anon. Distilleries des Deux-Sevres, E. P. 330026; abst. C. A. 1930, **24**, 6002; J. S. C. I. 1930, **49**, 807-B; Chem. Zentr. 1930, II, 2215. Belg. P. 374646. F. P. 679442; abst. C. A. 1930, **24**, 3898.
2. *Ibid.* Can. P. 307004.
3. Soc. des Produits Chim. de Clamecy and E. Charles, F. P. 696803; abst. C. A. 1931, **25**, 2738; Chem. Zentr. 1931, I, 2674.
4. Societe des Usines Chimiques Rhone-Poulenc, E. P. 323869; abst. C. A. 1930, **24**, 3368; Cellulose, 1930, **1**, #7, 198; J. S. C. I. 1930, **49**, 319-B.
5. *Ibid.* E. P. 328259; abst. C. A. 1930, **24**, 5496; J. S. C. I. 1930, **49**, 760-B; Brit. Plastics, 1930, **2**, #17, 101; Chem. Zentr. 1930, II, 1306. Can. P. 303242.

For the production of crotonylcellulose[1], a crotonic acid pretreatment of cellulose with crotonic acid is given (see p. 807, n. 2; 833, n. 7; 835, n. 5), and subsequently esterified with crotonic anhydride in the presence of a catalyst (sulfuric acid, sulfonic acid, zinc chloride), with or without diluents (benzene, toluene or melted crotonic acid). These esters may be subjected to a partial saponification in solution in a solvent containing water[2], and preferably in the presence of saponification catalysts, to produce cellulose crotonates of modified solubilities. In preparing cellulose acetocrotonates[3], cellulose is treated with crotonic anhydride in the presence of acetic acid and a catalyst, with or without a solvent or diluent at 15-75°. Cellulose diacetocrotonate has been described. In a similar manner of procedure, methods for the preparation of cellulose palmitate, stearate, laurate, or phenylacetate have been described[4] (see p. 200, n. 6; 234, n. 2; 648, n. 6), esterification being facilitated by pretreatment of the cellulose with chlorhydrin or chloracetic acid at 90° for 16 hrs., the esters obtained softening or melting at 65-135° without decomposition. Cellulose acetocrotonates may also be prepared by treating cellulose with crotonic anhydride in the presence of acetic acid and a catalyst[5].

Safety glass is made by dipping two sheets of glass and an intermediate plastic acetylcellulose sheet[6], superficially softened and free from volatile solvents, into a bath

1. Soc. des Usines Chimiques Rhone-Poulenc, E. P. 328508; abst. C. A. 1930, **24**, 5496; J. S. C. I. 1930, **49**, 655-B; Chem. Zentr. 1930, II, 1803. Can. P. 305507.

2. *Ibid.* E. P. 329704; abst. C. A. 1930, **24**, 6014; J. S. C. I. 1930, **49**, 858-B; Brit. Plastics, 1930, **2**, #16, 183; #17, 230; Chem. Zentr. 1930, II, 1803. Can. P. 305508.

3. *Ibid.* E. P. 331260, Addn. to 328588; abst. C. A. 1931, **25**, 204; J. S. C. I. 1930, **49**, 943-B; Brit. Plastics, 1930, **2**, #18, 278. Can. P. 305509. F. P. 684550; abst. C. A. 1930, **24**, 5306.

4. *Ibid.* E. P. 330575; abst. C. A. 1930, **24**, 6014; J. S. C. I. 1930, **49**, 900-B; Chem. Zentr. 1930, II, 2333. F. P. 689244; abst. C. A. 1931, **25**, 1082.

5. *Ibid.* F. P. Addn. 37606 to 684550; abst. C. A. 1931, **25**, 4706.

6. *Ibid.* F. P. 690803; abst. C. A. 1931, **25**, 1351. Compare F. P. 688884. F. Addn. 36863 to 658563.

composed of plastifiers for the plastic material, removing air bubbles, pressing the sheets lightly together, and then removing them to an autoclave in which a heated gas under pressure is introduced. Tri-*m*-hydroxyphenyl phosphate has been introduced as an acetylcellulose plasticizer and fire-retarding agent[1].

Cellulose butyrates have been described (see pp. 185, 328, 360, 495, 529, 559, 588, 621, 667, 811, 832)[2], by the use of butyric anhydride, butyric acid and monochloracetic acid. As a pretreatment of cellulose for acetylation, a method has been evolved in which the cellulose is reduced to the colloid state[3], and then esterified in a non-solvent medium. If the cellulose is partially acetylated at a temperature below 30°, and then esterified to the triacetate stage at a higher temperature, both operations being carried out at a pressure of 50-180 pounds, an ester of unusually high stability and low viscosity is said to result[4]. Cotton, linen or rayon may be immunized to direct dyestuffs in a single operation without weakening the fibers[5], by subjecting the material without any preliminary treatment, to the anhydride or chloride of an aromatic carboxylic acid (phthalic anhydride, phthalyl chloride, benzoyl chloride), in the presence of a tertiary base (pyridine, quinoline, triethylamine, diethylamine). If, for example, cotton is treated with phthalic anhydride and pyridine, the product is immune to direct and acid dyes but has a strong affinity for basic dyes. Maleic or succinic anhydrides may also be used.

Crepe effects on acetylcellulose fabrics are formed at least in part of highly twisted yarns by treatment of the

1. Soc. des Usines Chimiques Rhone-Poulenc, F. P. 691337; abst. C. A. 1931, **25**, 1082; Chem. Zentr. 1931, II, 3691.
2. Societe des Brevets Etrangers Lefranc & Co., Belg. P. 368431.
3. Soc. Dispersoid Francais, F. P. 692106; abst. C. A. 1931, **25**, 1379; Chem. Zentr. 1931, I, 1698.
4. Soc. Lyonnaise de Soie Artificielle and P. Chevalet, Holl. P. 21864.
5. Soc. Industry in Basle, E. P. 319584; abst. Chem. Zentr. 1930, I, 1377. Belg. P. 374858. Compare E. P. 284358.

material in a bath having a marked swelling action, but little or no peptizing action on the cellulose acetate (see p. 62, n. 1; 270, n. 4; 302, n. 6; 701, n. 4)[1]. Suitable substances are methyl or ethyl alcohols, their aqueous mixtures, benzene, toluene, trichlorethylene, carbon tetrachloride, guaiacol or aniline emulsions, or ethyl acetate. Fabrics formed in part of viscose and of cellulose acetate may be treated as above. If it is desired to induce mat effects on cellulose acetate[2], there is dissolved in the spinning solution a small quantity of soluble acid as stearic acid or a soluble anhydride, dry-spinning the solution obtained, and treating the filaments with aqueous solutions of salts which form water-insoluble compounds with the acid used.

A paper appeared in 1930 containing exhaustive experimental data on the relation between thermal condition and thickness for compressed pads of loose acetylcellulose[3], and relation between thermal conductivity and density at constant thickness and the effect of weave and various finishing processes thereon, and the specific conductivities. A study has been made of the acetolysis of cellulose[4], and the influence of temperature, duration of acetolysis and sulfuric content of the reaction mixture upon the yield of cellobiose octa-acetate. Yields of 42.3% of theoretical were obtained, in some instances with the formation of a considerable quantity of glucose penta-acetate. A plasticizer for use in the manufacture of cellulose ester plastics[5] comprises *b*-naphthyl-diphenyl (or dicresyl) phosphate.

1. 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.

2. *Ibid.* F. P. 695490; abst. C. A. 1931, **25**, 2849; Chem. Zentr. 1931, I, 1699. F. P. 695491; abst. C. A. 1931, **25**, 2849; Chem. Zentr. 1931, I, 1700. D. R. P. 502320; abst. C. A. 1930, **24**, 4932; Chem. Zentr. 1930, II, 1926.

3. J. Speakman and N. Chamberlain, J. Textile Inst., 1930, **21**, 29-T; abst. C. A. 1930, **24**, 4937.

4. C. Spencer, Cellulosechemie, 1929, **10**, 61; abst. C. A. 1929, **23**, 5038; J. S. C. I. 1929, **48**, 389-B.

5. Spicers, Ltd., F. P. 696603; abst. C. A. 1931, **25**, 2848; Chem. Zentr. 1931, I, 2291.

Multicolored screens are applied to a film of acetyl- or nitro-cellulose[1] by applying on the surface of the film a coloring material and afterwards printing successively on the surface of the film, lines or other geometric designs by means of an agent containing a compound capable of reacting with this constituent to form a differently colored dye. Or[2], a greasy resist containing a dye is applied as by printing to the film surface, the dye migrating 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 patterns remains on the film. H. Stadlinger[3] has made a comprehensive comparison with illustrations, of various brands of cellulose acetate silks[4], and discussed the significance of

1. Spicers, Ltd., F. P. 698258; abst. C. A. 1931, **25**, 2930; Chem. Zentr. 1931, I, 2572. Spicers, Ltd., J. Goldsmith, T. Baker and C. Bonamico, E.P. 333865; abst. C.A. 1931, **25**, 652; J.S.C.I. 1930, **49**, 1093-B.

2. J. Goldsmith and Spicers, Ltd., Chem. Zentr. 1930, II, 3891. Compare E. P. 217557, 322432.

3. H. Stadlinger, Melliand, 1930, **2**, 1106. Textilber. 1930, **11**, 450; abst. J. S. C. I. 1930, **49**, 707-B. Kunstseide, 1930, **12**, 383; abst. C. A. 1931, **25**, 3829.

4. He has found that the physical and dyeing properties of Setilose (Fabr. de Soie Artificielle de Tubize), Celanese, Fr. Rhodiaseta (Soc. pour la Fabr. de la Soie Rhodiaseta, Rousillon), G. Rhodiaseta (Deutsche Acetat-Kunstseide A.-G. "Rhodiaseta," Freiburg), Aceta (Aceta Ges. m. b. H., Berlin-Rummelsberg), Apex, and "Drya" (N. V. Nederlandsche Kunstzijdefabriek) silks. The acetyl contents (%) of the silks are: Setilose (53.2), Celanese (53.8, Fr. Rhodiaseta (54.4), G. Rhodiaseta (54.3), and Aceta (54.9), and the viscosities of their 2% solutions in acetone are 5.70, 5.80, 5.55, 5.75 and 8.85, respectively. The dry and wet tensile strengths, and also the dry tensile strength after immersion for 0.5 hr. in boiling water (g. per 1 denier at 20° and R. H. 60%), are, respectively: Setilose (1.22, 0.64, 1.08), Celanese (1.23, 0.64, 1.08), Fr. Rhodiaseta (1.25, 0.76, 1.12), G. Rhodiaseta (1.33, 0.78, 1.22), and Aceta (1.34, 0.90, 1.36). Under similar conditions the extensibilities were 28.2, 31.7 and 20.5%; 26.0, 32.2 and 19.4%; 27.7, 38.5 and 21.5%; 24.7, 32.8 and 19.9% 26.4, 36.4 and 19.9%, respectively. Celanese and Fr. Rhodiaseta silks lost much luster and became woolly, whereas Setilose and G. Rhodiaseta silks lost but little luster and became only slightly woolly, and Aceta silk was almost unaffected when boiled in water for 0.5 hr. Setilose silk had the highest affinity for Cellit (cellulose acetate) dyes, Celanese having the next highest affinity, and the other silks considerably less affinity; Celanese showed an abnormally high affinity for Cellit Fast Blue A when dyed with a mixture of dyes containing this dye. Setilose and Aceta silks have the softest handle, and G. Rhodiaseta the harshest. The fluorescence of the silks in ultraviolet light was affected by means of lubricating oils added to the silk, but after extraction with ether, Setilose and Aceta silks showed the strongest fluorescence (violet). The cross-sections of Apex, Enka-

fiber cross-section in acetylcellulose filament manufacture[1].

A method for the spray-drying of cellulose acetate solutions has been devised[2], in which fine droplets of a flowable reaction mixture comprising acetylcellulose, acetic acid and an organic liquid as ethylene dichloride which is miscible with these and is highly volatile, are sprayed into a dessicating, gaseous vehicle which absorbs acetic acid vapors and the volatile liquid with great rapidity, causing disruption of the particles with production of a fine powder, the particles of which are rough surfaced and highly permeable to liquids. C. Staud[3] has discussed acetylcellulose plasticizer and solvents and enumerated their properties and applicability, together with tests for determining the stability[4], while H. Staudinger, K. Frey, R. Signer, W. Starck and G. Widmer[5] have delineated the highly polymerized compounds of cellulose, including molecular

Drya and La Soie de Clairoix are similar in that they are ribbon-like and free from indentations; those of Celanese, Aceta, Setilose and Fr. and G. Rhodiaseta are circular and slightly indented.

1. Stadlinger, Jentgen's Rayon Review, 1930, **2**, 240; Kunstseide, 1930, **23**, 310; abst. C. A. 1931, **25**, 1679, 3829.

2. C. Staud, U. S. P. 1762937; abst. C. A. 1930, **24**, 3901; J. S. C. I. 1931, **50**, 261-B; British Plastics, 1931, **2**, #23, 529; Plastics, 1930, **6**, #8, 457; #11, 672. Cites U. S. P. 1516225.

3. Cellulose, 1930, **1**, #6, 166; #7, 191.

4. C. Staud, Paint, Oil and Chem. Rev. 1930, **89**, #18, 8; abst. C. A. 1930, **24**, 3111; Chem. Zentr. 1930, II, 476.

5. Ber. 1930, **63**-B, 2308; abst. C. A. 1931, **25**, 280; J. S. C. I. 1930, **49**, 1415-A. The viscosity of more or less degraded triacetylcelluloses in chloroform was determined. The products were dissolved in glacial acetic acid (in which according to Hess they are monomeric at great dilution), the solvent largely removed by vacuum, and the solute precipitated by water. Since the viscosity of the products in chloroform is not affected by the treatment, it is considered that the cellulose acetates are different substances and that their difference does not depend on varying state of aggregation of one and the same molecule. Attempts were made to prepare polymeric-homologous series of cellulose derivatives. The acetates are unsuitable for this purpose. Fission of triacetylcellulose with hydrogen chloride leads to the production of degraded products of differing mean mol. wt. and varying chlorine content; solutions of the simpler products are less viscous than those of equally concentrated solutions of the more complex products. Allylation of cellulose proceeds more easily than methylation, but does not lead to fully alkylated products. Starch and cellulose react incompletely with sodamide in liquid ammonia and treatment of the products with methyl iodide affords only incompletely alkylated compounds.

Degradation of cellulose, starch, lichenin, etc., and their deriva-

weight determinations of cellulose acetates[1], and an attempt to determine the molecular size of cellulose[2].

tives lead to series of polymeric-homologous products for which the following nomenclature is proposed. They are regarded as derivatives of polymeric glucans, mannans or lævulans. The chains can be terminated by hydroxyl, methoxyl, acetyl, chlorine, etc., as with the polyoxymethylene and polyethylene oxide chains. The compounds $OR.[C_6H_{10}O_5]_x.R'$ are thus polyglucan dihydrate (R=R'=H), polyglucan diacetate (R=R'=Ac), polyglucan dimethyl ether (R=R'=Me). The position of the free hydroxyl groups is indicated by numerals, thus poly-(2:3:6-glucan) dihydrate. The degradation products of cellulose, starch and lichenin are polycelloglucan, polyamyloglucan and polylichenoglucan compounds.

1. H. Staudinger and H. Freudenberger, Ber. 1930, **63**-B, 2331; abst. C. A. 1931, **25**, 280; J. S. C. I. 1930, **49**, 1416-A. Cellulose was treated with acetic anhydride and zinc chloride at 60° and 80° respectively and, at definite intervals, portions of the solution are withdrawn, diluted with glacial acetic acid to a concentration of 0.25 or 0.29 mol., and subjected to viscosity measurements. With the series of polytriacetylcelloglucan diacetates, the mol. wt. of the simpler members is determined by the method of Bergmann and Machemer, which is valid for degrees of polymerisation of 20-60. With more complex products the terminal groups form so insignificant a part of the molecule that their accurate determination is no longer possible. Viscosity measurements with these hemicolloids permit relationships to be established between viscosity and mol. wt. which can be applied to determination of the mol. wt. of the more complex products.

Initially, degradation of the cellulose molecule occurs very rapidly under the action of acetic anhydride and zinc chloride, but the simpler products are much more resistant. The initial, highly viscous solutions contain cellulose triacetates of mean degree of polymerisation 60-100; after 120 hrs. action the degree is reduced to 10. At the ordinary temperature reaction proceeds extremely slowly, giving products with degree of polymerisation 150. After 7 days at 30° the degree is 130 and after 10 days it is 100. Since native cellulose is more highly polymerised than the most complex of the acetates, its mol. wt. must be above 24,000; it appears probable that the cellulose molecule contains a chain of 500-1000 glucose residues and thus has dimensions similar to those of the caoutchouc molecule.

The simpler cellulose acetates dissolve without swelling to mobile solutions the viscosity of which increases proportionally to the concentration over a large range. Slightly degraded cellulose acetates swell very markedly; their viscosity in solution increases far more rapidly than the concentration, so that very viscous solutions can be obtained at relatively great dilution. In them, the total region of the macromolecules is greater than the available volume in relatively dilute solution. In place of sol solutions in which the macromolecules have free movement, they represent gel solutions in which the macromolecules impede one another. A 10-triacetylcelloglucan diacetate behaves in solution like a simple substance and the gel condition is not reached until the concentration attains 22%. With a 150-triacetylcelloglucan diacetate the transition between sol and gel lies at 1.4%.

2. H. Staudinger and O. Schweitzer, Ber. 1930, **63**-B, 3132.

In the manufacture of acetic acid by oxidizing acetaldehyde with O, the concentration of peracid is kept below about 0.2% by a continuous circulation of crude acetic acid[1]. The peracid in this form is placed into contact with acetaldehyde on a large surface to be transformed. Chlorination of acetic acid may be effected in the presence of a chlorinating catalyst (sulfur, sulfur chloride, phosphorus, or acetic anhydride) to form monochloracetic acid[2], and the chlorination is then continued at successively higher temperatures (suitably up to 160°) to form the trichlor-compound. Wood may be acetylated in the absence of an inorganic catalyst (see p. 647, n. 4; 664, n. 12; 725, n. 1; 836, n. 3), especially in the presence of a tertiary organic base[3], the acetylated product retaining the appearance of natural wood and is insoluble in all solvents. It does not give the color tests for lignin, and is more resistant than natural wood to light, water and splitting. Wood acetate, butyrate and benzoate are described.

An artificial silk has been described in which filaments[4], obtained either by the dry- or wet-spinning of cellulose acetate are drawn under adequate tension in the presence of swelling agents (methylene chloride, chloroform, tetrachlorethane) and organic substances (carbon tetrachloride, benzene, toluene, xylene) which have the power of diminishing the solvent action of the agents. Tackles Freres[5] have described a photographic film comprising a coating of white wax or ox gall applied to a strip of paper or thin, flexible metal, followed by a pasty coating of cellulose acetate in admixture with wood fiber. The sensitized emulsion is then applied. The film thus obtained may readily be removed from the supporting base.

1. W. Strecker, F. P. 688417; abst. C. A. 1931, **25**, 714; Chem. Zentr. 1931, I, 156.
2. C. Strosacker, U. S. P. 1757100; abst. C. A. 1930, **24**, 3250; Chem. Zentr. 1930, II, 981.
3. H. Suida and H. Titsch, Aust. P. 122499; abst. C. A. 1931, **25**, 4104; Chem. Zentr. 1931, II, 1224.
4. H. Suter, F. P. 696306; abst. C. A. 1931, **25**, 2849; Chem. Zentr. 1931, I, 1699. F. addn. 40105 to 696306.
5. Belg. P. 366501; abst. C. A. 1930, **24**, 4474.

The velocity of swelling of acetylcellulose film has been determined[1], maximum swelling being obtained in a 20% ethyl alcohol solution. The elongation of strips of the film under a given load was proportional to the degree of swelling. The load-elongation curves of acetone-soluble acetylcellulose films prepared from cellulose acetate in acetone and triacetin[2] resemble those of Cellophane steeped in acetone-water mixtures, the former film containing triacetin showing both elastic and plastic elongation. The tensile strength of a film containing the plasticizer was unaltered by immersion in water.

In a study of the properties of cellulose acetate and Cellophane film as dialysis membrane[3], the diffusion rates of certain acids and salts are proportional to the diffusion coefficients of the solutes, except where the latter have a specific action on the membrane, making its passage easier. Experiments on the rate of diffusion $N/10$ lithium chloride and of sodium hydroxide are given. A. Tate[4] has given directions for finishing acetate fabrics, including the removal of creases and wrinkles and imparting to the goods a soft "handle."

H. Tatu[5] has outlined methods for the differentiation of artificial silks, his conclusions being that greater reliance must be placed upon a few simple tests, as solubililty of acetate in acetone, the diphenylamine test for nitrocellulose, boiling viscose with dilute sulfuric acid and testing for hydrogen sulfide formed, and finally, if negative results have been obtained with all three of the above, looking for copper in the ash to determine copperammonia cellulose.

1. K. Tanemura, J. S. C. I. Japan, 1930, **33**, 497; Caout. et Gutta. 1930, **28**, 15464; abst. C. A. 1931, **25**, 2560; J. S. C. I. 1931, **50**, 479-B; Brit. Plastics, 1931, **3**, #28, 63.
2. *Ibid.* J. S. C. I. Japan, 1930, **33**, 499; abst. C. A. 1931, **25**, 2560; Brit. Plastics, 1931, **3**, #28, 179.
3. K. Tanemura and S. Miyoshi, J. S. C. I. Japan, 1930, **33**, 432; abst. C. A. 1931, **25**, 2560; J. S. C. I. 1931, **50**, 340-B.
4. Melliand, 1930, **2**, 111; abst. C. A. 1930, **24**, 3376.
5. Ann. chim. anal. chim. appl. 1930, **12**, 129; abst. C. A. 1930, **24**, 4150; Chem. Zentr. 1930, II, 1800.

A raw material suitable for phonograph records[1] comprises gelatinized acetylcellulose with camphor or camphor substitute, dried at 40-80° for 24 hours for each 0.1 mm. thickness, details of manufacture being given in the original patent. In 1930 G. Tocco and A. Nyssens[2] published their method of analysis of cellulose formate by treating the dry ester at 135-150° with *N*/1 potassium bichromate for 2 hours, then slowly and with cooling with sulfuric acid, excess of bichromate being determined by iodometric titration. The cc. of *N*-bichromate required for 1 gm. is 148.14, 136.78, 128.43 and 121.95 for cellulose, and the mono-, di- and tri-formates respectively.

Water-soluble cellulose and starch sulfates are prepared by treating the dry carbohydrates with sulfur dioxide dissolved in an inert liquid diluent as carbon bisulfide[3]. J. Trillat[4] has made an X-ray study of cellulose acetate and nitrate in such a way as to obtain different diagrams as a function of the degree of esterification, results using powdered acetylcellulose showing that films have a structure sufficiently different from the fibrous ester to allow of identification of the products. The molecular condition of cellulose di- and tri-acetate has been investigated[5], each being dispersed by spreading on a clean mercury surface a drop of the suspension suitably dissolved. When the dispersing liquid has evaporated the area covered by the dispersed substance was measured and its thickness calculated. The limiting thicknesses in A. U. were: cellulose nitrate, 2.5-5; cellulose triacetate 9.85, cellulose diacetate 3.8-4.2. The behavior of these substances agrees with Staudlinger's

1. A. Thomae, E. P. 337437; abst. C. A. 1931, **25**, 2255; J. S. C. I. 1931, **50**, 171-B; Brit. Plastics, 1931, **2**, #23, 531.

2. G. Tocco and A. Nyssens, Giorn. Chim. Ind. Appl. 1930, **12**, 124; abst. C. A. 1930, **24**, 3641; J. S. C. I. 1930, **49**, 607-B.

3. W. Traube, E. P. 322003; Addn. to E. P. 294572; abst. Chem. Zentr. 1930, I, 3355.

4. J. phys. radium, 1930, **1**, 340; abst. C. A. 1931, **25**, 3828; J. S. C. I. 1931, **50**, 27-A. J. Phys. Radium, 1931, **2**, 65; abst. J. S. C. I. 1931, **50**, 548-A.

5. S. Sheppard, A. Nietz and R. Keenan, Ind. Eng. Chem. 1928, **21**, 126; abst. C. A. 1929, **23**, 1796; J. S. C. I. 1930, **49**, 287-A.

conception of extended chains of atoms held by homopolar primary valences.

In the manufacture of stratified bodies as strengthened glass[1] (see p. 294, n. 5; 480, n. 4; 525, n. 5; 690, n. 6; 735, n. 4; 740, n. 7; 754, n. 5; 789, n. 1), the inner surfaces of two or more sheets of glass are first coated with gelatin and a cement containing a cellulose ester, the surfaces being then sprayed with a solvent which will cause swelling of the gelatin and ester. The sheets are then coapted by fluid pressure, finally with heat and pressure, and allowed to remain in this condition for a number of hours to assure complete and uniform adhesion. When sheets of ash-free cigaret paper 40 microns thick, made from pure cellulose[2] were irradiated with cathode rays perpendicular to the surface of the paper, no diffraction pattern was observed, but when part of the electron bundle was passed through a pinhole in the paper, an electron diffraction pattern, due to the cellulose crystals at the edge of the pinhole, was formed, similar to that obtained by S. Kikuchi with mica. Tangential irradiation of cellulose acetate gave a similar diffraction effect.

In the esterification of cellulose[3], manufacturing costs are said to be reduced by the use of liquid sulfur dioxide (see p. 566, n. 4; 620, n. 8; 669, n. 5), in that it avoids the large amounts of dilute acetic acid values resulting in the usual processes. The cellulose is acetylated in the presence of the SO_2, the ester produced being hydrolyzed in the same medium to the desired solubility by the addition of water,

1. Triplex Safety Glass Co., W. Lyttleton, J. Wilson and H. Dick, E. P. 328919; abst. J. S. C. I. 1930, **49**, 664-B; Kunst. 1931, **21**, 93; Chem. Zentr. 1930, II, 2296.

2. C. Trogus, H. Halberschadt and K. Hess, Naturwiss. 1930, **18**, 846; abst. C. A. 1931, **25**, 876; J. S. C. I. 1930, **49**, 1353-A. G. Thomson, Proc. Roy. Soc. (London) 1928, A-**117**, 600. S. Kikuchi, Proc. Imp. Acad. Tokyo, 1928, **4**, 271. F. Kirchner, Naturwiss. 1930, **18**, 706.

3. U. S. Industrial Alcohol Co., E. P. 329718; abst. C. A. 1930, **24**, 6014; J. S. C. I. 1930, **49**, 708-B; Brit. Plastics, 1930, **2**, #16, 183; Chem. Zentr. 1930, II, 2719. L. Burghart, U. S. P. 1816564; abst. C. A. 1931, **25**, 5557. Can. P. 305232. F. P. 686491, 695401; abst. C. A. 1931, **25**, 591, 2847. Cites E. P. 306531.

with or without the addition of acetic acid or alcohol. By abrupt liberation of the SO_2, as gas the ester is discharged from the reaction vessel in a light and fluffy form. Acetic acid is obtainable in the anhydrous state[1] by employing a solvent which is only slightly soluble in water and whose boiling point is higher than acetic acid, and which does not form an azeotropic mixture with the anhydrous acid, amyl acetate for acetic acid, and ethyl or amyl propionate for propionic acid being recommended.

A. Van Heuckeroth[2] has examined "all resins" available on the American market for acid value, softening point, color and solubility and miscibility with cellulose acetate and lacquers containing them, and correlated the data obtained into available form. Acetic acid is producible on a commercial scale by the interaction of sulfuric acid and calcium acetate in the presence of added water at 80-105°, the resulting calcium sulfate being separated by filtration[3]. A process has received patent protection for the production of dental plates (see p. 107, n. 4; 614, n. 7)[4], in which dissolved acetylcellulose is combined with pigments, coloring matter and suitable plasticizing bodies. Acetic acid and methyl acetate result by catalytic synthesis from acetone and CO or gases containing them[5], at 250-450° and 300-500 atm. pressure, chromium or aluminum phosphates being the preferred catalysts.

In one method for decomposing ethylidene diacetate into acetic anhydride and acetaldehyde[6], by the catalytic action of acid in the presence of an indifferent diluent,

1. U. S. Industrial Alcohol Co., Can. P. 303890, 320860.
2. A. Van Heuckeroth, Am. Paint & Varnish Manufrs' Assocn. Circ. 369, 1930, p. 354; abst. Plastics, 1931, **7**, #3, 173.
3. R. Van Schaack and R. Calvert, U. S. P. 1765318; abst. C. A. 1930, **24**, 4052; Chem. Zentr. 1930, II, 1770.
4. Vercingetorix Auguste Lapierre, F. P. 692400; abst. C. A. 1931, **25**, 1348; Chem. Zentr. 1931, I, 650.
5. Verein fur Chemische und Metallurgische Produktion, F. P. 698098; abst. C. A. 1931, **25**, 3015; Chem. Zentr. 1931, I, 2934.
6. Verein fur Chem. Ind. A.-G. and H. Walter, D. R. P. 495384; abst. C. A. 1930, **24**, 3251; Chem. Zentr. 1930, II, 465. See Verein fur Chem. Ind. A.-G. and E. Loew, D. R. P. 504722; abst. C. A. 1931, **25**, 413; Chem. Zentr. 1930, II, 2215.

phenol is employed. Nitrobenzene is added to the ethylidene diacetate before distillation to prevent resinification. Yield of acetaldehyde, 90%. An apparatus designed for the saponification of acetylcellulose has been patented[1]. In the production of fast dyeings and printings on acetylcellulose silk[2], the latter is treated with a solution of 2-(4-aminophenylamine)-7-(4-aminophenylaminoanaphthalene) chloride, and subsequently oxidized as with sodium bichromate, a blue-grey being produced. Other examples are given in the original patent for producing blue, greenish-black, blue-black or black. By scaping, the luster of the acetate silk is improved. E. Viviani in 1930 reviewed the methods of manufacture of various types of artificial filaments[3], stressing the advantages of that made from cellulose acetate.

The method of partial hydration of acetylcellulose as devised by S. Vles[4], comprises adding a mixture of 5 cc. sulfuric acid, sp. gr. 1.84, 46 cc. water and 55 cc. glacial acetic acid to a liter of cellulose acetate solution in glacial acetic acid containing 160 gm. ester, maintaining a temperature of 20° until the degree of solubility desired has been attained. The multicolor photographic screen of H. Wade[5] is fabricated by applying to an acetylcellulose film a nitrocellulose lacquer, allowing solvent to dissipate, then treating the coating to produce a multiplicity of differently colored regions.

It has been found that if a cellulose ester as the acetate is dissolved in a solution which contains a suitable aromatic acid and digested at an appropriate temperature in this solution, some of the acid groups which are combined with the cellulose will be displaced by the aromatic acid, and

1. Verein fur Chem. Ind. A.-G. and K. Werner, D. R. P. 515779; abst. C. A. 1931, **25**, 2567; Chem. Zentr. 1931, I, 2416.
2. P. Virck, U. S. P. 1774621; abst. C. A. 1930, **24**, 5167; Chem. Zentr. 1930, II, 3644. E. P. 306637; abst. Chem. Zentr. 1929, II, 1077.
3. Girm. chim. ind. applicata, 1930, **12**, 293; abst. C. A. 1930, **24**, 5153; Chem. Zentr. 1930, II, 3218. Atti III congresso naz. chim. pura applicata, 1930, 150; abst. C. A. 1931, **25**, 1072.
4. U. S. P. 1782796; abst. Plastics, 1931, **7**, #3, 177; Chem. Zentr. 1930, II, 2705.
5. H. Wade, Can. P. 298966.

mixed cellulose esters result. Tartaric, racemic, malic, glycollic, glyceric, pyruvic, *a*-ketobutyric, *a*-ketovaleric, *a*-ketocaproic, levulinic, *o*-, *m*-, and *p*-toluic, benzoic, mandelic, salicylic and cinnamic acids are said to be suitable, an example being cellulose acetotartrate[1]. The presence of ethylene chloride facilitates the reaction.

Two crystalline forms of *a*-glucose penta-acetate have recently (1930) been isolated from the chloroformic extract of the precipitation liquid from the acetolysis of cellulose without reacetylation[2]. The inflammability of celluloid is sought to be reduced by a method which comprises impregnating the swollen pyroxylin plastic with cellulose acetate dissolved in acetone to which 3-6% of acetic anhydride has been added[3]. A surface gloss may be induced by a final treatment with an alcoholic solution of shellac. Both celluloid and acetylcellulose are soluble in acetone and in acetic acid and anhydride. The viscosity of cellulose esters (primarily the nitrate[4], is materially reduced by treatment for some days with aqueous ammonia, sodium bicarbonate, calcium carbonate or zinc oxide. W. Weltzien[5] in 1930 published a review embracing the methods with comments for dyeing cellulose and acetylcellulose.

In the production of cellulose acetate, propionate and butyrate[6], water is removed from air-dried cellulose before esterification by intimately mixing in a ball or roller mill at temperatures up to 50° with sufficient fatty acid and anhydride to complete the esterification, but with catalyst

1. C. Webber and C. Staud, U. S. P. 1785466; abst. C. A. 1931, **25**, 592; J. S. C. I. 1931, **50**, 877-B. E. P. 338202. Can. P. 312806. New Zeal. P. 63304, 63305.
2. C. Webber, C. Staud and H. Gray, J. A. C. S. 1930, **52**, 1542; Abridged Scientific Pub. Kodak Research Lab. 1930, **14**, p. 69; abst. C. A. 1930, **24**, 2433; J. S. C. I. 1930, **49**, 749-A; Cellulose, 1930, **1**, #5, 149.
3. A. Weber, H. Hoppner and H. Weich, Can. P. 306819.
4. J. Weidig and Cellulose Utilities Corp., U. S. P. 1775179; abst. C. A. 1930, **24**, 5157; Cellulose, 1930, **1**, #9, 246.
5. W. Weltzien, Kolloid-Z. 1930, **52**, 110; abst. J. S. C. I. 1930, **49**, 815-B; Chem. Zentr. 1930, II, 2189.
6. K. Werner, E. P. 336349; abst. C. A. 1931, **25**, 1993; J. S. C. I. 1931, **50**, 16-B; Brit. Plastics, 1931, **2**, #21, 432.

insufficient to promote the reaction (0.02-0.05% of sulfuric acid or 0.05% sulfuryl chloride based on the weight of the cellulose); esterification is gradually carried out by gradual addition of a weak catalyst (sulfuryl chloride, phosphorous oxychloride), the temperature being allowed to rise to 60-70°. N. White in 1930 published an article on the dyeing and finishing of rayon and acetylcellulose based on his practical experience, containing various methods of procedure[1].

The results of experimentation on rats as to the antirachitic effect of winter sunshine through Celoglass (glass laminated by the interposition of an acetylcellulose sheet) has been reported upon[2]. The Wisconsin Alumni Research Association[3] has been granted patent protection for the manufacture of acetic and lactic acids by the fermentation of pentoses and hexoses obtained from wood, sawdust, straw and corncobs. In the formation of an inexpensive, substantially waterproof paper insulated electrical conductor[4], a metallic core is coated with a layer of loose fibrous material and a layer of textile material, the whole being impregnated with a plurality of acetylcellulose coats. The novelty involved in the cellulose esterification process of B. Wylam and J. Thomas[5], resides in the employment of pyridine sulfuro-anhydride (*N*-pyridinium sulfonic acid)[6].

The physical and chemical properties of immunised cotton, in which about half of the cellulose is in the form of the toluene-*p*-sulfonyl ester have been recorded[7], this "re-

1. Cotton, 1930, **94**, 575; abst. C. A. 1931, **25**, 596; Chem. Zentr. 1930, I, 3612. Cotton, 1930, **94**, 327; abst. C. A. 1930, **24**, 1743.
2. T. Wilder and C. Vack, Am. J. Diseases Children, 1930, **39**, 930; abst. C. A. 1930, **24**, 4328.
3. Wisconsin Alumni Research Foundation, E. P. 335596; abst. C. A. 1931, **25**, 1630; Chem. Zentr. 1931, I, 177.
4. E. Wood, U. S. P. 1762941. Cites U. S. P. 1615417.
5. U. S. P. 1748689; abst. Plastics, 1930, **6**, #5, 276; Chem. Zentr. 1930, II, 1803.
6. P. Baumgarten, Ber. 1926, **59**, 1166.
7. A. Woodhead, J. Soc. Dyers Col. 1930, **46**, 68; abst. J. S. C. I. 1930, **49**, 411-B.

serve cotton" being obtained by the action of benzoyl or phthaloyl chloride on alkalicellulose, while "immunized cotton" results from the action of toluene-*p*-sulfonyl chloride. The fibers are superficially esterified and resist the action of direct cotton dyes, but otherwise resemble untreated cotton. "Passive cotton" is said to consist of "cellulose mono- and di-acetates," which, since they are insoluble in the esterifying mixture, largely retain the original form of the cotton. The dyeing properties agree with those of acetate silk, the most important colors for the purpose being the SRA, Duranol, Setacyl, Cellit, Cibacet and other ranges. Mention is made of Karrer's amidated cotton formed by the action of ammonia on immunized cotton (see p. 278, n. 2).

W. Young[1] has contributed a general descriptive article on cellulose acetate dyeing problems, developing shades, scouring, and precautions in dyeing crepe-back satins (in which the satin is acetylcellulose and the crepe is silk), while G. Young the same year (1930) has analyzed the two major reasons for finishing aircraft fabric with acetylcellulose dope with details of application[2]. G. Zuccari[3] has succeeded in preparing a reagent of a mixture of several dyes, whereby the various artificial fibers may be differentiated, cellulose acetate being colored yellow.

Anonymous articles appearing in 1930 have covered information on the cellulose acetate plastic "Cellosite"[4], insulating with acetylcellulose[5], aniline black dyeing on acetate silk[6] and its affinity for dyestuffs in general[7], pro-

1. 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. For the manufacture of a high *a*-cellulose product from wood cellulose see Zellstofffabrik Waldhof and A. Bernstein, E. P. 337445; abst. C. A. 1931, **25**, 2288; Chem. Zentr. 1931, I, 1698.
2. Industrial Finishing, 1930, **6**, #10, 18.
3. La seta Artificiale, 1930, #1, 6; Progr. ind. Tint. tessili, **29**, 56; abst. C. A. 1930, **24**, 2607.
4. British Plastics, 1930, 327; Chem. Age, 1930, **23**, 231.
5. Melliand, 1930, **2**, 1170.
6. Rayon Record, 1930, **4**, #3, 161.
7. Rayon Record, 1930, **4**, #3, 163.

duction of acetate filaments resistant to delustering[1], scouring of acetate fabrics[2], dyeing and finishing acetylcellulose-cotton unions[3], the Eastman acetate yarn[4], micelle orientation in acetylcellulose silk[5], comparison of acetate fabrics[6] and mechanics of stretching[7], desizing difficulties in the acetylcellulose industry[8], lustering acetylcellulose[9], methods of cellulose acetylation[10], ornamental effects on acetate textiles[11], saponification methods for cellulose acetate[12], and details of mordanting treatments[13].

Advancement in the Organic Cellulose Ester Field, 1931. The number and importance of papers published and patents granted exceed those of any similar period in this art, attention being especially directed to the esters of cellulose with the higher aliphatic acids, endeavors to reduce the inflammability while still conserving the stability and other desirable characteristics of the nitrocellulose by means of the formation of mixed esters as the acetonitrates (nitroacetylcelluloses), and advancements in the production of artificial filaments and the fabrication into textiles, especially union goods which upon dyeing, induce differential effects of great beauty. The multiplicity and scope of the investigations are indicated by upwards of eight hundred individual contributions recorded in this period.

To reduce the electric charge carried by textile fibers sized with drying oils and resins[14], the fibers are treated after sizing with a solution containing an hygroscopic elec-

1. Rayon Record, 1930, **4**, #5, 282.
2. Rayon Record, 1930, **4**, #6, 331.
3. Rayon Record, 1930, **4**, #7, 377.
4. Rayon Record, 1930, **4**, #10, 516.
5. Rayon Record, 1930, **4**, #11, 609.
6. Rayon Record, 1930, **4**, #13, 710.
7. Rayon Record, 1930, **4**, #13, 711.
8. Rayon Record, 1930, **4**, #14, 749.
9. Rayon Record, 1930, **4**, #17, 909.
10. Rayon Record, 1930, **4**, #21, 1088, 1137.
11. Rayon Record, 1930, **4**, #23, 1212. See E. P. 274584.
12. Rayon Record, 1930, **4**, #24, 1260.
13. Rayon Record, 1930, **4**, #24, 1260.
14. Aceta, G. m. b. H., D. R. P. 531078, 1930; abst. C. A. 1931, II, 3059.

trolyte. Thus, cellulose acetate sized with linseed oil and Japan wax may be sprayed with an aqueous solution containing sodium lactate 10% and glucose 10%. Acetylcellulose of predetermined viscosity is prepared by maintaining a standard water content during acetylation[1]. For this purpose, the acetylation mixture including the catalyst, is allowed to stand before the cellulose is added, until its water content has entirely disappeared, or to the desired degree, the water content of the cellulose being adjusted with regard to that of the acetylation mixture. The viscosity of the acetate increases with diminution of the water content of the mixture.

An apparatus for producing acetylcellulose has been devised[2], in which a vertical cylinder with an inlet at the top and an outlet at the bottom has a central shaft to which are attached a number of rotatable stirring elements, which vary in form and increase in size from inlet to outlet according to the texture of the cellulose to be treated. Thin acetylcellulose films of 0.009-0.02 mm. diameter[3] are formed by flowing a plastic solution on a rapidly revolving wheel, the film either being cast colorless and afterwards dyed, or dyestuff introduced in the ester solution prior to film formation. J. Anderson[4] has furnished details concerning acetate lining fabrics.

Seraceta acetate warp yarns are usually heavily sized with gelatin[5], its removal being essential. The ideal method is said to be to first soak in water a short time, jig treat in water raising the temperature to 80°. Pad with "Courtauld's Desizing Compound" (4.5 lbs. Monopole soap No. 1, 4 pints NaOH 40° Tw, 2.75 pints xylene), let stand over night and then scour in the usual manner. In a series of

1. Algemeene Kunstzijde Unie, N. V. and J. Stockly, D. R. P. 530470, 1931; abst. Nitrocellulose, 1931, **2**, 165; Chem. Zentr. 1931, II, 2678; C. A. 1931, **25**, 5287.
2. J. Altwegg, U. S. P. 1792059; abst. C. A. 1931, **25**, 1993; J. S. C. I. 1931, **50**, 968-B.
3. Aluminum Walzwerke Singen, Lauber, Neher Co., F. P. 708539; abst. Chem. Zentr. 1931, II, 2807.
4. Textile World, 1931, **80**, 1204; abst. C. A. 1931, **25**, 5995.
5. J. Soc. Dyers Col. 1931, **47**, 5; abst. C. A. 1931, **25**, 1389.

studies on cellulose acetate[1], the specific conductivity, molecular condition, specific gravity, relative viscosity and surface tension were determined on a number of different acetylating baths and the results found incorporated in a series of tables and graphs. During the ripening of acetylcellulose the degradation of the cellulose residue and saponification of cellulose acetate were greatest in baths containing acetic anhydride, were moderate in baths containing only a trace of acetic anhydride or water, and very slight in baths containing an excess of water. In the earlier stages of ripening in a bath containing considerable acetic anhydride, increase in anhydride and considerable cellulose degradation occur because of cellulose acetolysis. It was found that sulfuric acid is essential to ripening, but if it is precipitated as $BaSO_4$, the ripening action ceases, the acetic content of the ester and the viscosity of the regenerated cellulose remaining nearly constant. The activity of sulfuric acid as a catalyst in ripening depends upon its ratio to water.

In the concentration of acetic acid and its recovery[2], *iso*propyl ether is recommended. As an insulating material[3], the use of acetylcellulose with artificial resins with acetone and phenyl acetate has been brought forward, or[4] an insulator may be used comprising cotton flock kneaded with an artificial resin of the phenol-aldehyde type plasticized by the reaction product between a phenol and tung oil in the presence of a promoter as phosphoric acid, until the fibrous structure of the cellulose has been destroyed. The activity of the resinoid may be retarded by incorporating cellulose acetate. Thiourea, partly replaced by urea if desired is condensed with anhydrous formaldehyde[5] in the

1. K. Atsuki and N. Ishii, J. S. C. I. Japan, (Suppl. binding) 1931, **34**, 335, 337, 351; abst. C. A. 1932, **26**, 297; J. S. C. I. 1931, **50**, 1087-B.
2. E. B. Badger & Sons Co., Belg. P. 378467. F. P. 713698.
3. Bakelite Corp. and H. Bender, E. P. 355318; abst. Chem. Zentr. 1931, II, 3405.
4. Bakelite Corp., E. P. 358120; abst. J. S. C. I. 1931, **50**, 1147-B.
5. *Ibid.* E. P. 358898; abst. J. S. C. I. 1932, **51**, 118-B.

presence of a monoalkyl glycol ether (e.g. Cellosolve) and ethyl lactate, and this incorporated with acetylcellulose.

In the Spicer-Dufay process of natural color photography[1], the film base is of the acetylcellulose type and is said to retain its suppleness and whiteness indefinitely and mature rapidly. The base is collodion coated with a green dye, the films are made in thousand feet lengths, 21 inches wide. Duplication is effected by a projection printer. As a cement for uniting glasses of bi-focal spectacle lenses[2], a mixture is used comprising acetylcellulose, glucose and acetone oil. The L. Bartelstone method of lamination consists in conditioning a glass surface by depositing thereon a thin acetylcellulose film[3], dissipating the volatile solvent therefrom and then interposing a sheet of celluloid, the whole being fabricated into a unitary layer by combined heat and pressure.

The viscosities of 6% solutions of cellulose acetate in acetone-water mixtures have been determined[4] and pure acetone solutions containing up to 30% ester examined. Methyl alcohol depresses the viscosity of acetone solutions of acetylcellulose more than water or absolute ethyl alcohol. The high viscosity of this ester in methylene chloride, dichlorethylene and tetrachlorethane are greatly reduced by methyl alcohol, the minimum in 6% solutions being attained when 20 volume-percent is present. The viscosities of 25% solutions in acetone can be determined by the ball-fall method, the difference between the true and apparent viscosity of such a solution being a measure of its rigidity.

In the partial hydration of acetylcellulose after the preliminary esterification has been completed[5], the process is carried out in two phases to minimize the formation of cellulose sulfacetates and augment the stability of the ester,

1. T. Baker, Nature, 1931, **127**, 821.
2. A. Banister, E. P. 338555; abst. C. A. 1931, **25**, 2531.
3. U. S. P. 1835747.
4. H. Barthelemy, Chim. et Industrie, 1931, **25**, 819; abst. C. A. 1931, **25**, 3827; J. S. C. I. 1931, **50**, 905-A. Cites H. Barthelemy, Mon. Sci. 1913, (5), **3**, 549.
5. *Ibid.* U. S. P. 1844417.

the first comprising destroying excess of acetic anhydride by the introduction of water, and the second phase consisting in adding a bath composed of a mixture of water, formic or acetic acids and HCl, in proportions strictly complying with the requirement that the number of H-ions introduced by the HCl is at least equal to the number of H-ions introduced by the sulfuric acid used as the esterification catalyst. Hexachlorethane may be made by introducing metallic aluminum and aluminum chloride into carbon tetrachloride[1], and subjecting the mixture to 65-75°. In the coloring of acetate silk[2], a di- or poly-aminoanthraquinone chloride is heated with dicyanodiamide, or the mixed bases are treated with halogen halide and heated at 150-200°. Products from 1.4-diaminoanthraquinone (yellow), 1-amino-4-hydroxyanthraquinone (red), 2.3-dichlor-1.4-diaminoanthraquinone, and 1.3.8-triamino-2-methylanthraquinone give colors of great fastness on acetylcellulose.

Acetic acid in acetylcellulose may be determined by hydrolyzing 0.5 gms. by shaking with 20 cc. of 89% phosphoric acid on the waterbath until all is dissolved, steam, free from CO_2, is passed over the hot mixture until the volume in the flask is between 75-100 cc., and the distillate measures 450 cc. The acetic acid is then titrated with 0.2*N* barium hydroxide using phenolphthalein[3]. E. Berl and H. Staudinger[4] have stressed that the mechanical and physical properties of acetylcellulose silks should be made the basis of judging their value and quality, and have detailed a series of suitable tests for evaluating acetate silk. In a mathematical elucidation of viscosity-tempera-

1. G. Bartlett, U. S. P. 1800371; abst. Chem. Zentr. 1931, II, 629.
2. E. Beckett, P. Baugham, J. Thomas and Scottish Dyes., Ltd., E. P. 348661; abst. J. S. C. I. 1931, **50**, 834-B; Chem. Zentr. 1931, II, 1357.
3. E. Berl, G. Rueff and W. Wahlig, Chem. Ztg. 1931, **55**, 861; abst. J. S. C. I. 1932, **51**, 96-B.
4. Chem. Ztg. 1931, **55**, 749; abst. C. A. 1932, **26**, 602.

ture relations of cellulose acetate and nitrate solutions[1], the esters dissolved in tetrachlorethane, butyl acetate and acetone have been determined. The formula $\log_n = kc$, and $\log_n = B/T\text{-}A$ (where c denotes volume/concentration, T the absolute temperature, k, A and B being constants) expresses the results satisfactorily. Values of the viscosity are accurately reproducible provided no free acid is present in the solvent.

Concentration of acetic acid is effected in a plurality of stages by extraction with solvent media as ether and methylene chloride[2], and in the various stages media are employed such that the ratio of solubility of the acid in the extracting medium in the ternary mixture increases successively from stage to stage. In the catalytic oxidation of acetaldehyde by O_2, the aldehyde in the acetic acid produced is oxidized by a counter-current of O_2 in presence of catalyst[3], while the aldehyde from the main reaction chamber is similarly oxidized, the whole being thus effected in a series of catalytic reaction vessels in which oxygen passes in counter-current to liquid acetaldehyde.

To increase the elasticity of objects formed from plastic masses as billiard balls[4], acetethylanilid (ethylacetanilid) is combined with acetylcellulose, and then treated with a solvent for the plasticizer as ethyl ether or benzene, to remove it from the surface. The solubility of the chloroform-soluble cellulose triacetate may be altered to the acetone-soluble form[5] by treatment with comparatively con-

1. E. Berl, H. Umstaetter and E. Karrer, Z. physikal. Chem. 1931, **152**, 284; abst. C. A. 1931, **25**, 1989; J. S. C. I. 1931, **50**, 302-A. Compare E. Berl and H. Umstaetter, Z. physik. Chem., Abt. A, 1930, **148**, 471; abst. C. A. 1930, **24**, 5151; J. S. C. I. 1930, **49**, 1115-A.

2. J. Billing, U. S. P. 1805127; abst. C. A. 1931, **25**, 3669; Chem. Zentr. 1931, II, 1632. Cites U. S. P. 1696432.

3. C. Boehringer & Sohne G. m. b. H., E. P. 350874; abst. J. S. C. I. 1931, **50**, 965-B; Chem. Zentr. 1931, II, 1754. F. P. 708906; abst. C. A. 1932, **26**, 997. Belg. P. 376640. See also F. P. 707835; abst. C. A. 1932, **26**, 736.

4. *Ibid.* E. P. 354957; abst. J. S. C. I. 1931, **50**, 936-B; Chem. Zentr. 1931, II, 3062.

5. *Ibid.* E. P. 355419; abst. J. S. C. I. 1931, **50**, 1006-B. F. P. 698548; abst. Chem. Zentr. 1931, II, 3178. Belg. P. 378351.

centrated inorganic acids (about 60% anhydrous acid) in the presence of salts or esters which are soluble in the acid, but have no solvent action on acetylcellulose. These salts, the function of which is to retard the solvent and degrading action of the acid, are used in quantities approaching saturation point. Suitable solutions include a saturated solution of potassium nitrate in 80% nitric acid, and a mixture of 10 gm. of 96-97% phosphoric acid with 9 gm. cyclohexyl acetate.

Acetaldehyde is formed by the catalytic dehydrogenation of ethyl alcohol, using a catalyst having a basis of copper intimately impregnated with cerium oxide in the proportion of not more than 1 (preferably 0.2) part by weight of cerium oxide to 100 of copper[1]. The viscosity may be materially lowered[2] by subjecting cellulose acetate, substantially free from volatile solvents, to a temperature of 120-180°. H. Brandenburger[3] has described and discussed the appearance and causes of various faults in acetate fabrics, the recognition and study of which is greatly facilitated by previous extraction of the dyes from the acetate filaments by means of absolute alcohol, this treatment accentuating the faults and enabling a clearer examination of the fibers.

Delustered acetate filaments may be relustered by treating the material with a liquid comprising water and acetic acid or other swelling agent, and subsequently, without material reduction of the ratio of swelling substance to water in the liquid retained by the filaments, the water is removed by evaporation[4]. To the diazo compound of 4-nitro-4′-aminodiphenyl sulfide is added 1-phenyl-3-methyl-

1. C. Boehringer & Sohne, A.-G., F. P. 705545; abst. C. A. 1931, **25**, 5178. E. P. 344554; abst. Chem. Zentr. 1931, I, 3169.
2. L. Branchen and C. Prachel, U. S. P. 1831795; abst. C. A. 1932, **26**, 844. Cites U. S. P. 1516225.
3. Kunstseide, 1931, **13**, 99; abst. C. A. 1931, **25**, 4408. Farber-Ztg., 1931, **67**, 619; abst. Chem. Zentr. 1931, II, 3268. Cites O. Braun, Farber-Ztg., 1931, **67**, 241; abst. Chem. Zentr. 1931, I, 3176.
4. J. Briggs, C. Palmer and J. Kidd. U. S. P. 1808098; abst. C. A. 1931, **25**, 4415. Cites U. S. P. 1554801.

5-pyrazolone, a dyestuff resulting which colors acetylcellulose a yellow shade[1]. In the insulation of electric wires and cables according to the F. Brislee process[2], a cellulose acetate in hard and substantially solvent-free form is applied in layers with textile supports around a conductor under approximately atmospheric pressure, the material then heated to 100° at which temperature the composition softens and flows so that adjacent layers unite and impregnation of the textile supporting material is effected. The trademark "Mylanit" for thread, yarns and knitted piece goods of cellulose acetate has been registered[3].

Acetic acid in vapor form may be converted into anhydride[4] by being brought into contact with a catalyst comprising silica gel which may be encased in a tube of fireclay, silica, copper, or chromium-nickel steel, heated to 300-1000°. Pumice or kieselguhr may be used as fillers and phosphoric acid as auxiliary catalyst. Or[5], the acid may be prepared by the action of CO on ethyl alcohol, either in the free or combined state in the absence of inorganic acid catalysts, "promotors" as vanadium, chromium, nickel or copper compounds being added. In the concentration of acetic acid by the azeotropic-mixture method[6], vapors of the entraining liquid are led into the dilute acid, the mixed vapors passing into a fractionating column. Suitable liquids are benzene, xylene, ethyl acetate and di- or tri-chlorethylene.

In the production of cellulose formate, acetate, propionate and butyrate[7], cellulose is agitated in a pretreating

1. R. Brightman, U. S. P. 1821255; abst. C. A. 1931, **25**, 5997. E. P. 296047; abst. Chem. Zentr. 1929, I, 304. See also F. Kehrmann and E. Bauer, Ber. 1896, **29**, 2362.
2. F. Brislee, U. S. P. 1795994; abst. C. A. 1931, **25**, 2498.
3. British Celanese, Ltd., Trade Mark, Sept. 9, 1931.
4. British Celanese, Ltd., H. Oxley and L. Fallows, E. P. 340484; abst C. A. 1931, **25**, 4893; Chem. Zentr. 1931, I, 2674.
5. British Celanese, Ltd., and H. Oxley, E. P. 343947; abst. C. A. 1932, **26**, 154; Chem. Zentr. 1931, II, 312.
6. British Celanese, Ltd., H. Oxley and L. Fallows, E. P. 356741; abst. J. S. C. I. 1932, **51**, 94-B; Chem. Zentr. 1931, II, 3393.
7. British Celanese, Ltd., E. P. 346292; abst. C. A. 1932, **26**, 343; J. S. C. I. 1931, **50**, 672-B; Silk J. and Rayon World, 1931, **8**, #88, p. 34.

chamber with acetic acid, and then discharged directly and gradually into the esterification vessel. If the ester is prepared by the use of sulfuric acid or other sulfur-containing catalyst[1], the ester may be freed from combined sulfur by dissolving in acetic acid and adding to the solution a metal salt (barium, strontium or lead acetate) which will react with the sulfur compounds to give an insoluble precipitate. Cellulose acetate thus purified has a heat test about 70° higher than the untreated ester. Or the cellulose may be subjected to successive pretreatments with nitric acid for an hour at about 50°, and an aliphatic anhydride (acetic, propionic, butyric), and may then be esterified by addition of a catalyst as sulfuric acid or zinc chloride[2].

Cellulose acetate may be purified by fractional precipitation from solutions, as by the addition of a non-solvent or by cooling[3], yielding fractions differing markedly in physical properties, the portions that precipitate first having a higher viscosity and clarity and a greater resistance to heat than those that separate towards the end of the precipitation. Or[4], separation into portions may be effected by repeatedly extracting with a liquid which has a selective solvent action on the esters of lower viscosity. Thus, by repeatedly extracting the ester which is mainly acetone-soluble with warm chloroform, a purified acetate is obtained which gives solutions in acetone of high clarity, and is particularly suitable for films and laminated glass.

Cellulose aceto-, propio- and butyro-nitrates are obtained by simultaneously treating cellulose with organic esterifying and nitrating agents[5], of such strength that at least 3% of N is present in the esterified product. The cellulose is pretreated with formic, acetic, propionic

1. Brit. Celanese, Ltd., E. P. 355690; abst. J. S. C. I. 1931, **50**, 1005-B.
2. *Ibid.* E. P. 338745; abst. C. A. 1931, **25**, 2566.
3. *Ibid.* E. P. 345408; abst. C. A. 1932, **26**, 304; J. S. C. I. 1931, **50**, 582-B; Silk J. and Rayon World, 1931, **8**, #87, p. 52.
4. *Ibid.* E. P. 357781; abst. J. S. C. I. 1931, **50**, 1135-B. 1931, **50**, 1135-B.
5. *Ibid.* E. P. 341147; abst. C. A. 1931, **25**, 5030; J. S. C. I. 1931, **50**, 343-B.

or butyric acids, then with the corresponding aliphatic anhydrides in conjunction with nitric acid and sulfuric acid as a catalyst. The mixed esters formed are very stable, and especially suitable for explosives, lacquers and film formation. In order to purify cellulose acetate[1], the ester is ground to pass a 5-mesh sieve, and then either graded through a series of screens (6-200 mesh) or simply separated into two fractions on a screen of about 40-mesh. The coarser the screen the higher is the purity of the ester retained thereon, most of the impurities being in the fraction which passes 100-200 mesh. The coarse particles of acetylcellulose give solutions of high clarity and are particularly suitable for photographic films.

A polish for acetylcellulose surfaces consists of an abrasive, benzene as diluent, and a liquid which has a softening effect on the surface. Where resins are used with the cellulose ester, substituted sulfonamides are used as softeners; for phenol-formaldehyde resins ethyl phthalate, diphenylolpropane or triacetin may be used[2]. The molding or working of cellulose acetate under heat and pressure[3], as in the production of laminated glass, is facilitated by pretreating with a non-solvent of acetylcellulose at room temperature, but becomes a solvent at higher temperature. Suitable compounds include butyl or amyl alcohol, cyclohexanol, and hydrocarbons of medium or low boiling point. Small quantities of plasticizing agents or compatible synthetic resins, as diphenylolpropane-formaldehyde resins, may be added to the treating liquid. Improved fire-resisting properties are imparted to acetate films by incorporating therewith 2-25% (on the weight of ester) of a bromine derivative of an aromatic or a lower fatty acid, particularly tribromphenyl acetate[4]. Cellulose acetate films containing

1. Brit. Celanese, Ltd., E. P. 344327; abst. C. A. 1932, **26**, 303; J. S. C. I. 1931, **50**, 480-B.
2. *Ibid.* E. P. 352547; abst. J. S. C. I. 1931, **50**, 895-B.
3. British Celanese, Ltd., E. P. 357567; abst. J. S. C. I. 1931, **50**, 1135-B.
4. *Ibid.* E. P. 357667; abst. J. S. C. I. 1931, **50**, 1136-B.

3% of this compound do not discolor after prolonged exposure to ultraviolet light.

In the preparation of acetate silk filaments by the wet-spinning process[1], the filaments are partially coagulated in a suitable liquid to indurate the periphery only, and after washing free from coagulant, are softened by means of a solvent in liquid or vapor form and subjected to a stretching which is confined to the softened portion. The setting is afterwards completed by liquid coagulating agents or by evaporation, a further stretching being applied if required. Filaments of fine denier or increased strength are obtained by extruding acetylcellulose solutions into an evaporative atmosphere[2], applying to the material, after formation of a skin-layer on it, a softening agent and completing the stretching before the solvent has been removed. A union fabric has been described[3] in which natural silk is dissolved in an acid, projected through orifices for filament formation into a coagulating solution comprising one or more alcohols. This filament is then worked into fabric with acetylcellulose threads, and when dyed gives pleasing differential effects. The upward dry-spinning of acetylcellulose in volatile solvents[4] is initiated by use of a liquid coagulating bath containing water, methyl or ethyl alcohols, benzene or carbon tetrachloride together with soap, which is afterwards withdrawn. Filaments are dry-spun into an evaporative medium[5], the whole or a definite part of which is caused to pass through the immediate vicinity of the spinning orifices solely by means of the suction applied to withdraw it from the spinning cell, while additional

1. British Celanese, Ltd., H. Dreyfus and W. Taylor, E. P. 342651; abst. J. S. C. I. 1931, **50**, 481-B.
2. *Ibid.* E. P. 342712; abst. C. A. 1931, **25**, 5559; J. S. C. I. 1931, **50**, 480-B.
3. British Celanese, Ltd., E. P. 349220; abst. Silk J. and Rayon World, 1931, **8**, #90, 51; Textile Mfr., 1931, **57**, #682, 381.
4. *Ibid.* E. P. 351718; abst. J. S. C. I. 1931, **50**, 836-B.
5. British Celanese, Ltd., H. Dreyfus, E. Kinsella, J. Bower and W. Taylor, E. P. 352922, Addn. to E. P. 300998, 304674 and 326232; abst. J. S. C. I. 1931, **50**, 877-B; Textile Mfr., 1931, **57**, #684, 461.

evaporative medium is also introduced into the neighborhood of the spinning orifice.

Or[1], the solution may be 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. Ornamental and pleasing effects are producible on acetate filaments by applying to them while still in a sticky condition of very finely divided metals (bronze, aluminum, colored luminous or phosphorescent powders as calcium, barium or zinc sulfides)[2]. Dull or mat effects may be induced by incorporating barium sulfate, titanium or zinc oxides, or organic products as the condensation products of urea or thiourea with benzidine, α-dinaphthyl urea or thiourea, diacetyl- or dibenzoyl-benzidine. Continuously with their production[3], acetylcellulose filaments while in a sticky condition brought about by incomplete evaporation of solvent, by treatment with a softener or by heat, are stretched and caused to emerge into a single filament, which is afterwards treated with a lubricant to remove stickiness. Other threads as wool or metal may also be incorporated in this composite thread.

In order to impart to acetate threads improved extensibility, tenacity, type and regularity of cross-section[4], a liquid (water, paraffin, glycerol, olive oil) is applied to the filaments during an early stage of drying, and while they contain a relatively high proportion of solvent. By using acetylcellulose containing 48-58% fixed acetic acid[5], filaments may be obtained which have a moisture regain of about 7%, a safe ironing point 25-30° above normal, and

1. British Celanese, Ltd., E. Kinsella, J. Bower, J. Briggs and R. Roberts, E. P. 341075; Addn. to E. P. 325233; abst. J. S. C. I. 1931, **50**, 342-B.
2. British Celanese, Ltd., and W. Taylor, E. P. 341057; abst. J. S. C. I. 1931, **50**, 346-B; Silk J. 1931, **7**, #84, 53.
3. *Ibid.* E. P. 349999; abst. J. S. C. I. 1931, **50**, 754-B.
4. *Ibid.* E. P. 355652, Addn. to 327740; abst. J. S. C. I. 1931, **50**, 1044-B; Textile Mfr. 1932, **51**, #686, 78.
5. British Celanese, Ltd., E. P. 356170; abst. J. S. C. I. 1931, **50**, 1044-B; Textile Mfr., 1932, **51**, #686, 79.

an increased affinity for dyes. In the preparing and spinning of yarns from rayon[1], the machine parts over or near to which the materials pass while in a substantially untwisted state are made of or covered with acetylcellulose to prevent attraction towards those parts of the fiber which have become electrified during the preparing or spinning operation. The calender rolls and guide-funnel of a carding engine, gill-box or drawing frame, the carding engine doffer-knife and the lower roller of the last pair of drawing rollers in a drawing or slubbing frame are specified as being acetylcellulose coated.

To give ample warning of the safe ironing temperature[2], yarn or fabrics of acetylcellulose have incorporated therein an organic substance other than an animal or vegetable oil, which causes scorching at a temperature below that at which the ester begins to melt. Suitable products are, oleic and stearic acids and their sodium and potassium salts; sodium, potassium and aluminum acetates; spermaceti and beeswax, or albumen and gelatin. All types of textile yarns may be sized by aqueous solutions or dispersions of cellulose oxalate or maleate, or by modification of cellulose acetate by treatment with organic acids[3]. Yarns thus sized are readily de-sized by scouring with an aqueous soap solution to which a small amount of alkali may be advantageously added.

Yarns to which a treating liquid—for example, a size, has been applied, are wound into hank form and dried during winding, the drying agency being concentrated in the neighborhood of the hank. With acetate yarn, starch size or gelatin size is recommended, with or without the addi-

1. British Celanese, Ltd., W. Dickie and F. Hale, E. P. 349990; abst. Text. Mfr. 1931, **57**, 419.
2. British Celanese, Ltd., E. P. 352058; abst. J. S. C. I. 1931, **50**, 836-B; Text. Mfr. 1931, **57**, 459. H. Dreyfus, F. P. 694750; Chem. Zentr. 1931, I, 1973.
3. British Celanese, Ltd., H. Dreyfus, W. Dickie and P. Sowter, E. P. 344775; abst. J. S. C. I. 1931, **50**, 535-B; Silk J. and Rayon World, 1931, **8**, #86, 54; Rayon Record, 1931, 421

tion of castor oil or glycerol as softener[1]. Products showing different degrees of saponification and hence suitable for differential dyeing effects[2] are formed of cellulose formate, acetate, propionate or butyrates associated with fibers of wool, silk or cotton. Portions of the esters may be saponified wholly, and other portions partly or not at all. The dyeing properties of the treated esters depend on the depth and extent of the saponification[3]. To preserve the luster of acetate filaments produced by the wet-spinning process[4], coagulation is induced under such conditions that the filaments contain a high-boiling solvent which is but slowly dissipated in the heated zone in proximity to the filament forming jets. The shrinking tendency of acetate fabrics when exposed to aqueous liquids[5], is diminished or overcome by incorporating with the fibers from which the fabrics are made, long staple (0.5-8 inch) fibers of normal cellulose.

To produce crepe effects in textile materials[6], threads of acetylcellulose or of degummed silk are impregnated with materials containing casein or rubber, which are then treated with formalin, or tannin to prevent softening during the swelling process. The coated threads, after highly twisting, are incorporated 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. If it is desired to produce

1. British Celanese, Ltd., S. Fulton and G. Tyce, E. P. 355794; abst. Text. Mfr. 1932, **51**, 79.
2. British Celanese, Ltd., and R. Roberts, E. P. 343953; abst. C. A. 1932, **26**, 306; J. S. C. I. 1931, **50**, 486-B.
3. British Celanese, Ltd., and S. Fulton, E. P. 351417; Addn. to E. P. 316521, 318468; abst. J. S. C. I. 1931, **50**, 837-B; Text. Mfr. 1931, **57**, 458.
4. British Celanese, Ltd., E. P. 356343; abst. Text. Mfr. 1932, **51**, 80.
5. British Celanese, Ltd., E. P. 356681; abst. Text. Mfr. 1932, **51**, 80.
6. British Celanese, Ltd., and W. Dickie, E. P. 348589; abst. J. S. C. I. 1931, **50**, 716-B.

crepe, pebble or cockled effects[1], yarns are used in the warp or weft which have been permanently stretched in combination with unstretched yarns or by alternating yarns which have been stretched to one degree only. Subsequent treatment of the fabric with water or aqueous soap solutions effects a shrinkage of the stretched yarns and a consequent crinkling of the unstretched. Low or high twist acetylcellulose yarns may be used.

Crepe effects may also be produced in fabrics containing highly twisted crepe threads with acetylcellulose threads[2] when the latter are locally padded with dehydrating liquids as calcium or zinc chlorides, sodium acetate, sodium phosphate (NaH_2) or HCl. Desirable effects on mixed yarns are obtained, when formed in part only of acetylcellulose[3], when treated with a reagent which causes greater shrinkage of the other material—caustic soda being used where a part cotton fabric is operated upon. The scroop of woven, knitted or net fabrics, especially taffeta[4], containing acetylated cellulose, is increased by treatment with salts of polybasic organic aliphatic acids, as sodium or potassium tartrate, potassium or calcium oxalate with an olive oil emulsion, or barium oxalate alone.

The pliability of ribbons, tapes and straw-like products from acetylcellulose[5] is improved by adding 2.5-10% of a highboiling solvent liquid used for moistening the filaments. Coalescence is then effected by application of both heat and pressure. Waterproof properties are induced by passing between smooth rollers coated with carnauba wax. Two or more layers of acetylcellulose fabric may be superposed and subjected to heat and pressure under such con-

1. British Celanese, Ltd., E. P. 349121; abst. Silk J. and Rayon World, 1931, **8**, Nov. 61. E. P. 352113; abst. J. S. C. I. 1931, **50**, 836-B.
2. British Celanese, Ltd., W. Dickie and R. Moncrieff, E. P. 357084; abst. J. S. C. I. 1931, **50**, 1090-B.
3. British Celanese, Ltd., E. P. 345022; abst. C. A. 1932, **26**, 319; Chem. Zentr. 1931, II, 3176; J. S. C. I. 1931, **50**, 584-B; Silk J. and Rayon World, 1931, **8**, #86, 54.
4. British Celanese, Ltd., E. P. 354200; Text. Mfr. 1932, **58**, 38.
5. British Celanese, Ltd., E. P. 354233; abst. J. S. C. I. 1931, **50**, 1044-B.

ditions that they coalesce to give a compound fabric retaining on one or both sides the woven structure of the original material[1].

In plasticizing selvages[2], one or both edges of a cellulose acetate fabric being woven in a shutterless loom are treated with a solvent or softening agent which plasticizes the warp and/or woof threads at the edge treated, and renders them sticky or tacky so that they coapt to contacting threads in the fabric edge. Pressure and heat are essential. Ornamental effects are producible in fabrics in which the warp or weft contains acetylcellulose yarns and yarns of another fiber as silk, cotton or wool[4], when treated with a reagent that causes shrinkage of one of the materials, further effects being induced by the use of dyes having a selective affinity for one of the materials.

Dispersed, relatively insoluble coloring agents having an affinity for unsaponified acetylcellulose are used for dyeing materials as mixed goods containing the partially saponified ester[4], which may be associated cotton or other fibers, the non-ester portion being dyed with suitable dyes. Or[5], the cellulose acetate may first be partially and uniformly saponified, and colored by dyes having a greater affinity for the unsaponified esters, as by the use of dispersed, insoluble dyes. Where part or all of the halogen in halogenated anthrarufins is replaced by OH by heating with sulfuric acid[6], and the products obtained aminated or alkylaminated, acetate silk dyes result. 6-Chlor-1.4.5-trihydroxyanthraquinone from 4.6-dichloranthrarufin, is converted into the 6-methylaminohydroxyanthraquinone, green-

1. British Celanese, Ltd., E. P. 355860; abst. J. S. C. I. 1931, **50**, 1005-B.
2. British Celanese, Ltd., W. Dickie and F. Hale, E. P. 343436.
3. British Celanese, Ltd., E. P. 342075; abst. C. A. 1931, **25**, 5043; J. S. C. I. 1931, **50**, 391-B.
4. *Ibid.* E. P. 339997; abst. C. A. 1931, **25**, 2859; J. S. C. I. 1931, **50**, 534-B; Silk J. and Rayon World, 1930, **7**, #83, 52; Chem. Zentr. 1931, I, 2270.
5. *Ibid.* E. P. 340982; abst. C. A. 1931, **25**, 5042; Chem. Zentr. 1931, II, 3046.
6. British Celanese, Ltd., G. Ellis, H. Olpin and E. Kirk, E. P. 343444; abst. J. S. C. I. 1931, **50**, 623-B; Chem. Zentr. 1931, I, 3296.

blue dyes result, the methyl ether dyeing yellow. Likewise[1], diazotized amines of the benzene or naphthalene series are coupled with non-sulfonated hydroxyalkylated-*a*-naphthylamine and form acetylcellulose dyestuffs; chlor-*b*-hydroxy-*n*-propyl-1-naphthylamine with diazotized *p*-nitroaniline (red-violet), with 5-nitro-*o*-anisidine (violet), with 5-nitro-*o*-phenetidine (violet), with 4-amino-4′-dimethylaminoazobenzene (blue-red), and with benzeneazo-*a*-naphthylamine (violet grey).

It has been found that woven or knitted acetate fabrics may be dyed in rope form without the formation of permanent crease marks[2], provided they are first partly (3-5%) saponified. The fibers may be delustered by impregnation or printing with aqueous mono-, di-, or triethanolamine[3], followed by steaming or other treatment with a hot, aqueous medium. Relustering may be effected with steam having a degree of superheat of at least 20°, and at ordinary, or preferably higher pressure[4]. The luster of acetylcellulose may also be modified by precipitating zinc sulfide therein[5], the necessary zinc salt being introduced into the fiber in the presence of a swelling agent, or zinc chloride may be used as the swelling agent. A firm handle (stiffening) and glossy appearance are conferred on cellulose acetate by steeping in a cold solution of gelatin or casein, followed by treatment with formaldehyde[6].

Laminated glass permeable to ultraviolet rays consists of external sheets of quartz glass and an intermediate one

1. 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.
2. British Celanese, Ltd., E. P. 339429; abst. C. A. 1931, **25**, 2576; J. S. C. I. 1931, **50**, 390-B; Chem. Zentr. 1931, II, 1355; Chim. et Ind. 1931, **25**, 956.
3. *Ibid.* E. P. 355466; abst. J. S. C. I. 1931, **50**, 1008-B; Textile Mfr. 1932, **51**, 78.
4. British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 349980, Addn. to 332231; abst. J. S. C. I. 1931, **50**, 838-B.
5. British Celanese, Ltd., E. P. 344093; Addn. to 318467; abst. J. S. C. I. 1931, **50**, 438-B; Silk J. and Rayon World, 1931, **8**, #85, 54.
6. British Celanese, Ltd., G. Langdon, A. Flower and S. Fulton, E. P. 358593; abst. J. S. C. I. 1932, **51**, 19-B.

of acetylcellulose plasticized with dibutyl tartrate[1]. Or the reinforcing layer may comprise acetylcellulose which has been subjected to a bleaching treatment and then plasticized with triacetin (see p. 260, n. 1)[2], or vinyl acetate. Or a glass sheet may be coated with gelatin on the inner side and an acetylcellulose film with gelatin on both sides[3] and then united, or the reinforcing layer may comprise cellulose acetate and at least 50% plasticizer (triacetin, ethyl or butyl tartrate or phthalate), the whole being softened by soaking in a high-boiling liquid (butyl alcohol, cyclohexanol, dioxan) and then uniting the two sheets by heat and pressure without other adhesive[4]. The inner adhesive layer may consist of a synthetic urea-phenol-aldehyde resin and a plastified acetyl- or nitro-cellulose film[5] (see p. 260, n, 4). The coatings are dried at 50-100° for 15-60 minutes.

In the production of rubberized materials comprising acetylcellulose[6], a firmly adherent film of rubber is applied to the acetate fabric by coating one or both sides with a solution of rubber containing sulfur as a vulcanizing agent and an accelerator, and afterwards vulcanizing at a temperature of 100° or above, but below that at which the fabric is damaged by heat. Rubberized cellulose acetate fabrics have a diminished tendency to crease. A liquid adhesive has been described[7], containing acetylcellulose, a phenol-aldehyde resin with suitable solvents, and, if desired, a plasticizer is applied to the surfaces to be united. When this coating has become tacky, a finely-divided pow-

1. British Celanese, Ltd., E. P. 340927, Addn. to 306397; abst. J. S. C. I. 1931, **50**, 350-B; British Plastics, 1931, **3**, #26, 82.
2. *Ibid.* E. P. 341891; abst. J. S. C. I. 1931, **50**, 395-B; British Plastics, 1931, **3**, #26, 82.
3. *Ibid.* E. P. 347777; abst. British Plastics, 1931, **2**, #30, 271; Chem. Zentr. 1931, II, 3244.
4. *Ibid.* E. P. 347972; abst. British Plastics, 1931, **2**, #30, 271; Chem. Zentr. 1931, II, 3244.
5. *Ibid.* E. P. 342337; abst. C. A. 1931, **25**, 4374; J. S. C. I. 1931, **50**, 395-B; British Plastics, 1931, **3**, #26, 82; Chem. Zentr. 1931, II, 2921.
6. *Ibid.* E. P. 347422; abst. J. S. C. I. 1931, **50**, 801-B; Chem. Zentr. 1931, II, 1365.
7. *Ibid.* E. P. 347445; abst. J. S. C. I. 1931, **50**, 587-B.

der of cellulose acetate and ethyl phthalate is sprinkled on the surface, and the article united by pressure.

The uninterrupted production of acetic acid through the oxidation of acetaldehyde in the liquid stage is possible by means of nascent oxygen and inert gases[1]—the oxygen being in excess—at temperature of 60-75°. Insulated electrical conductors may be coated with acetylcellulose[2] by immersing a cotton coated wire in an acetylcellulose solution, an electric current being passed through the conductor and bath. The conductor is then passed through another bath of acetylcellulose and through a drying chamber. By this method unusually tenacious adhesion is said to result. As a useful plasticizer for cellulose derivatives, the use of condensation products of glycerol with pimelic, suberic, azelaic or sebacic acid incorporated with a phenol-aldehyde resin has been described[3].

According to A. Caille[4] the difference between the amounts of water absorbed in a non-saturated atmosphere by cellulose sulfates and regenerated cellulose are maintained when the atmosphere is saturated. The sulfuric acid content of nitro- and acetyl-cellulose precipitated by water from the residues and filtrates after ultrafiltration of their acetone solutions seems to show that the smaller micelles contain most sulfuric acid. Cellulose acetate in a half-saturated atmosphere at 15° absorbs 6% moisture. Specifications of maximum limits of total sulfate and ash in acetylcellulose are inadequate as indicating proper quality, it being essential to specify a minimum decomposition point which should preferably not be below 195°. As cellulose acetate plasticizing bodies, butyl propionate[5], cyclohexanol[6] and nitro-*p*-xylene[7] have received patent pro-

1. British Industrial Solvents, Ltd., Can. P. 315016.
2. D. Brobst, U. S. P. 1808520; abst. C. A. 1931, **25**, 4403.
3. H. Bruson, U. S. P. 1783166; abst. British Plastics, 1931, **3**, #30, 272; Chem. Zentr. 1931, I, 1680.
4. A. Caille, Chim. et. Ind. 1931, **25**, 276; abst. C. A. 1931, **25**, 3161; J. S. C. I. 1931, **50**, 798-B.
5. S. Carroll, U. S. P. 1841311.
6. *Ibid.* U. S. P. 1841312.
7. *Ibid.* U. S. P. 1841313.

tection. Satunese[1] was trade-marked for fabrics composed wholly or partially of acetylcellulose.

A fire-resisting abrasive composition has been described[2], moldable under heat and pressure, comprising acetylcellulose, 25-75 parts of a plastifier or modifier and 100-1000 of abrasive material; fire-resisting agents (triphenyl phosphate, calcium sulfate and aluminum fluoride) are added. In the decorative treatment of acetate silk fabrics[3], white resist or discharge effects are obtained by overall-printing the fabric, before or after the printing with zinc acetate or oxide, with dyes having an affinity for acetylcellulose but forming no insoluble complex with metal compounds. The F. Hahn coating composition involves the combination of cellulose acetate with glyceryl benzoylbenzoate[4] (see p. 202, n. 3), or mono-[5] or di-ethyleneglycol monoethyl ether[6]. A celluloid substitute has been described[7] involving the use of cellulose acetate intumesced by means of a volatile swelling agent, the plastic ester being molded and otherwise fabricated while in the swollen condition. In the marking or decorating of such plastic bodies[8], decorative "characters" of acetylcellulose are applied to thermoplastic articles of the same material, the characters having a lower or inferior plasticity than the article to which they are applied, then welding in place under heat and pressure.

Flexible, non-blooming coatings which do not become sticky at high temperatures[9] are obtained by incorporating 100% or more (on the weight of cellulose ester) of relatively water-insoluble, non-volatile tartaric ester (butyl or

1. Celanese Corp., U. S. Trade-Mark, Ser. No. 316292.
2. Celluloid Corp., E. P. 359324; abst. J. S. C. I. 1932, **51**, 24-B.
3. Calico Printers' Assoc., Ltd., and J. Whinfield, E. P. 348715; abst. J. S. C. I. 1931, **50**, 755-B; Silk J. and Rayon World, 1931, **8**, #89, 56; Textile Mfr., 1931, **57**, #682, 380; Chem. Zentr. 1931, II, 2936.
4. Canadian Industries, Ltd., and F. Hahn, Can. P. 312568.
5. *Ibid.* Can. P. 312569.
6. Canadian Industries, Ltd., and W. Lawson, Can. P. 312570.
7. Celanese Corp. and A. Eichengruen, Can. P. 316309.
8. Celluloid Corp., E. P. 357457; abst. J. S. C. I. 1931, **50**, 1107-B.
9. *Ibid.* E. P. 358428; abst. J. S. C. I. 1931, **50**, 1147-B.

phenyl tartrates). Other solvents are a mixture of ethyl acetate, ethyl alcohol and water[1]; and triphenyl phosphate with diethyl phthalate[2]. A slide for a photographic plate or film holder has been described[3], made of plastic acetylcellulose.

In the production of acetylcelluloses[4], cellulose is pretreated below 20° with acetic acid and a relatively small quantity of SO_2 (not more than 5% on the weight of the acetylating bath), with addition of concentrated sulfuric and acetic acids, and afterwards esterified in the usual manner. H. Chadwick[5] has discussed the various methods proposed and in use for the removal of identification tints from cellulose acetate, and P. Chaumeton and V. Yarsley (see p. 757, n. 4; p. 856, n. 4) the various methods for influencing viscosity of these esters[6]. Cellulose fibers may be immunized to direct dyes by treating them with boiling NaOH or KOH solutions, and then esterifying with acid chlorides[7].

In order to obtain a uniform acetylcellulose film readily stripped off[8], a mixture of fusel oil and gallipoli oil (inferior olive oil) is applied by means of rollers to the casting surface (drum or band) before deposition of the film material. G. Choisy[9] has given a number of formulas for

1. Celluloid Corp., J. Walsh and A. Caprio, Can. P. 312793.
2. Celluloid Corp., J. Walsh and K. Flynn, Can. P. 314577, 315656.
3. Celluloid Corp. and K. Flynn, Can. P. 316713.
4. Cellulose Acetate Silk Co., Ltd., P. Chaumeton and G. Wakefield, E. P. 348292; abst. J. S. C. I. 1931, **50**, 714-B; Silk J. and Rayon World, 1931, **8**, #89, 56; British Plastics, 1931, **3**, #30, 268; Chem. Zentr. 1931, II, 2087. For concentration of acetic acid, see Cellulose Acetate Silk Co., Ltd., and D. Hayes, E. P. 352585; abst. J. S. C. I. 1931, **50**, 1085-B; Chem. Zentr. 1931, II, 2932.
5. H. Chadwick, Dyer, Calico, Printer, 1931, **65**, 677, 685; abst. C. A. 1931, **25**, 5295; Chem. Zentr. 1931, II, 1930. Dyer, Calico Printer, 1931, **66**, 43; abst. Chem. Zentr. 1931, II, 3044.
6. British Plastics, 1931, **2**, #21, 407; #22, 452, 522, **3**, #25, 35, 53.
7. Chemische Fabrik vorm. Sandoz, E. P. 345052; abst. C. A. 1932, **26**, 302; Chem. Zentr. 1931, II, 3271.
8. A. Chiverton and F. Chiverton, Ltd., E. P. 353136; abst. J. S. C. I. 1931, **50**, 877-B.
9. Russa, 1931, **6**, 979, 981; abst. C. A. 1931, **25**, 5568; Chem. Zentr. 1931, II, 1494.

printing acetate-cotton fabrics with vat dyes and indigo solutions. The cellulose acetate composition of H. Clarke[1] involves the use as a combustion retarder of compounds formed from chloral and urea or acetamide, or chloral may be incorporated with the ester, ureas and urethanes; or methyl, ethyl, propyl and butyl carbamate. Lacquers and films are formed from the above of high strength and great gloss. For recovering cellulose acetate from an acetic acid solution containing it[2], the solution is added to an aqueous precipitating bath containing initially about 33% acetic acid, and this acid concentration maintained throughout the precipitation.

Mixed organic esters of cellulose have been described which contain the acetic acid radical in conjunction with propionic, *n*- and *iso*-butyric, *n*- and *iso*-valeric, *n*-heptylic, lauric, myristic, palmitic, stearic, cyclohexanecarboxylic, crotonic, cinnamic, hydrocinnamic, undecylenic, *o*-methoxybenzoic and benzoic acids[3]; 15 parts of the relatively higher acid are dissolved in monochloracetic acid 15-25, acetic anhydride 15 and magnesium perchlorate hydrate 0.05, the reaction being maintained at 60-65° (for 2 hrs. with benzoic acid to 48 hrs. with cyclohexanecarboxylic acid). The simplest member would be cellulose aceto-propionate or propioacetate. The acetic anhydride may be replaced by propionic anhydride, yielding a series of esters of which the lowest member is cellulose propiono-*n*-butyrate. Cellulose aceto-palmito-stearate and propiono-palmito-stearate are also described. These esters are purified by means of methyl alcohol.

Cellulose esters of acetic, propionic, butyric, valeric, caproic and heptylic acids may be prepared by heating normal, or preferably modified cellulose as from the viscose

1. U. S. P. 1809234; abst. C. A. 1931, **25**, 4403. Cites O. Jacobsen, Leibig's Annalen, 1871, **157**, 243.
2. H. Clarke, U. S. P. 1823348; abst. C. A. 1932, **26**, 304.
3. H. Clarke and C. Malm, U. S. P. 1800860; abst. C. A. 1931, **25**, 3481; Plastics, 1931, **7**, 524. Cites U. S. P. 1591590.

process[1] under the esterification-impelling influence of an organic anhydride in the vapor phase at a temperature range of 100-200°, air or atmospheric oxygen being excluded, until the acyl group in the ester reaches at least 8%—the vapor being the sole acylating agent. In the dehydration of acetic acid[2], ethylene dichloride is mixed with the aqueous acid and water, and ethylene dichloride distilled from the mixture.

R. Clavel claims that in dyeing cellulose acetate with azo development dyes[3], the ester should be treated with the developer component at a temperature above 60°, which serves to facilitate the dyeing. Delustered acetylcellulose may be re-lustered by treatment with swelling agents as formic, acetic or propionic acids, especially in the presence of calcium thiocyanate[4]. If piece goods containing delustered acetylcellulose are printed with a paste made by emulsifying together 650 gms. acacia (50%) with 300 cc. ethyl alcohol and 15 gms. Rhodulin orange, and the well dried piece goods steamed at a pressure of 1.4 atmospheres absolute and finally cold washed, the pattern then comes up as a lustrous figure on a lusterless ground. E. Clayton[5] has discussed the application in the textile and allied industries of such solvents as cyclohexanol, methylcyclohexanol, dioxan and benzyl alcohol.

Cellulose may be pretreated for acetylation purposes[6] by heating at 100-145° under pressure with water containing 1-2% acetic acid, and after washing and drying, the product is then esterified in the usual manner. An ink for cellulose acetate comprises a cellulose ester solvent boiling

1. H. Clarke and C. Malm, U. S. P. 1823350; abst. C. A. 1932, **26**, 303. Cites U. S. P. 1668944, 1668945, 1687059.
2. H. Clarke and D. Othmer, U. S. P. 1804745; abst. C. A. 1931, **25**, 3669; J. S. C. I. 1932, **51**, 94-B.
3. U. S. P. 1811576; abst. C. A. 1931, **25**, 5042.
4. R. Clavel, U. S. P. 1844204.
5. E. Clayton and C. Clarke, Textile Mfr. 1931, **57**, #684, 454. See also U. S. P. 1681861. Fort, Journal Soc. Dyers and Colourists, 1918, **34**, 226.
6. L. Clement and C. Riviere, E. P. 343712; abst. J. S. C. I. 1931, **50**, 480-B; Chem. Zentr. 1931, II, 3177. F. P. 700478, and Addn. 38582; abst. Chem. Zentr. 1931, II, 3177.

between 140-225° (diacetone alcohol, ethyl lactate, diethyleneglycol)[1], National nitrosine base N, spirit blue or Malachite green with orange shellac. It has been calculated that for every 100 lbs. of cellulose treated there is available for recovery 558.5 lbs. acetic acid in a 15-40% solution[2]. The procedures of converting to glacial acetic acid by distillation with concentrated sulfuric acid or converting to acetic anhydride by the action of sulfur dichloride are unsatisfactory because of the various chemicals required, the low yield, the necessary concentration of the solution, and the high cost. Other processes employ a solvent of lower boiling point than acetic acid, extracting the acid from its solution, and subsequently distilling off the solvent. A satisfactory method is where a solvent of higher boiling point than the acid is used, the acid being fractionated from the solvent by distillation.

The permeabilities of such packing materials as cellophane, duratex and triacel (an acetylcellulose product)[3], as compared with that of parchment have been determined, the data obtained being so irregular that only general conclusions can be drawn. The permeability to moisture is inversely related to the electrical insulating power, both being connected with the presence or absence of free hydroxyl groups.

A study of the partial alkaline hydrolysis of acetylcellulose silk preparatory to dyeing has been made[4], hydrolysis being effected by immersion in dilute NaOH containing sodium acetate as a leveling agent, whereby it acquires an affinity for Benzopurpurin 4B which is a maximum when the resulting loss in weight is about 1.7%.

1. J. Clewell, U. S. P. 1806965; abst. Plastics, 1931, **7**, 577; Chem. Zentr. 1931, II, 2820.
2. H. Clotworthy, Ind. Chemist, 1931, **7**, 111; abst. C. A. 1931, **25**, 2560; Rayon Record, 1931, July 3, 421; J. S. C. I. 1931, **50**, 437-B; British Plastics, 1931, **3**, #28, 179.
3. R. Cohen, Chem. Weekblad, 1931, **28**, 159; abst. J. S. C. I. 1931, **50**, 340-B.
4. W. Coltof, H. Waterman and I. Wolf, Z. angew. Chem. 1931, **44**, 163; abst. J. S. C. I. 1931, **50**, 1007-B.

Cross-sections of partly hydrolyzed fibers dyed with Benzopurpurin 4B and Cellit Fast Red (dyes having affinities for cellulose and cellulose acetate respectively) show that the degree of hydrolysis increases from the surface to the center of each fiber. From an examination of the acetone soluble portion of partly hydrolyzed fibers, lower acetates than cellulose triacetate were shown to be present. It is concluded that from the surface to the center of each fiber the acetic acid content of the cellulose acetate gradually increases, except in highly saponified fibers where an outer layer of pure cellulose exists. The degree of hydrolysis increases with the alkali concentration and temperature of the solution, but the lower the concentration, the less the proportion of alkali which reacts.

Acetaldehyde is formed when an excess of acetylene is led through aqueous sulfuric acid of 6-35% concentration containing a mercury compound[1], the acid being maintained at 60-80°. Acetaldehyde is removed from the gases leaving the reaction vessel, and the excess of acetylene returned to the system. In the manufacture of acetic anhydride by reaction between a vinyl ester and a carboxylic acid (see p. 626, n. 3)[2], the ethylidene ester obtained as a by-product is mixed with fresh vinyl ester and carboxylic acid, and returned to the process[3]. The aldehyde also obtained is not removed immediately from the reaction mixture, the latter being first heated under reflux until its boiling point has increased considerably, the aldehyde being then distilled off. A resume of the patents and processes recently exploited for dyeing and finishing acetylcellulose silk has been contributed by "Consultant"[4].

1. Consortium fur Elektrochem. Ind. G. m. b. H., E. Baum and M. Mugdan, D. R. P. 518290; abst. C. A. 1931, **25**, 2441; Chem. Zentr. 1931, I, 2933.
2. Consortium fur Elektrochem. Ind. G. m. b. H., H. Deutsch and W. Herrmann, D. R. P. 526795; abst. C. A. 1931, **25**, 4559; Chem. Zentr. 1931, II, 1490. Swed. P. 72045.
3. *Ibid.* D. R. P. 526797; abst. C. A. 1931, **25**, 4559; Chem. Zentr. 1931, II, 1490.
4. "Consultant," Silk J. and Rayon World, 1931, **7**, #84, 39; **8**, #86, 44; #87, 48.

In the separation of ethylidene diacetate[1], the crude product from acetylene and acetic acid is agitated with aqueous sodium acetate solution of density greater than that of ethylidene diacetate, and the upper layer separated and dried over anhydrous sodium acetate. Delustering of acetylcellulose filaments may be brought about, when dry-spun from an acetone solution containing 1% arachis oil (peanut or earthnut oil)[2], by treating with an aqueous soap solution at or near the boiling point. Or[3], amyl stearate or glucose penta-acetate, or hydroxyethyl oleate[4] may be used. Novel effects in artificial fibers are said to result when paraffin or spermaceti in the melted state is homogenized with acetylcellulose in solution[5] and the product dry-spun the temperature being maintained above the melting point of the wax until after it has passed the spinning jet. A. Crispe[6] published practical operating directions for producing artificial crepes containing acetate silk, and F. Curtis[7] the complex competitive situation now prevailing in the acetic acid manufacturing industry.

Foils of lacquers 0.6-30 microne diameter of nitro- or acetyl-cellulose with polar mols., prepared by evaporation on a pure mercury surface[8], show static changes when torn off the mercury. The side next to the Hg. is negative the other side positive, indicating polarization of the outer film. If the foil is placed upside down on the Hg. and heated for 25 minutes at 125-130° the orientation reverses conforming to the new position. Orientation follows equal-

1. Courtaulds, Ltd., and J. Brown, E. P. 353318; abst. J. S C. I. 1931, **50**, 1086-B; Chem. Zentr. 1931, II, 2658.
2. Courtaulds, Ltd., and C. Diamond, E. P. 338269; abst. C. A 1931, **25**, 2305; Chem. Zentr. 1931, I, 1699.
3. Courtaulds, Ltd., C. Diamond and W. Glover, E. P. 352412 352610, 352611; Addn. to 338269; abst. J. S. C. I. 1931, **50**, 878-B; Textile Mfr. 1931, **57**, #684, 450.
4. Courtaulds, Ltd., and C. Diamond, E. P. 356299; abst. J. S C. I. 1931, **50**, 1044-B; Textile Mfr. 1932, **58**, #686, 79.
5. *Ibid.* E. P. 360626; abst. J. S. C. I. 1932, **51**, 142-B.
6. Russa, 1931, **6**, 243; abst. C. A. 1931, **25**, 2571.
7. Chem. Met. Eng. 1931, **38**, 38.
8. G. Daletzky, Naturwissenschaften, 1931, **19**, 251; abst. C. A 1931, **25**, 3217.

ly well by evaporation on solid Hg. When heated, sandwiched between Hg. layers, the foil turns out to be negative on both sides. Preparations of acetylcellulose on glass give the opposite sign of charge. Foils from a nonpolar lacquer do not show charges.

M. Denis[1] has discussed the four important methods of acetone recovery in acetate silk spinning, e.g. (1) washing out with water, (2) absorption with such organic solvents as *m*-cresol and tetralin, (3) absorption by active charcoal, and (4) absorption by silica gel. In the normal process of acetylcellulose hydrolysis[2], when insufficient water to convert the residual acetic anhydride into acetic acid is added, a secondary acetate richer in acetyl than the ordinary primary acetate is obtained, but with larger amounts of water a product poorer in acetyl results. The acetyl content also fails as hydrolysis is prolonged. High acetyl content is accompanied by low sulfuric acid percentage and conversely, the higher acetyl content being ascribed to the more ready decomposition of the cellulose sulfates present. The stability of secondary acetates increases with decreasing sulfuric content. Hydrolysis with larger amounts of water gives produdcts of high viscosity. When 7.5% instead of 15% sulfuric acid is used as catalyst in preparing the primary acetate, the effect of concentration of the hydrolysis mixture on the viscosity of the secondary acetate is the same, but the *rate* of hydrolysis is very slow and must be accelerated by the addition of more sulfuric. Secondary acetates are soluble in acetone when the yield of acetic acid is between 60% and 49%.

A crepe effect is given to artificial silk fabrics by using as weft highly twisted acetylcellulose fibers which have been spun from solutions containing sodium acetate which gives a high solution tension in water[3]. If an acetylcellu-

1. L'Avenir Textile, 1930, 372.
2. A. Deripasko, Cellulosechem. 1931, **12**, 254; abst. J. S. C. I. 1931, **50**, 1278-A.
3. Deutsche Acetat-Kunstseiden A. G. "Rhodiaseta," D. R. P. 529800; abst. C. A. 1931, **25**, 5301; Chem. Zentr. 1931, II, 3564.

lose containing esterifiable OH groups is treated with a chloride of an acid ester of a polybasic acid[1], which may be added as such or formed in the reaction mixture from the acid ester, e.g., butyl hydrogen phthalate and a catalyst, mixed cellulose esters result. Thus, a mixture of cellulose dinitrate, monobutyl phthalate, acetic ester and sulfuryl chloride when allowed to react, the chloride of the acid ester is formed and reacts with the cellulose derivative, forming (probably in this instance) cellulose phthalyl-dinitrate. Textile fabrics have been described characterized by the employment in the fabric of yarns or threads comprising a number of artificial filaments of cellulose acetate mixed with rayon, merged or coalesced to form by their physical union, a single unitary filament of larger denier[2].

The C. Dreyfus and G. Miles method of producing cellulose acetonitrates[3] comprises simultaneously treating cellulose with glacial acetic acid, acetic anhydride and fuming nitric acid free of catalyst from 0° to room temperature until the degree of esterification desired has been attained. In order to insure a predetermined amount of moisture in acetate plastics[4], a hygroscopic substance as zinc chloride is incorporated with the ester, subsequently allowing the mixture to acquire such water as the zinc chloride absorbs and retains. Where cellulose is acetylated with acetic anhydride in the presence of acetic acid as diluent and sulfuric acid as catalyst[5], water is added to the resulting mass and part of the acetic acid distilled off, the distillation being interrupted while the acetylcellulose is still in solution. The amount of acetic acid remaining in the mass corresponds substantially to the acetic anhydride originally employed.

1. Deutsche Celluloid-Fabr., E. P. 355172; abst. J. S. C. I. 1931, **50**, 968-B. F. P. 709958.
2. W. Dickie and W. Taylor, U. S. P. 1848560. See C. Dreyfus and W. Whitehead, Can. P. 312669.
3. Can. P. 318757.
4. C. Dreyfus and G. Miles, Can. P. 312024.
5. C. Dreyfus and G. Schneider, Can. P. 312026; abst. C. A. 1931, **25**, 3832.

Cellulose propionate of high clarity and soluble in benzene and butyl acetate is prepared by treatment of cellulose with formic, acetic or propionic acids, a small amount of sulfuric acid and propionic anhydride[1] at 10°, allowing the temperature to rise to about 35°, when, after a few hours, the mass is transformed into a translucent, heavy, syrupy mass, which completes the reaction. If the cellulose is treated with nitric acid and then acetylated in the usual manner[2], a cellulose acetate carrying little or no combined nitric acid is formed which gives solutions of great clarity.

Cellulose acetate of high resistance to heat is prepared by acetylating in a bath in which sufficient non-solvent is present so that the acetylcellulose upon formation does not pass into solution[3]. The cellulose acetate is mechanically separated and treated in the solid form with a solution of nitric, phosphoric or oxalic acids at elevated temperature. The tensile strength of cellulose acetate is said to be augmented by employing a saponifying treatment of submitting the ester at not above 30° to the action of an atmosphere resulting from the vaporization of 28% aqueous solution of ammonia[4]. Or[5], the ester may be saponified by treatment with methyl alcohol containing 3% NaOH for not more than 10 hrs. at approximately 25°.

In producing hollow yarns or filaments[6], they may be formed from acetylcellulose solutions under such conditions that solidification takes place in two stages, the former being less drastic than the latter. Acetylcellulose lacquers and aldehyde in the presence of stannous chloride[1], in a junction with a phenol-aldehyde resin prepared from phenol

1. C. Dreyfus and G. Schneider, U. S. P. 1824877; abst. C. A. 1932, **26**, 305. Can. P. 312906; abst. C. A. 1931, **25**, 4401.
2. C. Dreyfus, H. Martin and L. Lee, Can. P. 314310.
3. C. Dreyfus and L. Lee, Can. P. 313340; abst. C. A. 1931, **25**, 4706.
4. C. Dreyfus and W. Whitehead, Can. P. 313338; abst. C. A. 1931, **25**, 4706.
5. *Ibid.* Can. P. 313336; abst. C. A. 1931, **25**, 4706.
6. *Ibid.* Can. P. 316422.

and aldehyde in the presence of stannous chloride[1], in a volatile solvent for both. In stabilizing acetylcellulose[2], the ester is precipitated from the primary solution in which it is formed, dissolved, and adding thereto a soluble barium salt (chloride or acetate) to combine with the cellulose sulfates. In order to economize on volatile solvents, a surface may be coated with acetylcellulose by applying a mass containing the ester in very finely divided powder and a plastifier to the surface under pressure and at an elevated temperature[3]. The surface may be polished and smoothed by submission to the action of an abrasive in the presence of a latent solvent for the ester[4].

An insulating composition has been outlined[5], in which articles to be coated are provided with a jacketing of acetylcellulose fibers. In order to fabricate yarns of acetylcellulose resistant to the delustering action of boiling water[6], the ester is dissolved in a mixed solvent containing not more than 5% ethyl alcohol. The maximum of luster and transparency in filaments are said to be obtained by extruding a solution of acetone-soluble acetylcellulose in acetone and triacetin through orifices into an aqueous precipitant[7], and then contacting the filament with a heating device. If the ester has an acetyl value of 45-48% it is recommended to extrude a solution of the ester in a solvent mixture comprising 60-85 acetone and 40-15 water through orifices into a drying evaporative atmosphere[8].

Pattern effects on fabrics containing acetylcellulose and

1. C. Dreyfus, Can. P. 307989.
2. C. Dreyfus and C. Haney, Can. P. 309756; abst. C. A. 1931, **25**, 3167.
3. C. Dreyfus and G. Schneider, Can. P. 310250, 310251.
4. C. Dreyfus, Can. P. 310930.
5. *Ibid.* Can. P. 315581.
6. C. Dreyfus and W. Whitehead, Can. P. 316423.
7. *Ibid.* Can. P. 314312; abst. C. A. 1931, **25**, 5289.
8. C. Dreyfus, W. Whitehead and H. Martin, Can. P. 312668; abst. C. A. 1931, **25**, 4402.

other fibers as cotton or linen[1] are possible by printing on the fabric a saponifying agent as NaOH in a paste with tragacanth or acacia, so that the ester is converted into regenerated cellulose, the fabric being then given a carbonization treatment as by passing through a bath containing

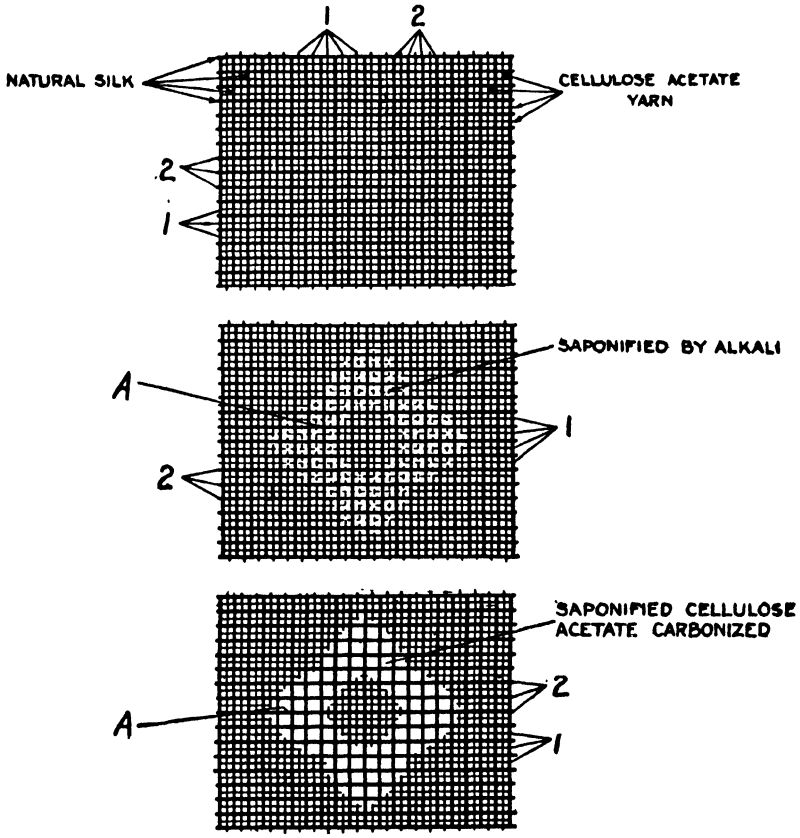


Fig. 1. Pattern Effects on Cellulose Acetate Fabrics.

HCl, aluminum chloride or sodium bisulfate, thus making possible the production of beautiful effects. Fig. 1 is explanatory. In weaving a pile fabric containing natural silk

1. C. Dreyfus, U. S. P. 1804529; abst. C. A. 1931, **25**, 3849; Chem. Zentr. 1931, II, 1766. Can. P. 314909. C. Dreyfus, R. Dort and H. Platt, Can. P. 320249. F. P. 716671; abst. C. A. 1932, **26**, 2328.

and acetylcellulose yarns[1], the tendency of the ester to become delustered when exposed to boiling water is overcome in the appearance of the finished fabric by partially degumming undyed natural silk to the desired extent and then weaving this with acetate yarn in such a manner as to form a pile fabric which need not be subjected to a degumming process, the finished fabric taking on the natural sheen and luster of the cellulose acetate. Fabric containing acetylcellulose has the "sticking" point increased by treatment for 45 min. at 40° with a solution containing 1-5% basic aluminum acetate and 5-10% acetic acid[2].

A fabric has been described[3], composed, at least in part, of a thermoplastic acetylcellulose having a hole or holes therein, the edge of which has been partially liquefied and then permitted to solidify. To permanently emboss such a thermoplastic fabric[4], the latter is treated with a softening agent as a dilute acetone solution, and then embossed. If it is desired to adapt the fabric to be used as a stiffening material[5], the individual acetate yarns are stiffened before weaving. Such a fabric may be pressed without appreciably affecting the luster[6], by subjecting the fabric in dry condition to a dry, hot ironing treatment below the fusion point of the cellulose acetate.

An ornamental fabric has been described having one of the components of the warp or weft of acetylcellulose yarns and the other of acetate silk with natural silk fibers[7], the acetylcellulose being uncolored while the natural silk has been dyed dark. If it is desired to induce a crepe effect[8], the fabric is formed by weaving together acetylcellulose fibers with highly twisted, degummed natural silk yarn and then subjecting the fabric to a creping bath.

1. C. Dreyfus, U. S. P. 1818540; abst. C. A. 1931, **25**, 5580. Can. P. 312945.
2. *Ibid.* Can. P. 308437; abst. C. A. 1931, **25**, 1686.
3. *Ibid.* Can. P. 308436.
4. *Ibid.* Can. P. 308623.
5. *Ibid.* Can. P. 311185.
6. C. Dreyfus and C. Palmer, Can. P. 312667.
7. C. Dreyfus and C. Palmer, Can. P. 313341.
8. C. Dreyfus, Can. P. 313166.

If an acetone-soluble acetylcellulose having acetyl value of 52.5-56% is dried until it contains less than 1% of water, dissolved in substantially pure acetone, filtered and dry-spun at 50-55°, yarns are formed that are highly resistant to the delustering action of boiling water, and which have a strength that is 15-25% greater than that of yarn produced from a cellulose acetate solution in 95% acetone[1]. Instead of acetone, methyl alcohol or a mixture of acetone and methyl alcohol may be used[2], or a mixture of acetone 65%, with 35% of 95% denatured ethyl alcohol[3].

Instead of immersing acetylcellulose filaments and fabrics directly in a dye bath, the dye may be dissolved in a swelling agent for the ester and sprayed on[4]. To increase the color and clarity of cellulose acetate, the cellulose is pretreated with a mixture of nitric and acetic acids, the nitric acid evaporated off, and then further esterified in the usual manner[5]. Instead of dyeing in a hot aqueous solution, the dyestuff may be dissolved in a solvent which is both a solvent for the dye and acetylcellulose[6].

Methods for the manufacture of laminated glass have been patented by C. Dreyfus in which the cellulose acetate intermediate film between the sheets of glass has applied thereto a sulfonamid-aldehyde resin[7], a synthetic resin compatible with the cellulose ester[8], or a plasticizer as dibutyl tartrate[9]. An acetylating apparatus has been protected[10], being the combination of a container with agitator, an acetylizer with mixing members and means for connecting to the container and for delivering the material

1. C. Dreyfus and W. Whitehead, Can. P. 310732; abst. C. A. 1931, **25**, 3169.
2. *Ibid.* Can. P. 309131; abst. C. A. 1931, **25**, 1994.
3. *Ibid.* Can. P. 309130; abst. C. A. 1931, **25**, 1994.
4. *Ibid.* Can. P. 308605; abst. C. A. 1931, **25**, 1685.
5. C. Dreyfus and L. Lee, Can. P. 314309; abst. C. A. 1931, **25**, 5287.
6. C. Dreyfus and W. Whitehead, Can. P. 312666.
7. C. Dreyfus and W. Moss, Can. P. 318145.
8. *Ibid.* Can. P. 317919.
9. *Ibid.* Can. P. 311770. See C. Dreyfus and W. Whitehead, Can. P. 316587.
10. C. Dreyfus and G. Schneider, Can. P. 316841.

from the former to the latter, this connection being adapted to be swung into and out of alignment.

To impart a differential color to a fabric containing acetate yarns[1], there is locally applied a diazotizable amine in the presence of an acetylcellulose swelling agent, and then developing. Or[2], the local color effect may be induced by locally applying a readily volatilizable dyestuff in a transfer medium, then moistening, and applying a heated surface to predetermined places thereon. If it is desired to lubricate acetylcellulose yarns[3], there is applied thereto an aqueous solution of a polyhydric alcohol in which at least one of the hydroxyl hydrogens is replaced by an alkyl group. In forming "spun" yarn[4], filaments of acetylcellulose are cut while they are stretched under tension, and then associated together by the usual spinning operation for staple fiber.

A phonograph record has been devised (p. 822, n. 6) having a reproducing surface of thermoplastic acetylcellulose with about 35-60% plastifier contained therein, and free from hard filling material[5], it being claimed that such a composition amplifies sound vibration with great fidelity of reproduction and freedom from distortion. It would appear that such a record would have a comparatively low softening degree. Dibenzyl tartrate as an acetylcellulose plastifier has been patented[6]. A toluenesulfonamid-formaldehyde resin, polymerized vinyl compound and cellulose acetate dissolved together in a volatile solvent[7], has been put forward as a desirable lacquer and liquid coating composition. A process for bleaching cellulose acetate by treatment with aqueous oxalic acid has been devised[8].

1. C. Dreyfus and H. Platt, Can. P. 317114.
2. C. Dreyfus and R. Dort, Can. P. 317115.
3. C. Dreyfus and W. Whitehead, Can. P. 317116. See C. Dreyfus and W. Whitehead, Can. P. 318521.
4. C. Dreyfus and G. Schneider, Can. P. 317920. See C. Dreyfus and F. Williams, Can. P. 318146.
5. C. Dreyfus, Can. P. 317959.
6. C. Dreyfus and G. Schneider, Can. P. 318147.
7. C. Dreyfus and W. Moss, Can. P. 318758.
8. *Ibid.* Can. P. 319149.

According to W. Moss[1], a useful coating composition results from combining cellulose acetate with a resin formed by the condensation of lactic acid, both being dissolved together in a volatile solvent. Or[2], the resin may comprise toluenesulfonamid-aldehyde resin with excess of toluenesulfonamid and a volatile solvent, or an aromatic sulfonamid-furfural resin[3]. The safe ironing point of a textile material containing acetylcellulose may be increased by partially saponifying the ester and adding weighting material[4], of which a list of the latter has been given as suitable for employment with the organic cellulose esters[5].

As a cellulose acetate plastifier, dihydroxybenzophenone[6] and a ketone of the general formula CH_3COR, wherein R represents an aromatic radical containing at least two carbon atoms having a hydroxyl group[7] have been granted patent protection. Artificial resins in conjunction with acetone-soluble acetylcellulose as coating compositions have been evolved, such as combining the ester with naphthalene and a synthetic resin[8]; with a toluenesulfonamid-aldehyde resin which is hard and does not deposit toluene sulfonamid from a solution in benzene[9]; a diphenylolnaphthene-formaldehyde condensate[10]; and an aromatic sulfonamid with benzaldehyde[11], all in conjunction with volatile solvent combinations.

Open work fabric of predetermined design may be prepared by treating acetylcellulose textiles having a pattern of acetylcellulose and a vegetable fiber[12], with a carbon-

1. C. Dreyfus and W. Moss, Can. P. 319150.
2. C. Dreyfus, W. Moss and B. White, Can. P. 319151.
3. *Ibid.* Can. P. 319152.
4. C. Dreyfus and W. Blume, U. S. P. 1818466; abst. C. A. 1931, **25**, 5580. C. Dreyfus and G. Rivat, Can. P. 320913.
5. C. Dreyfus and H. Platt, Chemicals, 1931, **35**, 29.
6. C. Dreyfus and W. Moss, Can. P. 319733.
7. C. Dreyfus, W. Moss and G. Seymour, Can. P. 319734.
8. C. Dreyfus and W. Moss, Can. P. 319728.
9. C. Dreyfus, W. Moss and B. White, Can. P. 319731.
10. C. Dreyfus and W. Moss, Can. P. 319730.
11. C. Dreyfus, W. Moss and B. White, Can. P. 319729.
12. C. Dreyfus, R. Dort and H. Platt, Can. P. 320249.

izing promoting compound, and then subjecting the fabric to a carbonizing temperature.

To remove combined sulfur from cellulose acetate[1] a mixture of the ester and water is passed continuously through a heated passage at superatmospheric pressure, maintaining such conditions that the treated ester contains an amount of sulfur equivalent to less than 0.03% SO_4. A soldering powder has been invented[2] containing finely divided filtering material, acetylcellulose, and a plasticizer in intimate admixture. To prepare acetate filaments of great softness and suppleness[3], it is recommended to combine with the ester before spinning, diethylene glycol and an oleaginous substance, or the salt of a higher fatty acid which tends to assist solidification of the filaments when projected into an evaporative atmosphere[4].

Cellulose acetate textiles may be conditioned while wound in a package[5], by submission to the vapors of a conditioning agent generated within the package. In order to increase the filament stretch in acetylcellulose stretch-spun by the dry method[6], a liquid of lower volatility than the solvent used in the acetate solution before spinning, is applied to the filaments during their drying.

In acetic anhydride production[7], phenol ethers other than phenetole and anisole are used for scrubbing the reaction gases (see p. 633, n. 6; 770, n. 1). In the solvent method for concentrating dilute acetic acid[8], *a*- or *b*-naphthyl methyl (or ethyl or propyl) ether, anisole, phenetole, diphenyl oxide, *p*-tolyl ether or *b*-naphthyl ether, naphthol-*p*-tolyl ether, phenolphenyl ether, or cresolcresyl ether may be used. Acetic anhydride results when a reaction mix-

1. C. Dreyfus and G. Schneider, Can. P. 320914.
2. C. Dreyfus and W. Whitehead, Can. P. 320250.
3. *Ibid.* Can. P. 319735.
4. *Ibid.* Can. P. 319736.
5. C. Dreyfus and G. Blake, Can. P. 319737.
6. H. Dreyfus and W. Taylor, Can. P. 321116.
7. H. Dreyfus, E. P. 354199, Addn. to E. P. 279916; abst. J. S. C. I. 1932, **51**, 12-B; Chem. Zentr. 1931, II, 2658.
8. H. Dreyfus, E. P. 354198; abst. J. S. C. I. 1932, **51**, 12-B; Chem. Zentr. 1931, II, 2932. Swiss P. 63057, 63526.

ture comprising an aliphatic acid and metaphosphoric acid are subjected to a temperature not exceeding the boiling point of the mixture, the reaction being performed in the presence of a non-aqueous diluent[1]. Acetic acid may be made from formaldehyde vapor with CO subjected to 300-400 atmospheres pressure at 300-400°, a nearly theoretical yield being obtained. Or the aliphatic acid may be subjected to pyrogenic decomposition[2], the resulting anhydride being separated from water vapor present or formed in the reaction, by condensing the anhydride while carrying away the water vapor by a gaseous entraining liquid. Or[3], the acetic anhydride may be dissolved by a naphthyl ether, or a phenol-phenyl ether[4].

The succeeding five patents embrace acetic acid manufacturing processes as evolved by H. Dreyfus, and comprehend (1) heating formaldehyde with CO at 100-300 ats. to 300-400°[5]; homogeneously mixing the dilute acetic acid and the entraining liquid by adding sufficient concentrated acetic acid before distillation[6]; by admixing an alcohol, air or oxygen with steam and in presence of the oxides of manganese, cobalt, nickel, iron, lead, zinc or uranium[7]; passing dimethyl ether and CO under 100-200 atm. pressure through a copper lined reaction chamber filled with granules of zinc or tin oxide[8]; or by combining methyl alcohol and CO under pressure in the presence of phosphoric acid, the reaction vapors being absorbed by active charcoal or silica gel[9].

Aliphatic ketones as acetone are produced by subjecting ethyl alcohol vapor in the presence of water vapor to

1. H. Dreyfus, Can. P. 308432.
2. H. Dreyfus and C. Haney, Can. P. 316192.
3. H. Dreyfus, Can. P. 319581.
4. *Ibid.* Can. P. 319580.
5. H. Dreyfus, S. Green and R. Handley, Can. P. 316201.
6. H. Dreyfus, E. P. 356787; abst. J. S. C. I. 1932, **51**, 94-B; Chem. Zentr. 1931, II, 3393.
7. *Ibid.* E. P. 341031; abst. C. A. 1931, **25**, 4893; J. S. C. I. 1931, **50**, 385-B; Chem. Zentr. 1931, I, 2934.
8. *Ibid.* E. P. 340939; abst. C. A. 1931, **25**, 4893; Chem. Zentr. 1931, I, 2933.
9. H. Dreyfus, S. Green and R. Handley, Can. P. 316202.

relatively high temperatures in the presence of zinc oxide as catalyst[1]. Acetylation of cellulose is effected with acetic anhydride and sodium bisulfate[2], in the presence of an organic solvent as acetic acid, the temperature being kept at 25-30°. Cotton or wood pulp to be used for acetyl-cellulose production is pretreated with formic or acetic acids in the gaseous state, a portion of the acid being removed by air current before acetylating in the usual manner[3], or the esterifying agent may also be in the vapor form[4], liquid solvents and diluents being absent.

Valuable properties are claimed for acetated cellulose in which basic ferric chloride is used as catalyst[5], the cellulose being pretreated with less than 2% hydrogen halide (calculated on the weight of the cellulose)[6], or not to exceed 2% combined HCl and ferric chloride[7]. Stannic chloride and HCl may also be used as catalyst[8], or a mixture of 5% each HCl and zinc chloride[9], or a mixture of manganese and copper chlorides[10]. Cellulose acetate may be formed in the fibrous condition by esterifying cellulose in suspension and also ripening the primary esters in suspension in a liquid in which the ripening agent is miscible—at least to a sufficient extent to permit ripening[11]. Ripening may also be effected in the presence of tertiary organic bases as alkyl piperidines (methyl or ethyl), or dimethyl-*n*-hexylamine[12].

1. H. Dreyfus, Can. P. 319579.
2. *Ibid.* U. S. P. 1829822; abst. C. A. 1932, **26**, 843.
3. *Ibid.* U. S. P. 1831101; abst. C. A. 1932, **26**, 843. E. P. 343986; abst. C. A. 1932, **26**, 303. See also U. S. P. 1711110.
4. *Ibid.* U. S. P. 1831102; abst. C. A. 1932, **26**, 843.
5. *Ibid.* E. P. 342738; abst. C. A. 1931, **25**, 5557; J. S. C. I. 1931, **50**, 479-B; Brit. Plastics, 1931, **3**, #28, 179; Silk J. and Rayon World, 1931, **8**, #85, 54. Can. P. 316027.
6. *Ibid.* E. P. 342739; abst. C. A. 1931, **25**, 5557; J. S. C. I. 1931, **50**, 479-B; British Plastics, 1931, **3**, #28, 179; Silk J. and Rayon World, 1931, **8**, #85, 54. See E. P. 309201, 312095, 312096, 312098.
7. *Ibid.* E. P. 342740; abst. C. A. 1931, **25**, 5557; J. S. C. I. 1931, **50**, 479-B; British Plastics, 1931, **3**, #28, 179; Silk J. and Rayon World, 1931, **8**, #85, 54.
8. *Ibid.* Can. P. 316028.
9. *Ibid.* Can. P. 315358, 316026.
10. *Ibid.* Can. P. 315357.
11. *Ibid.* Can. P. 309594.
12. *Ibid.* Can. P. 315359.

Cellulose butyrate or propionate fabrics may be loaded and prepared for dyeing, printing or stencilling[1], by treatment in successive baths of stannic chloride and disodium phosphate, then dyed with a dyestuff which has but little affinity for unloaded acetylcellulose. A method of acetate silk fabrication has been described[2], comprising forcing the solution through a relatively large number of orifices simultaneously into a current of evaporative medium secluded from the atmosphere, a definite proportion of which is allowed to pass through the immediate vicinity of the spinning orifices. Or the proportion of air may be restricted only in the vicinity of the birth-zone of the filaments[3], so that a definite proportion of air is constrained to pass therethrough. Filaments may be stretched and reduced in denier by bringing into contact the acetate filaments directly after extrusion[4], with 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 their extrusion.

A regular or systematic variation in denier to acetate filaments or threads may be induced by delivering the spinning solution to the nozzles in pulsations[5], a suitably actuated member such as a diaphragm, piston or plunger being caused to vibrate, reciprocate, fluctuate or oscillate in contact with the spinning solution. Very interesting effects are stated to be obtainable in fabrics prepared from these irregular filaments.

In the production of threads, ribbons and films of acetylcellulose by the wet-spinning process[6], the coagulation is manipulated with non-solvent swelling agents whereby a

1. H. Dreyfus, U.S.P. 1805468; abst. Chem. Zentr. 1931, II, 3046.
2. *Ibid.* Belg. P. 377606. Can. P. 308434.
3. *Ibid.* Belg. P. 376997. Can. P. 308433.
4. H. Dreyfus and W. Taylor, Can. P. 315537. See H. Dreyfus, W. Dickie and P. Sowter, Can. P. 316198.
5. H. Dreyfus, W. Dickie and W. Taylor, Can. P. 315536.
6. H. Dreyfus, W. Dickie and P. Sowter, Can. P. 317110. H. Dreyfus, Can. P. 311410. H. Dreyfus, J. Briggs and R. Roberts, Can. P. 311592. See H. Dreyfus, W. Dickie and P. Sowter, Can. P. 314449.

maximum stretching of the partially coagulated filament is possible. The filaments are preferably stretched while they contain 20-40% of residual solvent[1], the filaments being caused to set under considerably reduced pressure, assisted by the application of heat[2]. The resistance of cellulose acetate silk in the form of yarns, skeins or fabrics to hot or boiling liquids is increased by stretching the finished filaments beyond their elastic limit[3], the stretching being assisted by pretreatment with swelling agents as acetone, alcohol, formaldehyde or glycerol, a stretch of 15-25% being suitable. Threads so treated are stated to retain their luster and do not become curly or wool-like in boiling water.

Pleasing effects in acetate textiles are producible where a portion of the fibers has been submitted to differential saponification, dyestuffs giving a variation in tint and depth of penetration[4]. The filament cross section is more uniform and more nearly circular if acetate filaments are extruded from the spinneret into a closed chamber in which a partial vacuum is maintained[5], the threads being led out through an opening in the chamber, and dry air fed into the zone of the opening to prevent the penetration of damp air into the opening. By modifying the evaporative conditions, especially as to atmospheric pressure[6], filaments of varied cross section are obtained.

To formulate plastic acetated cellulose compounds, the finely divided ester containing little or no solvent is impregnated with a plasticizer (toluenesulfonamide, alkyl phthalate) in a volatile liquid vehicle (ethyl ether[7]), which is not a solvent for or soluble in the cellulose ester, but

1. H. Dreyfus and W. Taylor, Can. P. 317108.
2. H. Dreyfus, Can. P. 311409.
3. *Ibid.* F. P. 697427; abst. C. A. 1931, **25**, 3167. Cites E. P. 206113, 246879, 277089. F. P. 678314, 679618.
4. *Ibid.* F. P. 701875; abst. C. A. 1931, **25**, 4136.
5. *Ibid.* F. P. 702509; abst. C. A. 1931, **25**, 4403.
6. *Ibid.* F. P. 702979; abst. C. A. 1931, **25**, 4402. See F. P. 704281; abst. C. A. 1931, **25**, 5708.
7. *Ibid.* E. P. 354860, 354861; abst. J. S. C. I. 1931, **50**, 936-B; Chem. Zentr. 1931, II, 3691.

evaporated before the material is worked. The plastifier is uniformly applied by spraying onto the finely divided ester (preferably itself as a spray), substantially in the absence of solvents or diluents. 2.4.6-Tribromdiacetanilide, stable to light, a cellulose ester fire-retarder melting at 124° is obtained by acetylating sublimed 2.4.6-tribromaniline[1]. A paste for the discharge printing of acetate silk has been patented[2] containing acacia 200, kaolin 50, water 210, deatured alcohol 250 and zinc formaldehyde-sulfoxylate 190 parts. Discharge effects on acetate silk are also obtainable by printing with a paste containing *p*-dihydroxy benzene compound[3].

If it is desired to weight acetylcellulose fabrics which also are to be colored[4], the fabric or yarn to be woven into fabric is first loaded with alkali metal stannates (sodium stannate) then locally coloring by applying separately both discharges and dischargeable dyestuffs. In producing colored discharge effects[5], a pyrazolone dye is incorporated with the discharge agent, which may be a formaldehyde-sulfoxylate, a hyposulfite or stannous chloride. Substances facilitating the discharge such an anthraquinone, or swelling agents as the thiocyanates may also be used. Example, 1-phenyl-3-methyl-6-pyrazolone coupled with diazotized amidobenzene. In printing acetate textiles[6], reagent penetration is facilitated by the use of *p*-dihydroxy compounds as hydroquinone, 2.5-dihydroxytoluene or derivatives, the process being particularly applicable to the local application of dyes or discharges.

Azo dyes are prepared by coupling diazotized aromatic amines with naphthylamine coupling components substituted in one amido group by one or more aliphatic groups

1. H. Dreyfus and B. Miller, Can. P. 316200.
2. H. Dreyfus, F. P. 702012; abst. Chem. Zentr. 1931, II, 3271.
3. H. Dreyfus and G. Ellis, Can. P. 317111.
4. H. Dreyfus and G. Ellis, Can. P. 316193.
5. H. Dreyfus, F. P. 706670; abst. C. A. 1932, **26**, 317.
6. *Ibid.* F. P. 706620; abst. C. A. 1932, **26**, 317.

containing OH[1]. Thus, *p*-nitroaniline diazotized and coupled with hydroxyethyl-*a*-naphthylamine give a scarlet shade on cellulose acetate. If it is desired to dye in the package or wound form[2], aqueous dispersions are applied containing relatively water-insoluble dyestuffs entirely in the colloid state.

High-melting organic compounds, preferably water-insoluble[3], are incorporated in the spinning solution to impart to acetylcellulose a subdued luster. Particularly suitable are diacetyl- benzidine or -tolidine, dibenzoylbenzidine, di-*b*-naphthylamine, diphenyloxamide, succinic-*a*-naphthylamide, thiocarbonylbenzidine, carbonylbenzidine, 4.4′-dicarbamidodiphenyl and 4.4′-*bis*phenylcarbamidodiphenyl. Phosphorescent or luminous substances may be affixed to acetate textiles while the latter are in a softened condition[4], acetone being recommended in this connection. In one method which has been described for the treatment of ornamental fabrics[5], an acetate textile composed of both shrunk and unshrunk yarn is immersed in nitric acid as a shrinking agent of sp. gr. 1.1-1.2.

Acetate ribbons or other flattened yarns result when a plurality of individual filaments are coalesced by means of treatment with an incipient volatile dissolving combination, and the filament aggregates submitted to pressure[6]. Pattern effects on acetate fabrics are producible by forming azo colors on the textile[7], diazotizing and developing the production of discharge resist effects by rendering the amino body, before diazotization and development, incapable of reaction in selected areas with the aid of a reduction dis-

1. H. Dreyfus, F. P. 701372; abst. C. A. 1931, **25**, 4134. See also F. P. 688623, 688624, 705161.
2. H. Dreyfus, G. Ellis and T. Ellison, Can. P. 314448.
3. H. Dreyfus, E. P. 346678; abst. J. S. C. I. 1931, **50**, 715-B; Silk J. and Rayon World, 1931, **8**, #88, 54.
4. *Ibid.* F. P. 704564; abst. C. A. 1931, **25**, 4718. H. Dreyfus and W. Taylor, Can. P. 317109.
5. H. Dreyfus, W. Dickie and R. Moncrieff, Can. P. 316203.
6. H. Dreyfus, Can. P. 316196. H. Dreyfus and W. Taylor, Can. P. 316195.
7. H. Dreyfus, G. Ellis and W. Miller, Can. P. 316194.

charge. A. Drinberg has shown[1] that intensity of dispersed light increases with increase in concentration of nitrocellulose, but does not show a maximum observed by E. Mardles (p. 561, n. 2) with acetylcellulose. The intensity decreases with increase in degree of solvation or depolymerization of the sol. Viscosity and degree of depolymerization decrease is attributed to the influence of electrolytes[2]. Increase in molecular weight of acid radicals in cellulose esters used as peptizing agents results in increase in viscosity of the sols[3], while viscosity and degree of solvation with a homologous series of peptizing agents augments with increase in molecular polarization, dipolar moment and the alcohol coagulation number.

If small quantities of water are successively added to an acetone solution of acetylcellulose[4], viscosity diminishes, and passes through a minimum when the amount of water is about 5% and then again increases when coagulation occurs. This effect is attributed to the state of association of the water. The plastifying action is ascribed to the hydroxyl groups of the water which react with the OH groups of the cellulose acetate, which are the absorbent components of these compounds. In the preparation of films of fossilized plants[5], a plasticizer and a small proportion of high-boiling solvent is used to prepare an acetylcellulose lacquer as an imbedding media. Clear films are obtained which are not brittle and do not contract, and allow permanent mounts to be made without distortion of the specimen.

A. Dunton[6] claims that if the right "type" of cellulose acetate is selected there need be no fear about the ageing

1. J. Applied Chem. (U. S. S. R.) 1931, **4**, 505; abst. C. A. 1932, **26**, 592.
2. *Ibid.* Zhur. Prikladnoi Khim, 1931, **4**, 293; abst. C. A. 1932, **26**, 357.
3. *Ibid.* Zhur. Prikladnoi Khim, 1931, **4**, 87; abst. C. A. 1931, **25**, 5820.
4. J. Duclaux and J. Barbiere, J. Chim. phys. 1931, **28**, 313; abst. C. A. 1932, **26**, 591.
5. H. Duerden, Ann. Bot. 1931, **45**, 376; abst. J. S. C. I. 1931, **50**, 886-A.
6. Electrician, 1931, **107**, 483.

properties of the ester. It has been found that the life of acetate foils actually exceeds that of many of the insulating materials now employed in the arts, being next to mica products in stability as an insulator. Mat or woolly effects on acetate threads are obtainable by treatment with aqueous calcium chloride followed by a boiling dilute acid solution of $N/10$ concentration[1]. An ink for cellulose esters has been brought forward[2] comprising diacetone alcohol, ethyl lactate, nigrosin and shellac.

Cellulose acetate is colored by means of the leuco-compounds of gallocyanine dyes[3], which have a greater affinity for acetate fibers than when in the fully oxidized form. The method of applying may be so modified that they dye cotton in conjunction with acetylcellulose (e.g. in mixed fabrics)[4], the fabrics being printed or padded with a paste containing the leuco form of the dye and sodium chlorate, then dried, steamed and after-chromed in 0.5% sodium bichromate. A capsule has been placed on the market intended for home use in the dyeing of cellulose acetate mixed fabrics[5], comprising a non-soluble dyestuff which colors in a very fine state of division suspended in gelatin or glycerol, and a substantive cotton dye, the whole being encased in a gelatin capsule.

The crude product obtained by acetolysis of cellulose is separable into a methyl alcohol, soluble and an insoluble portion[6], the latter corresponding with biosan acetate. Roentgen diagrams of the products obtained when fibrous cellulose acetate and *limit*-dextrin acetate are dissolved in ethyl malonate, methyl alcohol-chloroform and pyridine re-

1. Du Pont Rayon Co., Can. P. 308125.
2. Du Pont Viscoloid Co. and J. Clewell, U. S. P. 1806965; abst. Chem. Zentr. 1931, II, 2820.
3. Durand & Huguenin A.-G., E. P. 352808; abst. J. S. C. I. 1931, **50**, 923-B; Textile Mfr. 1931, **57**, 461; Silk J. and Rayon World, 1932, **8**, #83, 54. D. R. P. 526193; abst. C. A. 1931, **25**, 4413; Chem. Zentr. 1931, II, 1497. F. P. 701852.
4. *Ibid.* E. P. 359861; abst. J. S. C. I. 1932, **51**, 99-B. D. R. P. 534466; abst. C. A. 1932, **26**, 855.
5. Dyanese, Ltd., and S. Tootal, Can. P. 316728.
6. K. Dziengel, C. Trogus and K. Hess, Annalen, 1931, **491**, 52; abst. J. S. C. I. 1932, **51**, 47-A.

spectively, and the solutions evaporated at various temperatures, show that transformation of the diagrams for cellulose acetate I into those of cellulose acetate II occur between 35-45°, 30-45° and 60-75°[1]. Roentgen diagrams indicate that cellulose dextrins contain two substances, one of which appears to be cellulose acetate II. Acetate III is considered to be an additive compound of cellulose acetate II and a substance formed during acetolysis, which is not a glucose acetate or cellobiose acetate, but may be an acetyl derivative of the water-soluble carbohydrate described by Klages. J. Eccles has reviewed our knowledge concerning mildew growth on acetate fabrics[2], and the effects of *Aspergillus, Rhizopus, Penecillium, Mucor, Fusarium* and *Alternia* types of mould, and discussed the causes of warp streaks in fabrics with acetate warps, the usual cause being oxidation of lubricating oil[3].

A mixture of acetic and butyric acids may be separated and recovered by neutralizing, evaporating to dryness, dehydrating and distilling with sulfuric acid to liberate the acids in concentrated form[4]. Very thin foils and bands of acetylcellulose are obtainable[5] by casting a thin solution on a rapidly moving band, the ester being dissolved in a low-boiler solvent containing a high boiling nonsolvent so that setting of the film will be almost instantaneous, the bands being arranged in the form of loops

1. K. Hess, C. Trogus, W. Ostwald and K. Dziengel, Zts. physikal. Chem. 1930, B-**7**, 1, that if either fibrous cellulose triacetate I or the crystalline triacetate II (see p. 149, n. 1; 232, n. 4; 248, n. 1; 800, n. 7) is dissolved in pyridine and the solution evaporated at different temperatures give identical X-ray diagrams between 35-75°, a behavior noted with other solvents, but the temperatures vary. The transformation of triacetate I into triacetate II is therefore reversible and characterized by an equilibrium which depends upon temperature and solvent. By the acetylation of ramie, whether mercerized or not, fibrous bundles of either triacetate can be obtained, the nature of the product depending upon the temperature of acetylation, triacetate I preponderating at low temperatures, and triacetate II at high.

2. Am. Dyestuff Rep. 1931, **20**, 633; Textile Mfr. 1931, **57**, 184; abst. C. A. 1932, **26**, 310.

3. J. Eccles, Dyer, Calico, Printer, 1931, **66**, 39; abst. C. A. 1932, **26**, 851.

4. W. Edmonds and I. Krchma, U. S. P. 1835700.

5. A. Eichengrün and Celanese Corp., U. S. P. 1824337.

individually driven positively, and supported by its borders only. Or[1], the process may be adjusted for the manufacture of filaments of unusually fine denier.

For the rapid determination of the water adhesion of textile fibers containing acetylcellulose[2], a bundle of 25 fibers is held under tension in the center of a horizontal glass tube and the decrease in length recorded as all the water is driven out of the fibers by heating to about 135°. A calibration curve is required. A non-curling floor covering has been patented[3], comprising acetylcellulose, triacetin, ceresin, and a benzoyl-benzoic synthetic resin or similar resinous body, with compatible volatile solvents.

For dyeing acetylcellulose yarns or fabrics[4], a relatively water-insoluble unreduced indophenol coloring matter in the dispersed form obtained by treating with naphthenic or naphthenesulfonic acids or their sodium salts, as a dispersing agent, has been patented. Differential effects on acetate fabrics are obtainable by treatment with solvents (aniline, chloranilines, toluidine, anisidine, phenol, cresols, resorcinol, catechol, pyridine, quinoline) and dyestuffs which are likewise soluble, followed by a delustering treatment by moist steam[5]. For coloring[6], the acetate fabric is treated with an azo compound containing *α*-naphthylamine as end component, such as *p*-aminobenzeneazo-*α*-naphthylamine, the base being diazotized and coupled with a developer as *b*-hydroxynaphthoic acid. If an aqueous dispersion of a relatively insoluble dye is used[7], penetration of dye into acetate fiber is augmented by the addition of a solubilizing agent as sulforicinoleic acid or ammonium salt.

1. Celanese Corp. and A. Eichengrün, Can. P. 320555.
2. E. Einecke, Z. analyt. Chem. 1931, **85**, 45, no. 1-2-3.
3. C. Ellis, U. S. P. 1848329.
4. G. Ellis, U. S. P. 1818541, 1818542, 1818543. E. P. 224925; abst. Chem. Zentr. 1925, I, 1653.
5. *Ibid.* U. S. P. 1826608; abst. C. A. 1932, **26**, 605; Chemicals, 1931, **36**, 11.
6. *Ibid.* U. S. P. 1829130; abst. C. A. 1932, **26**, 855.
7. *Ibid.* U. S. P. 1840572. G. Ellis and W. Goldthorpe, U. S. P. 1803008; abst. C. A. 1931, **25**, 3847. Cites U. S. P. 1694414.

If it is desired to form colored patterns on acetate fabrics[1], the textile is locally treated with a composition comprising a swelling agent (formic acid, phenol, ammonium thiocyanate) and a printing composition capable of penetrating the ester in the intumesced condition. Conversion of primary into secondary cellulose acetates (by heating with 95% acetic acid at 100°) occurs without appreciable change in degree of molecular aggregation. When the true weight of cellulose in either the primary (cellulose 39.4, acetic acid 60.6) or secondary (cellulose 43.0, acetic acid 57.0) acetate is plotted against the viscosity of the sample, all the points lie on the same curve, hence the cellulose residue in both products is identical. Change in properties on conversation depends only on the fission of acetic acid, i.e., in the proportion of polar and non-polar groups in the molecule[2]. Enco[3] published a practical paper on the production of varying effects in the dyeing of fabrics containing acetylcellulose.

If cellulose acetate is mixed with any of the phosphoric acids (meta-, ortho, pyro-)[4], in small proportions in the presence of acetone as solvent, lacquers result of diminished inflammability and high stability. After boiling acetate silk 1 hr. in water and drying for 2 days at ordinary temperature[5], the breaking strain and elasticity are diminished and the extensibility increased. Treatment with certain dyes (Textile-test H and Picrocarmine K) affords a valuable test for the varying effect of boiling on the threads, depending upon the extent of surface hydrolysis; the amount of acetic acid formed, however, is too small to be determined. Decrease in luster is also quantitatively em-

1. G. Ellis and E. Greenhalgh, U. S. P. 1792152; abst. C. A. 1931, **25**, 2008. E. P. 244143; abst. Chem. Zentr .1926, I, 2970. Chemicals, 1931, **35**, 32.
2. E. Elod and A. Schrodt, Z. ang. Chem. 1931, **44**, 933; abst. J. S. C. I. 1932, **51**, 48-A.
3. Enco, Russa, 1931, **6**, 489; abst. C. A. 1931, **25**, 3173.
4. E. Farrow, S. Sheppard and H. Clarke, E. P. 342444; abst. C. A. 1931, **25**, 4421.
5. W. Fermazin, Chem. Ztg. 1931, **55**, 93; abst. C. A. 1931, **25**, 2000; J. S. C. I. 1931, **50**, 390-B.

ployed to determine the action of boiling liquids, the resistance to boiling being improved by the addition of calcium chloride to the liquor.

Pine oil, an oxidation product of turpentine boiling at 208-210°, at present mainly used for the manufacture of terpineol, has been found to be an excellent solvent for nitrocellulose and lacquers[1], a 0.5% addition to the size used for acetate silk improves the strength materially, a similar advantage being noted in adding 3% pine oil to the spinning bath. W. Fermazin[2] has described methods and apparatus for studying changes in the tensile strength and luster of acetate silk to determine its ability to withstand boiling. Monomethyl (or ethyl, propyl, *iso*propyl, butyl, *iso*butyl, amyl, *iso*amyl) propyleneglycol are excellent solvents for nitro- and acetyl-cellulose[3], and may be diluted with more than an equal volume of such non-solvents as benzene and toluene in the preparation of cellulose ester lacquers and films.

Cellulose butyrate, giving on hydrolysis 65-66% butyric acid[4], and hence intermediate in composition between the di- and tri-esters, is obtained by steeping cellulose in 80-95% formic acid for 24 hrs. at ordinary temperature, then esterifying with butyric anhydride and acid and zinc chloride, finally removing the formyl group by hydrolysis with 93% butyric acid. The product sinters at 172°, becomes clear at 208°, and begins to decompose at 225°, being soluble in the usual solvents with formation of highly viscous solutions. In the form of films or fine threads it has a much lower tensile strength and greater plasticity than cellulose acetate. Suitable apparatus and technique for the dry- and wet-spinning of cellulose acetate solutions, on

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, II, 2948.
2. Kunstoffe, 1931, **21**, 153; abst. C. A. 1931, **25**, 5555.
3. H. Finkelstein, U. S. P. 1812145.
4. G. von Frank and H. Cohn, Cellulosechemie, 1931, **12**, 68; abst. C. A. 1931, **25**, 5554; J. S. C. I. 1931, **50**, 606-A.

a laboratory scale, has been described[1]. The enhanced speed of formylation of cellulose in simultaneous presence of zinc chloride and HCl as compared with the sum of the rates in the presence of each catalyst singly[2], is due to the formation of a series of complexes. Formic acid in presence of zinc chloride can dissolve much greater amounts of HCl than in absence of the salt. The electrical conductivities of the acid containing $ZnCl_2$ or HCl is much grater than the sum of the corresponding conductivities of the acid containing $ZnCl_2$ or HCl singly, transport measurements showing that zinc wanders to the anode. The strongly acidic nature of the complex is shown by the coloration of a saffranine solution compared with those imparted by HCl and sulfuric acid of known concentrations. Parallelism exists between the strength of the acids and the rate of dissolution of cellulose. The mechanism of cellulose acetylation has been dealt with by H. Friese and K. Roos[3], who is not in accord with H. Rudy[4] on the subject.

The effect of the presence of sodium and potassium nitrates, sulfates and chlorides has been studied on the rate of acetylcellulose saponification in acetic acid[5], all retarded hydrolysis, the differences in molecular weight of the metals having no effect upon the degree of retardation. A greater retarding effect was noted with nitrates and sulfates than with chlorides. According to C. Gabriel who has obtained patent protection for so doing[6], an undercoat composition suitable for use with nitro- and acetylcellulose lacquers comprises shellac 2-4 lb., dibutyl phtha-

1. G. von Frank, H. Krueger and W. Wolff, Z. angew. Chem. 1931, **44**, 342; abst. C. A. 1931, **25**, 5984; J. S. C. I. 1931, **25**, 625-B. M. Friedmann, Kunstseide, 1931, **13**, 173; abst. C. A. 1931, **25**, 4400; Rayon Record, 1931, July 3, p. 421.
2. W. Frey and E. Eloed, Ber. 1931, **64**-B, 2556; abst. J. S. C. I. 1931, **50**, 1401-A.
3. Kunstseide, 1931, **13**, 52; abst. C. A. 1931, **25**, 4121.
4. Kunstseide, 1930, **12**, 420; abst. C. A. 1931, **25**, 3827.
5. J. Fuess and C. Staud, J. A. C. S. 1931, **53**, 1934; abst. C. A. 1931, **25**, 3162; Rayon Record, 1931, July 3, 421.
6. U. S. P. 1813735; abst. C. A. 1931, **25**, 5304; Chem. Zentr. 1931, II, 3554.

late 2-10 oz., and a volatile solvent as "methylated spirit" 1 gal.

Paper pulp receptacles impervious to hot or cold aqueous, oily or greasy materials[1], are provided with a coating of gelatin and an overlying coating of acetylcellulose containing tricresyl phosphate and castor oil to render the coats strongly adherent to each other. The preparation and properties of methyleugenol, methyl-, benzyl- and ethyl-*iso*-eugenol and eugenol formate and acetate have been published[2], of possible value as cellulose ester softeners and plasticizing bodies. The use of acetylcellulose films for cementing the plies of wood in veneer manufacture is said to render the finished veneer less susceptible to moisture and other atmospheric influences[3]. Methods of preparation and properties of mono-acetin, -propionin, -*n*-butyrin, -*iso*-butyrin, -*n*-valerin, -*iso*valerin, and -*n*-caproin have been published[4]. The processing of acetate silk has been detailed, accompanied by illustrations, by D. Gilmore[5]; suggestions given for modifications and adjustments of the machinery used in winding, twisting and tinting acetate yarn by S. Gilston[6]; and the mechanics of tannin and basic dye absorption on acetate silk by I. Ginsberg[7].

In the concentration of dilute acetic acid[8], after vaporization, the resulting mixture of acid and water vapor is brought into contact with fused acid sodium sulfate. Fibers of partially acetylated cellulose are rendered diazotizable and therefore in a more reactive condition[9], by swelling

1. M. Gentile, U. S. P. 1804555; abst. C. A. 1931, **25**, 3836. M. Gentile and S. Weis, E. P. 349724. D. R. P. 532734.
2. O. Gerhardt, Seifensieder-Ztg. 1931, **58**, 585; abst. Chem. Zentr. 1931, II, 3408.
3. O. Gerngross, Z. angew. Chem. 1931, **44**, 231; abst. British Plastics, 1931, **3**, #29, 75.
4. P. Gilchrist and H. Schuette, J. A. C. S. 1931, **53**, 3480.
5. Am. Dyestuff Rep. 1931, **20**, 647; Textile Mfr. 1931, **57**, #683, 412.
6. Textile World, 1931, **79**, 431; abst. C. A. 1931, **25**, 1677.
7. Rayon, 1931, **12**, #2, 14, 45; abst. C. A. 1931, **25**, 5994.
8. A. Gorhan, U. S. P. 1808600; abst. C. A. 1931, **25**, 4363.
9. C. Graenacher, E. P. 346385; abst. J. S. C. I. 1931, **50**, 672-B; Textile Mfr. 1931, **58**, #680, 306; Chem. Zentr. 1931, II, 1933.

with alkali, washing with water, then treating at about 100° with a nitrated benzyl halide in aqueous suspension or in an indifferent solvent, in the presence of an acid-binding agent as calcium or sodium carbonates; the nitrobenzylated fibers being afterwards reduced to the amido derivative. Aromatic *o*-dinitro-compounds may also be used[1], as 1.2-dinitro-4-brombenzene or -4.5-dichlorbenzene. To economize in the amount of glacial acetic acid used, H. Gray[2] acetylates cellulose in the presence of ethylene dichloride, or reacts upon cellulose with acetyl chloride with a stoichiometrical amount of anhydrous sodium acetate[3], acetic acid and anhydride being present in the usual amounts.

A new product dye of the anthraquinone series has been described[4], being 1-methylamino-4.8-diamino-5-oxyanthraquinone, a dark powder dyeing acetylcellulose greenish-blue. F. Grove-Palmer[5] has reviewed the various methods available for coloring compound fabrics containing cellulose acetate, and explained the Imperial Chemical Industries Altex dyes and their application to the above[6]. Esters of inorganic acids (cellulose phosphate and sulfate) are obtainable by acting upon mercerized cellulose with phosphorous oxychloride or sulfuryl chloride in benzene at low temperature, the esters being colloidally dispersed in the presence of water, and containing 16% PO_4 and 60% SO_4 respectively[7]. Yield, 80% on the weight of the cellulose. The W. Hagenbuch thesis on the acetylation of cellulose was published in Basel[8] in 1931.

Monomethylin, monoethylin, monopropylin and monobutylin oxalates, tartrates and phthalates[9] have been proposed combined with diethyl and dibutyl phthalates as de-

1. C. Graenacher, E.P. 347263; abst. Chem. Zentr. 1931, II, 3397.
2. U. S. P. 1823359; abst. C. A. 1932, **26**, 304.
3. U. S. P. 1836711.
4. P. Grossman, U. S. P. 1833250.
5. Am. Dyestuff Reptr. 1931, **20**, 587; abst. C. A. 1931, **25**, 5994.
6. Silk J. 1931, **8**, #85, 38; abst. C. A. 1931, **25**, 5994.
7. M. Hagedorn and E. Guehring, U. S. P. 1848524.
8. Thesis, Basel, pp. 534-71; abst. C. A. 1931, **25**, 3831.
9. F. Hahn, U. S. P. 1812335; abst. C. A. 1931, **25**, 5049; Plastics, 1931, **7**, #11, 636. Can. P. 312568; abst. C. A. 1931, **25**, 4422.

sirable with acetylcellulose. Glyceryl benzoylbenzoate[1] has also received patent protection (see p. 202, n. 3), as has monoethylin phthalate (see p. 202, n. 5; 203, n. 1)[2]. K. Hahn[3] has detailed a series of practical tests for the identification of the various artificial filaments.

As A. Hall has correctly pointed out[4], partial saponification of acetylcellulose increases its affinity for direct dyes to an extent depending on the degree of saponification, a 10% saponification giving a dyestuff receptivity equal to that of cotton, but reducing affinity for SRA dyes and other dyes commonly used for coloring this type of yarn. Almost complete saponification is required to destroy the affinity for SRA dyes, while conversely, a very slight degree of saponification appears to somewhat increase the affinity. Partial saponification increases the resistance of the yarn to hot ironing (by diminishing the acetyl percentage).

In measuring the wetting tension of cellulose esters[5], the inner walls of a capillary are wetted with the ester solution and a film allowed to form. Acetylcellulose films show a marked ageing effect. Liquid mixtures and solutions, especially of capillary active substances, behave differently from pure liquids. Artificial flowers are made by treating crepe paper with a composition containing rubber[6] or cellulose ester[7], and magnesia and lime, the coating being substantially colorless and having a mat appearance due to the presence of pigment. An acetylcellulose combined plasticizer and fire-retardant has been patented comprising mixed aryl phosphates[8] (diphenyl-*b*-naphthyl, phenyl-*m*-tolyl-*b*-naphthyl and mono-*b*-naphthyldicresyl phosphates) in conjunction with tricresyl phosphate and

1. F. Hahn, Can. P. 312568; abst. C. A. 1931, **25**, 4422.
2. *Ibid.* Can. P. 312569; abst. C. A. 1931, **25**, 4422.
3. K. Hahn, Dyestuffs, 1931, **32**, #2, 33.
4. Am. Dyestuff Reptr. 1931, **20**, 583; abst. C. A. 1931, **25**, 5995.
5. W. Haller, Kolloid-Z. 1931, **54**, 7; abst. C. A. 1931, **25**, 1137.
6. R. Ham and M. Ham, U. S. P. 1831559; abst. C. A. 1932, **26**, 847.
7. *Ibid.* U. S. P. 1831560; abst. C. A. 1932, **26**, 847.
8. H. Hands, E. P. 346339; abst. J. S. C. I. 1931, **50**, 672-B.

heptachlorpropane. Films are odorless and colorless and highly plastic.

An electrodynamic microphone has been described[1], involving the use of a conical diaphragm with a coil support at its smaller end united by an acetylcellulose cement. A product of high strength and flexibility is said to be obtained by spinning and stretching acetylcellulose threads, a tensile strength of over 2 gm. per denier being claimed[2], when the ester groups are saponified off to the extent of at least 10%. It is stated that spaces are thereby created between the cellulose crystallites. Filaments are spun from acetylcellulose solutions[3] and projected into a suitable precipitating bath so as to form a skin, the filament being then treated with a solvent as aqueous acetone which causes the core to swell to a greater extent than the peripheral layer. A diametrical expansion of the threads is thus produced with consequent disposition of the crystallites of the outer layers at right angles to the axes of the threads.

A plastic of cellulose acetate and/or nitrate has been patented with cashew nut shell liquid[4], in conjunction with copal[5] and alkaline material, sodium or ammonium hydroxide or carbonate, barytes or magnesia[6]. China wood oil may be added[7], the combination being used for the manufacture of electric insulators[8]. Acetic acid is prepared by oxidizing acetaldehyde with oxygen in presence of catalyzer, the upper gaseous layer of the reacting vessel being continually replenished with a non-reacting gas under pressure, and oxygen supplied into the reaction chamber

1. C. Hanna, U. S. P. 1792300; abst. C. A. 1931, **25**, 1958.

2. W. Harrison, E. P. 344874; abst. C. A. 1932, **26**, 306; J. S. C. I. 1931, **50**, 533-B; Chem. Zentr. 1931, II, 1517. Compare E. P. 309053, 344873.

3. *Ibid.* E. P. 351527; abst. J. S. C. I. 1931, **50**, 836-B; Chem. Zentr. 1931, II, 3565. Can. P. 318197. F. P. 703765; abst. C. A. 1931, **25**, 4707.

4. M. Harvey, U. S. P. 1838070, 1838071.

5. V. Ryan, U. S. P. 1838072. M. Harvey, U. S. P. 1838074.

6. M. Harvey, U. S. P. 1838075.

7. *Ibid.* U. S. P. 1838076. 8. *Ibid.* U. S. P. 1838077.

from the bottom[1]. Acetaldehyde, when freshly prepared, suffers immediate oxidation on contacting with oxygen or the air[2], a compound being formed which in aqueous solution acts like an organic peracid, and this has a pronounced effect upon the subsequent gas-phase of the acetaldehyde.

A form of glass substitute may comprise covering thin wire fabrics with a transparent cellulose ester film (see p. 625, n. 2)[3], which has certain disadvantages due to the fact that the undulating weave of the wire does not produce a flat surface. By diminishing the size of the wire and subjecting the same to pressure before coating, a substantially flat coated wire results. Methods for the formation of triacetylmethyl-, monoacetyldimethyl-methyl- and monoacetylmethyl-rhamnoside have been given[4], including methyl hexamethyldixylobionic acid and its hydrolysis to 2.3.4-trimethylxylophyranose[5].

A photomechanical screen has been described[6], of a transparent plate of acetylcellulose coated with a lead sulfide mirror on which a sodium bichromate-albumin layer is applied, the plate being then exposed through a ruled plate, and developed and etched in the normal manner.

The heat of combustion (in microbomb) of ramie fiber is 4193=5 cal./gm, ramie fiber triacetate, 4545=3 cal./gm., ramie fiber half acetate (0.43 mol. acetic acid) 4222=9 cal./gm., ramie tricapronate (actually 2.9 capronate) 6811=6 cal./gm., ramie trilaurate (2.73 laurate) 8250=6 cal./gm. Heats of formation per mol. acid (computed) are: triacetate, 600=1000 cal.; capronate, 20000=1000 cal.; trilaurate, 26500=4000 cal., the heat of formation increasing with augmentation of C atoms of esterifying acid. Cellulose

1. Nippon Chisso Hiryo Kabushiki-Kaisha and H. Hashimoto, Can. P. 318938.
2. W. Hatcher, E. Steacie and F. Howland, Can. J. Research, 1931, **5**, #6, 648.
3. E. Haver, U. S. P. 1842093.
4. W. Haworth, E. Hirst and H. Samuels, J. C. S. 1931, **137**, 2861.
5. W. Haworth and E. Percival, J. C. S. 1931, **137**, 2850; abst. C. A. 1932, **26**, 969.
6. J. Heidenhain, E. P. 351626; abst. J. S. C. I. 1931, **50**, 824-B. F. P. 701148; abst. Chem. Zentr. 1931, II, 372.

monoacetate formation is exothermic, 0.43 acetate 21000= 6000 cal., the first OH group being more energetically replaced than the second and third, the latter two being replaced endothermically. Cellulose acetate silk stretched, yielded greater heat of combustion (4440=9 cal./gm.) than the unstretched (4401=10 cal./gm), the higher energy content corresponding to work applied in the stretching process[1].

In the dyeing of acetylcellulose (see p. 168, n. 5)[2], there is applied a non-alkaline solution of a dye obtained by coupling the diazo compound of a dinitroaminophenol with an unsulfonated and noncarboxylated aminonaphthol, an example being coupling diazotized 4.6-dinitro-8-hydroxynaphthalene with 1-amino-8-hydroxynaphthalene in the presence of sodium carbonate, cellulose acetate being dyed deep black. Methods for the production of methyl, ethyl and propyl abietate (from resin acids) have been given[3]. Acetals are prepared by treating methyl or ethyl alcohol with acetylene in the presence of mercury sulfate while continuously removing the acetal from the reaction liquid by means of an excess of acetylene[4], and acetaldehyde by reacting acetylene upon water also in the presence of $HgSO_4$, adding ethyl alcohol and continuously removing acetaldehyde from the zone of reaction[5].

Acetic anhydride results when sodium acetate is mixed with 2-4 times its weight of liquid sulfur dioxide[6], then

1. E. Heisenberg, Cellulosechemie, 1931, **12**, 159; abst. C. A. 1931, **25**, 5982; J. S. C. I. 1931, **50**, 913-A.
2. W. Hentrich, U. S. P. 1827150; abst. C. A. 1932, **26**, 605. W. Hentrich, M. Hardtmann and H. Metzl, U. S. P. 1832208.
3. Hercules Powder Co., Swed. P. 72243.
4. W. Herrmann and H. Deutsch, U. S. P. 1796690; abst. C. A. 1931, **25**, 2441. E. P. 257622, 264791. F. P. 620594. Aust. P. 121997; abst. Chem. Zentr. 1927, II, 635. D. R. P. 502431; abst. C. A. 1930, **24**, 4793.
5. *Ibid.* U. S. P. 1816326; abst. C. A. 1931, 5436. D. R. P. 499507; abst. Chem. Zentr. 1930, II, 3080. F. P. 623665; abst. Chem. Zentr. 1928, I, 1229. W. Herrmann, H. Deutsch and W. Raehnel, U. S. P. 1810174; abst. Plastics, 1931, **7**, #12, 696. F. P. 593338; abst. Chem. Zentr. 1926, II, 1791. Aust. P. 103106.
6. B. Herstein and U. S. Industrial Alcohol Co., Can. P. 319138.

causing sulfuryl chloride to react with the salt. Measurements of the viscosity of cellulose acetate[1] of varied origin have been made[2], and fail to confirm H. Staudinger's data (see p. 813, n. 1), the constancy of the relationship observed by him being considered as depending on the progressive removal during acetylation of integumental matter resulting in a diminution in viscosity and increased ease of attack on the cellulose. Color effects on art velveteen, composed of acetylcellulose pile and on cotton backing, have been discussed by G. Holden[3], while W. Holst[4] has given directions for manipulating the Nacelan dyes on acetylcellulose textiles, with formulas for 12 mode shades.

A stencil sheet employing acetylcellulose has been patented by S. Horii (see p. 663, n. 3-9; 664, n. 1-11; 801, n. 3) comprising a fibrous base, a tempering agent as chlorinated naphthalene or naphthenic acid, and blown camelic, tsubaki, sasanqua or teaseed oils[5]. Naphthenic acid may be replaced by aluminum, iron, calcium or magnesium naphthenates[6]. The use of a cadmium phosphate as catalyst[7], leads to 91% conversion in one passage of acetylene with steam at 100 reciprocal hrs. into acetaldehyde and crotonaldehyde. The acetaldehyde may be transformed into acetic acid[8] by passing acetylene, H and O at 180-350 over a catalyst of tin, copper or silver chromate or vanadate[9].

1. K. Hess and E. Garthe, Naturwissenschaften, 1931, **19**, 180; abst. C. A. 1931, **25**, 2349.

2. K. Hess and I. Sakurada, Ber. 1931, **64**-B, 1183; abst. J. S. C. I. 1931, **50**, 828-A.

3. J. Soc. Dyers & Colorists, 1931, **47**, 222; abst. Rayon Record, 1931, **5**, 564.

4. Dyestuffs, 1931, **32**, 25; Textile Colorist, 1931, **53**, 481; abst. C. A. 1931, **25**, 5994; 1932, **26**, 309.

5. S. Horii, U. S. P. 1825798; abst. C. A. 1932, **26**, 569.

6. *Ibid.* U. S. P. 1829750; abst. C. A. 1932, **26**, 816.

7. G. Horsley and Imperial Chemical Industries, Ltd., E. P. 346288; abst. J. S. C. I. 1931, **50**, 666-B; Chem. Zentr. 1931, II, 631.

8. Holzverkohlungs-Ind. A.-G., E. P. 347323; abst. J. S. C. I. 1931, **50**, 710-B. F. P. 687789; abst. Chem. Zentr. 1930, II, 3848.

9. I. G. Farbenindustrie, A.-G., and H. Jochheim, D. R. P. 533466, Addn. to 509020, 524716; abst. C. A. 1932, **26**, 480; Chem. Zentr. 1931, II, 3156.

Formic acid is concentrated by passing it with formamide over gaseous HCl or concentrated sulfuric acid at 60-80°, filtered from ammonium salts, and vacuum distilled[1], and acetaldehyde formed by passing high-percentage acetylene at 0.8-1.5 atms. into acid mercury solution above 85° in the absence of an organic solvent[2]. When acetic acid with acetyl chloride or sulfuryl chloride are introduced into a column attached to a still containing boiling acetic anhydride[3], the latter condenses and is removed from the still by an overflow, the exit gases being washed to remove excess acetyl chloride.

Acetic anhydride results when acetic acid vapor is led into molten boryl phosphate, heat at 700-1000° being applied electrically by a current between the lead-in tube and the containing vessel which are made of copper or chromium-nickel[4]. When nitrile vapors are saponified by continually passing in contact with a current of inorganic acid as 50-90% sulfuric or phosphoric acids[5], acetic acid is formed and may be recovered by extracting with quinoline or dimethylaniline[6].

Cellulose may be esterified in liquid sulfur dioxide (see p. 466, n. 4; 620, n. 8, 9) by means of a free carboxylic acid or mixture of acids, under pressure higher than that due to the SO_2, in presence of a catalyst or oxidizing

1. I. G. Farbenind., A.-G., E. P. 348944; abst. J. S. C. I. 1931, **50**, 834-B. F. P. 705851; abst. C. A. 1932, **26**, 154.

2. *Ibid.* E. P. 349022; abst. J. S. C. I. 1931, **50**, 917-B; Chem. Zentr. 1931, II, 767. D. R. P. 514591, Addn. to 504862; abst. C. A. 1931, **25**, 2156.

3. *Ibid.* E. P. 354159; abst. J. S. C. I. 1931, **50**, 1132-B; Chem. Zentr. 1931, II, 2514. F. P. 710337; abst. C. A. 1932, **26**, 999. Belg. P. 376291. F. P. 703816; abst. C. A. 1931, **25**, 4559.

4. *Ibid.* E. P. 353688; abst. J. S. C. I. 1931, **50**, 1132-B. D. R. P. 535046; abst. C. A. 1932, **26**, 999. F. P. 698907; abst. Chem. Zentr. 1931, I, 2934. Belg. P. 376977.

5. *Ibid.* E. P. 339235; abst. C. A. 1931, **25**, 2440. D. R. P. 524716, Addn. to D. R. P. 509029; abst. C. A. 1931, **25**, 714, 4012. See E. P. 332258; abst. C. A. 1931, **25**, 115.

6. I. G. Farbenindustrie, A.-G., G. Schwaebel and F. Schleicher, D. R. P. 533312; abst. C. A. 1932, **26**, 480. F. P. 633817; abst. Chem. Zentr. 1928, I, 2305.

agent[1], the ester formed being capable of working up into acetate filaments without first isolating the acetylcellulose by precipitation. For example, a solution comprising liquid sulfur dioxide 55, cellulose acetate 22, acetic acid 16, water 5.6 and catalyst 1.2%, when filtered, may be dry-spun. It is preferable to carry on the esterification at increased pressure produced by means of compressed air or nitrogen, the acetylation being carried out with addition of a limited quantity of an oxidizing agent (chromic acid, hydrogen dioxide or potassium permanganate), followed by hydrolysis with water[2].

Cellulose may be esterified in absence of *free* fatty acid but in the presence of a water-insoluble chlorinated hydrocarbon boiling below 100° (dichlorethylene, chloroform), the amount of catalyst being less than ordinarily used[3]. Halides of saturated or unsaturated heterocyclic carboxylic acids may also be used[4], or dichlorethylene[5], or a halide of sulfurous acid in conjunction with zinc chloride or cuprous chloride[6].

In the acetylation of cellulose and starch it is recommended to drive the air out of the reaction vessel by gases or vapors which disappear on addition of the acylating liquid[7], as by vacuum. If a two-stage esterification is

1. I. G. Farbenindustrie, A.-G., E. P. 355144, Addn. to E. P. 301036; abst. J. S. C. I. 1930, **49**, 504; 1931, **50**, 968-B. E. P. 348931 and Addns. 348959, 348960; abst. J. S. C. I. 1931, **50**, 714-B; Silk J. and Rayon World, 1931, **8**, Nov. #90, 61; Tex. Mfr. 1931, **57**, 381.

2. *Ibid.* E. P. 343655, Addn. to E. P. 301036; abst. J. S. C. I. 1931, **50**, 480-B; Brit. Plas. 1931, **3**, #28, 179; C. A. 1931, **25**, 5557.

3. I. G. Farbenind., A.-G., and R. Hofmann, D. R. P. 528821, Addn. to D. R. P. 526479; abst. C. A. 1931, **25**, 4401, 5030. Nitrocellulose, 1931, **2**, 204.

4. I. G. Farbenind., A.-G., E. P. 347451, Addn. to E. P. 283181; abst. Silk J. and Rayon World, 1931, **8**, #89, Oct. 20, 54. Swed. P. 72292.

5. I. G. Farbenind. and R. Hofmann, D. R. P. 526479; abst. C. A. 1931, **25**, 4401.

6. I. G. Farbenind., A.-G., C. Ebert and T. Becker, D. R. P. 528140; abst. C. A. 1931, **25**, 4706.

7. I. G. Farbenind., A.-G., O. Ernst and K. Sponsel, D. R. P. 533939; abst. C. A. 1932, **26**, 735; Chem. Zentr. 1931, II, 3178.

used[1], and difficulty is experienced in controlling the temperature in the second stage, this may be obviated by using in this stage sodium sulfate, sodium bisulfate, pyridine sulfate or methyl sulfate, the salt being formed *in situ* by adding an acetic acid solution of sodium acetate to the reaction mixture. When cellulose is heated to 125° with naphthenic acid chloride, acetic acid and pyridine, cellulose acetonaphthenate results[2]. The ester is claimed to be unusually stable. The esterification may be conducted under 100°, the reaction mixture being afterwards heated to a temperature above 100° without isolating the ester, until the degree of solubility desired has been obtained[3].

Saving in acylating components is claimed where the cellulose is pretreated with not more than 2% sulfuric acid (on the weight of the cellulose) with acetic acid, afterwards esterifying to the point desired by addition of acetic anhydride and a salt or ester of sulfuric acid[4]. Cellulose acetonitrate (nitroacetate) is formed by acetylating cellulose at 50-100° by acetic acid and anhydride in the presence of a nitrate (ammonium, zinc, aniline or urea nitrates) with the addition of 0.2-1% free sulfuric acid. The esters have an N content of 0.1-1.8% and form "extraordinarily clear and viscous" films[5]. Instead of a nitrate, nitric acid may be used[6], and the esterification carried on simultaneously as to introduction of acyl groups into the cel-

1. I. G. Farbenind., A.-G., E. P. 356073; abst. J. S. C. I. 1931, **50**, 1006-B. D. R. P. 533593, Addn. to D. R. P. 515107; abst. C. A. 1931, **25**, 1671; 1932, **26**, 843.

2. I. G. Farbenind., A.-G., M. Hagedorn and P. Möller, D. R. P. 533463; abst. C. A. 1932, **26**, 843; Chem. Zentr. 1931, II, 3418. E. P. 338798; abst. C. A. 1931, **25**, 2566; J. S. C. I. 1931, **50**, 108-B. F. P. 687627; abst. C. A. 1931, **25**, 813, 2566. Can. P. 310405.

3. I. G. Farbenind., A.-G., D. R. P. 533127; Addn. to D. R. P. 515106; abst. C. A. 1931, **25**, 1671; 1932, **26**, 843.

4. *Ibid.* F. P. 707700; abst. C. A. 1932, **26**, 843.

5. I. G. Farbenind. and L. Lock, U. S. P. 1817994; abst. C. A. 1931, **25**, 5558. F. P. 681754; abst. Chem. Zentr. 1930, II, 2719. F. addn. 38797 to 681754. E. P. 344761; Addn. to E. P. 319285; abst. C. A. 1930, **24**, 2600; 1932, **26**, 304; J. S. C. I. 1931, **50**, 343-B, 672-B.

6. I. G. Farbenind., A.-G., and F. Becker, D. R. P. 529191; abst. C. A. 1931, **25**, 5030. Can. P. 313992. D. R. P. 533126; Addn. to D. R. P. 511208; abst. Chem. Zentr. 1931, I, 714; II, 3418.

lulose[1], by treating with a mixture of nitric and acetic acids, adding acetic anhydride and proceeding to the monoacetate stage, then adding catalyst and continuing until the degree desired in acetyl substitution has been reached.

Cellulose di- and poly-fatty acids and their salts are used as dressing agents for artificial silks[2], cellulose diacetic acid and sodium cellulose diacetate being specified. A plastifiable material of acetylated wood may be obtained by treating wood flour with acetic anhydride at 200° and 10-12 atms. pressure, with or without catalyzers[3]. A mixture of acetone and ammonium thiocyanate has been patented in Switzerland as an acetylcellulose solvent combination[4], as has the production of cellulose trilaurate and naphthenate (see p. 681, n. 4; 789, n. 4; 790, n. 1-4)[5]. Cellulose acetobutyrate (p. 284, n. 4; 529, n. 7; 559, n. 6) when dissolved in acetone and cast and cut into tapes[6], forms a material for the electrical insulation of cables. When dilute acetylcellulose solutions are allowed to spread over the surface of a liquid non-miscible with the solution in a thin layer[7], and the skin of cellulose ester collected it is found that the viscosity has been considerably reduced. Thus, cellulose acetate dissolved in chloroform and the solution allowed to spread over the surface of water.

Resinous materials exerting a plastifying effect on cellulose esters[8] result upon esterifying pentaerythritol with fatty acids, glycerides or naphthenic acids, pentaerythritol

1. I. G. Farbenind., A.-G., D. R. P. 535253, Addn. to D. R. P. 511208; abst. Nitrocellulose, 1931, **2**, 205. I. G. Farbenind., A.-G., and F. Becker, Can. P. 313477.
2. *Ibid.* D. R. P. 505629; abst. C. A. 1931, **25**, 606.
3. I. G. Farbenind., A.-G., K. Ott and H. Schüssler, D. R. P. 526793; abst. C. A. 1931, **25**, 5030. I. G. Farbenind., A.-G., H. Suida and H. Titsch, D. R. P. 526794; abst. C. A. 1931, **25**, 5026. E. P. 337791; abst. C. A. 1931, **25**, 2289. F. P. 685712.
4. I. G. Farbenind., A.-G., Swiss P. 143668.
5. *Ibid.* Swiss P. 139819, 143296, 143297.
6. *Ibid.* E. P. 348129; abst. J. S. C. I. 1931, **50**, 726-B; Brit. Plas. 1931, **3**, #30, 270. Can. P. 308356.
7. I. G. Farbenind., A.-G., and H. Mark, D. R. P. 521720; abst. C. A. 1931, **25**, 3481.
8. I. G. Farbenind., A.-G., E. P. 351945; abst. Brit. Plas. 1931, **3**, #30, 272.

naphthenate being an example. The desirable qualities of acetyl silk are augmented by charging the filaments with formic or acetic acids, stretching to about 50%, and removing the free acid by stages while under tension[1]. If liquid ethylene, propylene or butylene oxides are used as cellulose acetate solvents in conjunction with readily volatilizable, swelling liquids as acetone and ethyl alcohol[2], plasticized products are formed. By incorporating trialkyl phosphates containing different alkyl radicals (ethyldipropyl phosphate) with acetone-soluble acetylated cellulose[3], soft, plastic celluloids of low inflammability result.

For the manufacture of plastic masses, films and filaments[4] that are insensitive to water and difficultly combustible, use is made of unhydrolyzed mixed cellulose esters with acetic acid and saturated or unsaturated fatty acids having 3-5 C atoms in the molecule. Only the mixed esters prepared in the presence of an organic base are suitable, e.g., cellulose acetopropionate prepared by treating cellulose with acetyl chloride and propionyl chloride in chlorbenzene in the presence of pyridine bases, the esters being worked up with softening agents. Both cellulose acetopropionate and acetobutyrate when dissolved in acetone form lacquers of high clarity and transparency.

In producing hollow filaments[5], acetylcellulose dissolved in acetone with at least 20% of non-solvent (excluding ethyl alcohol) as toluene, is preheated before spinning

1. I. G. Farbenind., A.-G., 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; Chem. Zentr. 1930, I, 1726. See I. G. Farbenind., A.-G., E. Hubert, A. Röst-Grande and K. Weisbrod, D. R. P. 521598; abst. C. A. 1931, **25**, 3482.

2. I. G. Farbenind., A.-G., E. P. 346827; abst. C. A. 1931, **25**, 1672; J. S. C. I. 1931, **50**, 643-B; Silk J. and Rayon World, 1931, **8**, #88, 56; Brit. Plas. 1931, **3**, #30, 269; Chem. Zentr. 1931, II, 3178. D. R. P. 527736; abst. C. A. 1931, **25**, 5288; Nitrocellulose, 1931, **2**, 166.

3. I. G. Farbenind., A.-G., and C. Schonburg, Can. P. 311525. F. P. 700680; abst. Chem. Zentr. 1931, II, 3062.

4. I. G. Farbenind., A.-G., M. Hagedorn and O. Reichert, D. R. P. 531175; abst. C. A. 1931, **25**, 5557. F. P. 680860; abst. Chem. Zentr. 1930, II, 1306. E. P. 345970; abst. C. A. 1932, **26**, 610.

5. I. G. Farbenind., A.-G., E. P. 356327; abst. J. S. C. I. 1931, **50**, 1044-B.

into an atmosphere below the boiling point of the non-solvent where it is subjected to accelerated but localized evaporation. An ink suitable for printing on acetylcellulose is formed by dissolving nitro- or acetyl-cellulose with coloring matter and a solvent containing at least 70% ethyl alcohol, but free from aliphatic homologues of 1.4-dioxane (for patent infringement reasons)[1]. Methods of improving the handle (softness) of acetate rayon have been described[2].

When cyclohexylamine is condensed with a nitro derivative of 1-chlor-2.4-dinitrobenzene which contains a reactive halogen atom[3], HCl is split off and *N*-nitroarylcyclohexylamines are formed which can be reduced to the corresponding amino compounds, and dye acetate silk generally in yellow shades. A woolen fabric containing cellulose acetonitrate effect threads of low N content[4], may be dyed with Azogrenadine S, sodium sulfate and sulfuric acid, producing a clear red on wool while leaving the acetate threads pure white and of a silky luster. Stability is ensured in the presence of about 1% combined N in the acetonitrate. If black shades are desired which give clear white discharges with zinc formaldehydesulfoxylate[5], the acetylcellulose is treated with a dye of the type (4) $H_2NRN_2R'NX_2(4')$, where R and R′ are phenylene residues which may contain halogen or alkyl substituents, and X_2 an aliphatic residue as methylethyl, then diazotizing and coupling with *b*-naphthol-3-carboxylic acid. Yellowish, but not white, discharges result when both components are applied simultaneously to the silk and the black shade is then developed by treatment with nitrous acid.

1. I. G. Farbenind., A.-G., E. P. 339733; abst. C. A. 1931, **25**, 2865.
2. *Ibid.* E. P. 339858; abst. Silk J. and Rayon World, 1931, **7**, #81, 49.
3. *Ibid.* E. P. 340495; abst. C. A. 1931, **25**, 5040. F. P. 684417; abst. Chem. Zentr. 1931, I, 160.
4. *Ibid.* E. P. 340501; abst. C. A. 1931, **25**, 5042; J. S. C. I. 1931, **50**, 346-B; Silk J. and Rayon World, 1931, **7**, #83, 52. See E. P. 10706, 1912.
5. *Ibid.* E. P. 353592; abst. J. S. C. I. 1931, **50**, 1008-B.

Colors varying from marine-blue to black are obtained on cellulose esters by dyeing with 4-*p*-aminoarylazo-5.6.7.8-tetrahydronaphthylamines which are diazotized on the fiber, and coupled with 2-3-hydroxynaphthoic acid or derivatives[1]. Colored objects are formed by molding masses of chlorine derivatives of cellulose acetate with basic dyes[2]. 5.8-Di-monomethylamino-1.2-benzanthraquinone[3] dyes acetate silk. In dyeing mixed fabrics containing acetate silk[4], a sulfurized phenol is added to the bath whereby the acetate silk or natural silk is reserved. Methods of sizing acetate with cellulose hydroxyalkyl ethers[5] have been patented (p. 286, n. 5). Thin supports of paper are coated with solutions containing cellulose esters of saturated higher fatty acids together with resin and rubber, especially applicable for tipping cigarets[6]. A spatula mass is obtained by mixing these esters with resin[7], cellulose laurate dissolved in chlorbenzene and stirred with dammar in benzene, the consistency being governed by the addition of talc, slate meal and lithopone. When acetaldehyde 2, NaOH 1.25%, 1 part are passed through a series of four coils immersed in baths maintained at 3°, 8°, 15° and 20° respectively[8], aldol results.

1. I. G. Farbenind., A.-G., F. P. 703118; abst. C. A. 1931, **25**, 4409.

2. I. G. Farbenind., A.-G., and R. Kuhn, D. R. P. 520971; abst. C. A. 1931, **25**, 3481.

3. I. G. Farbenind., A.-G., P. Nawiasky and O. Chrzescinski, D. R. P. 533496; abst. C. A. 1932, **26**, 604. See D. R. P. 529970; abst. C. A. 1931, **25**, 5179.

4. I. G. Farbenind., A.-G., D. R. P. 526277; abst. C. A. 1931, **25**, 4413.

5. *Ibid.* F. P. 701868; abst. C. A. 1931, **25**, 4136. D. R. P. 523434; abst. C. A. 1931, **25**, 3498. (See p. 286, n. 5.)

6. I. G. Farbenind., A.-G., E. Richter, M. Hagedorn and W. Becker, D. R. P. 517451; abst. C. A. 1932, **26**, 305; Chem. Zentr. 1931, II, 3419.

7. I. G. Farbenind., A.-G., and E. Richter, D. R. P. 533802; abst. C. A. 1932, **26**, 861; Chem. Zentr. 1931, II, 3275.

8. I. G. Farbenind., A.-G., M. Müller-Cunradi and K. Pierch, D. R. P. 531295; abst. C. A. 1931, **25**, 5436. E. P. 298349; abst. Chem. Zentr. 1929, I, 575.

To hinder deterioration of the color of lead chromate pigments in cellulose ester lacquers[1], the inclusion of 20-25% of leaded zinc oxide in the total (inert) white pigments is recommended. When linseed, soya bean, cottonseed or tung oils are heated to 250-300° under 15-145 mm. pressure with sulfur dioxide, hydrogen sulfide, carbon dioxide or H, and the polymerized oil subsequently heated with a soap (sodium or magnesium stearate), air being excluded[2], the product after vulcanization may be incorporated with cellulose esters to form a varnish. The plasticizing effect of solid plastifiers on acetylcellulose has been reported upon[3], and by comparing the affinity to the ester, the physico-chemical properties and the plasticizing efficiency, it is recognized that the efficiency of a plasticizer is greater as the affinity, viscosity and surface tension increases, the increase in plasticity being ascribed to the permanent swollen state of the cellulose acetate. In this state, the mutual cohesive power of the micelle is decreased by the intra-micellar swelling, the spaces between the structural units is enlarged, and the slipping capability among the micelle or the structural units increased by the "inner lubricating effect" of the plasticizer.

A study of the fractional precipitation of acetylcellulose solutions indicates that the physico-chemical properties of the fractions (viscosity, solubility, melting point) are considerably different, whereas the acid contents are practically the same[4]. A theory of the ripening of cellulose acetate is based on these observations and on the micellar theory of K. Meyer and H. Mark. The immunization of

1. Imperial Chemical Industries, Ltd., E. P. 361918; abst. J. S. C. I. 1932, **51**, 118-B.
2. Imperial Chemical Industries, Ltd., and H. Bunbury, E. P. 343099; abst. C. A. 1931, **25**, 4428; Chem. Zentr. 1931, II, 504. F. P. 700074; abst. C. A. 1931, **25**, 3449; Chem. Zentr. 1931, II, 660.
3. N. Ishii, Cellulose Industry, Journal of the Cellulose Institute, Tokyo, Japan, 1931, **7**, #10, 51; abst. J. S. C. I. 1932, **51**, 96-B.
4. S. Iwasaki, J. S. C. I. Japan, 1931, **34**, 9-B; abst. C. A. 1932, **26**, 297; J. S. C. I. 1931, **50**, 469-A.

cotton has been described by O. Jaeck and F. Schuetz[1], which involves heating the cellulose to 50-95° with fused maleic anhydride alone or in conjunction with acetic acid, either with or without the use of a catalyst, it appearing that a superficial esterification of the fiber to cellulose maleate and acetomaleate results. The yarn thus treated can scarcely be dyed with substantive dyestuffs, but is strongly dyed by basic colors. They prepare acidylcellulose by treating cellulose first with copper sulfate and sulfuric acid[2] which is afterwards hydroextracted and dried, then acetylated in the usual manner. If a cotton fabric is superficially acetylated, it possesses valuable immunizing properties.

In a study on the adsorption capacity for cellulose and its esters for ions and the amphoteric properties characteristic[3], the potentials were measured by the electroendosmosis and streaming-potential methods. Acetylcellulose was found to show no maximum either in HCl or potassium chloride, while in NaOH solution there is a slight maximum. When cotton is treated with an acetylating agent in the presence of a formaldehyde "equalizer" to effect a partial acetylation sufficient to give immunity to substantive dyes[4], the outward appearance of the fiber remains unchanged.

The lattice variations with swelling of acetylated normal and mercerized ramie cellulose in aqueous lithium thiocyanate solutions has been investigated[5]. With solutions of less than 0.5% lithium salt, no change in the X-ray spectrum is evident, but as the solutions become more concentrated, interference points of a new spectrum become more intense, while those of the old diagram become weaker until at a concentration of 2.5 lithium thiocyanate only the

1. U. S. P. 1812790. 2. U. S. P. 1839967.
3. K. Kanamaru, Cellulose Ind. (Tokyo), 1931, **7**, 3; abst. C. A. 1931, **25**, 3895. J. Cellulose Inst., Tokyo, 1931, **7**, 42; abst. C. A. 1932, **26**, 601; J. S. C. I. 1931, **50**, 969-B.
4. P. Karrer, U. S. P. 1836254; abst. C. A. 1932, **26**, 1134. Compare E. P. 280493.
5. J. Katz and J. Derksen, Rec. trav. chim. 1931, **50**, 746; abst. C. A. 1931, **25**, 4701; J. S. C. I. 1931, **50**, 898-A.

new spectrum is present. The change in lattice structure indicates that besides absorption on the micelle, the salt enters within the micelle.

Intaglio direct or offset plates are made by coating thin metal or metallized waterproof card with 0.1 mm. cellulose nitrate, then 0.1 mm. cellulose acetate, saponifying with 30% NaOH at 60-70°, thus converting the acetate substantially into hydrate, washing, drying and sensitizing with chromate solution, exposing and developing[1]. Cellulose di- and tri-furoates have been prepared by treating cellulose with furoyl chloride in the presence of pyridine[2]. The esters are fibrous, dark colored and insoluble in the usual cellulose ester dissolvants. A considerable degradation of the cellulose takes place in the esterification with formation of furoylated cellulose products which are black, amorphous substances. The analysis of cellulose furoate by saponification is claimed to clearly show the fundamental difference of two of the alcohol hydroxyl groups in the hexose residue from the third or primary OH, thus confirming the present accepted theory of the hexose residue structure. Chlorides, nitrates, chlorates and bromides diminish the hydrolysis of acetic anhydride[3], but sulfates increase the velocity.

Mixed esters of cellulose are formed by treating cellulose formate, acetate, butyrate and benzoate with a solution of acid (oxalic, tartaric, lactic, pyruvic, maleic, glyceric, *m*-toluic, phenylglycollic, salicylic, malonic, succinic, glutaric, adipic, cinnamic or acrylic(having an ionization constant higher than that of the acid corresponding to the ester, and in the presence of a solvent for the ester as 1.4-dioxane[4]. The above 60 mixed esters, of which cellulose formyloxalate is an example, are said to produce excellent

1. A. Keller, D. R. P. 517141.
2. K. Kobe and R. Montonna, J. A. C. S. 1931, **53**, 1889; abst. C. A. 1931, **25**, 3162; J. S. C. I. 1931, **50**, 849-A.
3. J. Kocsis, Magyar Chem. Folyoirat, 1931, **37**, 41; abst. C. A. 1931, **25**, 2905.
4. Kodak-Pathe, F. P. 702116; abst. C .A. 1931, **25**, 4124; Chem. Zentr. 1931, II, 3061.

lacquers and transparent films, being soluble in a wide range of solvents.

Cellulose acetate may be precipitated from its acetic acid solutions in soft clumps, fibers or threads which are readily disintegrable and washable[1], by introducing the solution into an aqueous bath containing initially at least 20% acetic acid, the final acetic acid concentration being up to 50% without impairing the cellulose ester recovery. The resulting solution is then concentrated by mixing with dichlorethylene and distilling. A suitable acetylcellulose composition for film formation results by dissolving the ester in a mixture of methyl acetate 50, ethyl acetate 10-40 and acetone 40-10, to which plasticizers may be added[2].

Cellulose may be acetylated by mixing with a catalyst (sulfuric or *p*-toluenesulfonic acids)[3], and heating with saturated acetic anhydride vapor in a closed system from which the air has been substantially removed, the acetic acid formed during the reaction being retained in contact with the cellulose until acetylation is complete. Where cellulose is acetylated with a halogen derivative of an acid of high molecular weight (stearyl chloride) in the presence of pyridine, and after separation of the ester, submitted to acetation[4], preferably in the presence of tetrachlorethane or chloroform, a mixed ester, cellulose acetostearate (see p. 153, n. 6; 240, n. 3; 759, n. 1) is formed, insoluble in acetone and benzene, soluble in tetrachlorethane and chloroform.

Preliminary to acetation[5] cellulose is given a treatment with acetic acid, the mixture afterwards distilled with

1. Kodak, Ltd., E. P. 342596; abst. C. A. 1931, **25**, 4401; J. S. C. I. 1931, **50**, 388-B.
2. Kodak, Ltd., and Eastman Kodak Co., E. P. 345505; abst. C. A. 1932, **26**, 304; J. S. C. I. 1931, **50**, 597-B; British Plastics, 1931, **3**, #28, 63; Chem. Zentr. 1931, II, 3178.
3. *Ibid.* E. P. 345800; abst. J. S. C. I. 1931, **50**, 533-B; Silk J. and Rayon World, 1931, **8**, #87, 54; British Plastics, 1931, **3**, #28, 179.
4. Kodak, Ltd., E. P. 346816; abst. J. S. C. I. 1931, **50**, 626-B; Chem. Zentr. 1931, II, 3418. F. P. 687996.
5. *Ibid.* E. P. 349959; abst. J. S. C. I. 1931, **50**, 754-B.

dichlorethylene, forming an azeotropic mixture with water, esterification being completed by the addition of acetic anhydride and sulfuric or phosphoric acids as catalyst. After hydrolysis of the ester to the desired extent[1], a solution of HCl in acetic acid is added to the hydrolyzing bath, resulting in a cellulose acetate free from haze. The ester may be obtained in a fluffy form by including in the acetylation bath an inert, water-immiscible, volatile solvent and subsequently precipitating the ester in water at or above the boiling point of the volatile solvent[2]. The quantity of acetic anhydride in the acetylation bath should be insufficient of itself to dissolve the acetylcellulose formed, complete dissolution being effected by adjusting the proportion of volatile solvent present. Suitable solvents are trichlorethylene, chloroform, and particularly dichlorethane. If the cellulose is preliminarily heated in the vapor of a fatty acid containing 2-8 C atoms at 100-200° in absence of both oxygen and catalyst[3] until the product contains at least 4% combined acyl group, it may then be esterified in the usual manner with considerable economy in fatty anhydride required.

The back-hydrolysis of acetylcellulose to the acetone-soluble modification is effected by adding to the final reaction mixture, which preferably contains dichlorethane as diluent[4], enough methyl or ethyl alcohol to convert all of the acetic anhydride into the corresponding acetate—the reaction providing the water necessary for the hydrolysis of the triacetate—and leaves a sufficient excess of uncombined alcohol to form with the dichlorethane a solvent mixture in which the cellulose ester remains dissolved. Acetic acid may be dehydrated by treatment with sulfur dioxide

1. Kodak, Ltd., E. P. 350310; abst. J. S. C. I. 1931, **50**, 754-B.
2. *Ibid.* E. P. 351118; abst. J. S. C. I. 1931, **50**, 877-B; Chem. Zentr. 1931, II, 3287.
3. *Ibid.* E. P. 352054; abst. J. S. C. I. 1931, **50**, 837-B. F. P. 707473; abst. C. A. 1932, **26**, 843.
4. *Ibid.* E. P. 356012; abst. J. S. C. I. 1931, **50**, 1006-B. F. P. 704664; abst. C. A. 1931, **25**, 4706; Chem. Zentr. 1931, II, 1516.

and a nitrogen oxide until nitrosylsulfuric acid is formed[1]. Acetic solutions containing ions of high mobility (i.e. containing HCl or metallic salts)[2], are purified by electrolysis, the mobile ions traveling on a relatively short course through a porous wall to the corresponding electrode.

A process has been described for making roll films of cellulose acetate[3], characterized by coloring the back of the film with a coating of alcoholic solution of magenta and aurine, with or without the addition of naphthalene green. P. Krais and H. Markert[4] have given methods for the analysis and isolation of mixtures of rayons and acetate fibers; A. and N. Kramer a process for stocking and sock manufacture using acetyl silk[5], while D. Krueger[6] has pointed out the fundamental morphological chemical and colloidal differences between wood pulp and cotton linters as affecting the relative suitability for viscose, acetylcellulose, nitrocellulose and copperammonia filament manufacture.

Attention has been called to the fact that perchloric acid is much more effective than sulfuric acid as catalyst for the acetylation of cellulose[7], both acids being effective in so dilute concentration that the solubility of cellulose does not enter into the question, the acceleration of the process being attributed to a specific property depending on the structure of the acids. The formation of mixed esters, observed in the acetylation of cellulose in presence of sulfuric acid, is not a general property of acid catalysts,

1. Kodak-Pathe, F. P. 703003; abst. C. A. 1931, **25**, 4251; Chem. Zentr. 1931, II, 1922.
2. *Ibid.* F. P. 709662; abst. C. A. 1932, **26**, 926.
3. *Ibid.* D. R. P. 515533; abst. C. A. 1931, **25**, 2379.
4. Rev. Gen. Mat. Col. 1931, **35**, 281; abst. J. S. C. I. 1931, **50**, 875-B.
5. E. P. 338082.
6. Papier-Fabr. 1931, **29**, 509; abst. C. A. 1932, **26**, 592.
7. D. Krueger and E. Tschirch, Ber. 1931, **64-B**, 1874; abst. C. A. 1931, **25**, 5402; J. S. C. I. 1931, **50**, 1041-A. D. Krueger and F. Hoehn, D. R. P. 519877; abst. C. A. 1931, **25**, 3481. For the microchemical detection of minute quantities of perchloric acid in cellulose acetate, see D. Krueger and E. Tschirch, Zts. anal. Chem. 1931, **65**, 171.

primary acetylcelluloses obtained in homogeneous or heterogeneous systems in presence of perchloric acid being free from this acid. Acetylation takes place at a lower temperature and with a rapidity not previously observed when perchloric acid is used as catalyst. D. Krueger and E. Tschirch[1] have reviewed the methods for detecting cellulose acetate, particularly by the reactions of acetic acid, with a bibliography. Their uranyl formate test works satisfactorily. D. Krueger[2] has also reviewed the literature and patents in respect to mixed esters of cellulose, and discussed the outlook for the application of these esters in the rayon industry.

A phonograph record disc has been patented comprising cellulose acetate 10, triacetin 3, triphenyl phosphate 1, with 86% acetone[3], to which loading material may be added. In the storage of gasoline and other volatile organic liquids[4], it is absorbed by the stearates, oleates, palmitates and laurates of cellulose, hydrocellulose or oxycellulose. A new method of preparing cellulose stearate has been described, the ester being pressed into sheets, threads, pellets, or other desired form and then dried. When textile filaments, fabrics or other coherent structures are subjected to partial esterification by treatment with higher fatty acid chlorides[5], although the structure of the cellulose is not destroyed by the incipient esterification, great resistance to water is obtained. Esterification takes place at 80-120° in the presence of pyridine. Gasoline may be filtered through thin layers, plates, slabs or bags of cellulose laurate, oleate, stearate or palmitate of low degree of esterification[6], to

1. Dyestuffs, 1931, **32**, 91; abst. C. A. 1932, **26**, 298.
2. D. Krueger, Kunstseide, 1931, **13**, 83; abst. C. A. 1931, **25**, 4120.
3. H. Laffon, U. S. P. 1787484; abst. Plastics, 1931, **7**, #4, 236.
4. R. Lant, E. P. 342742; abst. C. A. 1931, **25**, 4328; Chem. Zentr. 1931, I, 3313.
5. *Ibid.* F. P. 707688; abst. C. A. 1932, **26**, 857. R. Lant and W. Koreska, E. P. 343104; abst. Chem. Zentr. 1931, II, 2399.
6. R. Lant and W. Koreska, E. P. 343105; abst. C. A. 1931, **25**, 4395; Chem. Zentr. 1931, II, 2956. Aust. P. 120875; abst. Chem. Zentr. 1931, I, 2149.

remove suspended matter. Or[1], cellulose distearate may be dissolved in xylol and fatty or mineral oils and waxes, to form a varnish especially applicable for the coating of tennis-racket strings and gut.

The luster may be restored to acetate silk by wetting and hot-calendering selected areas of a fabric containing dulled cellulose acetate[2] at temperatures of 125-170° and a pressure of 0.1-0.5 kgm./sq. cm, to produce pattern effects. Methods for the filtration and clarification of the liquids used in connection with acetate filament spinning have been given by La Soie de Clairoix[3]. Suitable baths for the dyeing of acetylcellulose are prepared, without sulfonated or other oils, by using a mineral oil compound which is soluble or dispersable in water to a clear solution[4], such a compound being formed by adding potassium oleate and oleic acid to a mixture of refined white mineral oil and a suitable solvent, preferably one which is partially soluble in both oil and water.

Cellulose butyrate is prepared (see pp. 185, 328, 360, 495, 529, 559, 588, 621, 667) by treating cellulose with butyric and acetic acids under vacuum in presence of acetone as diluent, the acetic acid retained by the material being removed by lixiviation with the diluting agent prior to esterification[5]. H. Levinstein in 1931 reviewed the production and uses of cellulose acetate[6]. The wrapping of packages with acetate film (Inceloid) has been detailed by H. Levy[7], a cellulose acetate sheeting 0.0009 inch thick transmitting

1. R. Lant and W. Koreska, E. P. 343117; abst. C. A. 1931, **25**, 4421; J. S. C. I. 1931, **50**, 438-B. F. P. 689991; abst. Chem. Zentr. 1931, I, 548.
2. G. Lardy, U. S. P. 1803672; abst. C. A. 1931, **25**, 3849; Chem. Zentr. 1931, II, 798.
3. F. P. 708673; abst. Chem. Zentr. 1931, II, 3061.
4. J. Leaper, Textile Colorist, 1931, **53**, 550; abst. C. A. 1931, **25**, 5994.
5. J. Lefranc and Soc. des Brevets Etrangers LeFranc & Cie, E. P. 350906; abst. J. S. C. I. 1931, **50**, 799-B; British Plastics, 1931, **3**, #30, 269; Chem. Zentr. 1931, II, 3288.
6. Am. Dyestuff Rep. 1931, **20**, 635; Chemicals, **35**, #24, 10; abst. C. A. 1931, **25**, 4120. The Times Trade and Eng. Suppl. 1931, **28**, #664, 8; abst. C. A. 1931, **25**, 2846.
7. Food Industries, 1931, **3**, #8, 349.

40 gms. water vapor in 24 hours. A paint and varnish remover[1] comprises methylene chloride 90, acetylcellulose 5, stearin or fat of similar effect 5 in the absence of an alcohol or ether.

In the concentration of acetic acid[2], the solution is mixed with an anhydrous, hydrate-forming salt as sodium sulfate which is inert to the acid, and the salt allowed to crystallize from the solution. The volatile substance is separated from the hydrated salt by means of a current of inert gas at a temperature sufficiently low to cause decomposition of the salt, and the acetic acid recovered from the inert gas. The preparation of cellulose glycollic acids has been described[3].

In the production of cellulose membranes containing proteins[4], 10% solutions of acetylcellulose and gelatin in cold glacial acetic acid are shaken together in the requisite proportions. The membranes are then prepared by desiccation in the usual way, and are transparent for 5%, and opalescent for 25% gelatin. For other proteins (casein, ovalbumin, gliadin, serum-proteins), the solutions are made in cold or warm formic acid. A perfectly dry membrane containing casein 20 and acetylcellulose 80 is clear and does not give the Tyndall effect. A clear, solid membrane may be made of proteins, glucides or lipins[5] by using a carefully selected ratio of certain solvents. Example, acetylcellulose 9 is dissolved in a mixture of acetone 47.6, and absolute methyl alcohol 33.4 and casein 1 in formic acid (all gms.) added with rapid stirring and poured on a plate, a clear membrane being obtained after dissipation of sol-

1. J. Lewy, E. P. 357184; abst. J. S. C. I. 1931, **50**, 1106-B; Chem. Zentr. 1931, II, 3555.
2. F. Lichtenthaeler, U. S. P. 1817993; abst. C. A. 1931, **25**, 5480.
3. L. Lilienfeld, D. R. P. 535393; abst. Nitrocellulose, 1931, **2**, #10, 205.
4. J. Loiseleur and L. Velluz, Compt. rend. 1931, **192**, 43; abst. C. A. 1931, **25**, 1723; J. S. C. I. 1931, **50**, 167-A.
5. *Ibid.* Compt. rend. 1931, **192**, 159; abst. C. A. 1931, **25**, 1861.

vent. Similarly membranes may be made from glycogen, gums and glycerides.

The affinity of cellulose esters for dyestuffs may be considerably augmented by adding a cellulose cyanacetate, or partially acetylating cellulose and adding to the esterizing bath cyanacetic acid, acetic acid and anhydride, when a cellulose acetocyanacetate is perhaps formed[1]. Nitrobenzoic or aminobenzoic acids may be used instead, resulting in the formation of a cellulose acetonitrobenzoate and acetoaminobenzoate. By subjecting aqueous formic acid to direct fractional distillation in the presence of a highly boiling organic base, an acid approaching the absolute is said to be obtained[2]. Or a formate may be treated with nitric acid at low temperature in the presence of urea[3], and the concentrated formic acid removed by fractionation.

Splinterless glass is formed by pretreating glass sheets by coating them with a very thin layer of hardened but still soluble gelatin, pretreating an acetylcellulose sheet with ether and coating both sides of this sheet with a thin gelatin layer, then pressing the acetate sheet between the glass in the presence of a volatile softening liquid for gelatin[4]. In hydrolyzing acetylcellulose[5], it is recommended to use ethyl alcohol in excess of that required to esterify any acetic acid present. The claim is made[6] that acetylcellulose may be prepared free from haze by conducting the acylation in an apparatus of a copper-chromium-nickel alloy.

A highly sensitized photographic film results when a silver halogen light-sensitive composition is incorporated in a hard drying lacquer or varnish having a cellulose acetate base, finely ground silver bromide emulsion being incor-

1. Lonza Elektrizitatswerke and Chemische Fabriken Akt-Ges., Can. P. 316549. F. P. 713908.
2. *Ibid.* Can. P. 319839.
3. *Ibid.* Can. P. 320394.
4. H. Mallabar, U. S. P. 1802213; abst. Plastics, 1931, **7**, #8, 469.
5. C. Malm, Can. P. 321228.
6. *Ibid.* U. S. P. 1840404; abst. C. A. 1932, **26**, 1782.

porated in the lacquer[1]. Gelatin or albumin may be used as the colloid vehicle. A cellulose ester plastifier, especially applicable with the nitric ester[2] is ethyl mandelate. Glass sheets may be juxtaposed by inserting between a cellulose acetate film coated with a mixture of acetin and benzoin[3]. Glucosone triacetates, oxyglucal tetra-acetate, glucosonehydrate triacetate and glucosone triacetate have been described[4]. J. McCloud[5] has detailed the requirements in airplane coatings, including dope mixtures for wing coverings, and J. McLaurin[6] expatiated on the various acetylcellulose coatings on paper in conjunction with rubber and artificial resins.

At room temperature cellulose acetate films when stretched to small elongations cool, but give off heat when elongated beyond their yield point. With strongly biaxial films the secondary heating effect is absent[7]. The thermoelastic properties of coagulated films are independent of their content of volatile solvent. In a series of measurements of the fluorescence of cellulose acetate, accompanied by photomicrographs[8], it was found that variations in the thickness of the film produce but little change in the photograph of the fluorescent light, the fluorescence of cellulose diacetate falling below that of the triacetate. This change in fluorescence is progressive as the triacetate is hydrolyzed to the diacetate ester. Solutions of acetylcellulose fluoresce when irradiated by ultraviolet light, increasing in intensity as the concentration of the solution becomes greater.

1. Masa Ges. zur Herstellung kunstlicher Oberflaechen, E. P. 340246; abst. Chem. Zentr. 1931, I, 2012.
2. H. Matheson, U. S. P. 1815655.
3. N. Mattingly and Lancegays Safety Glass, Ltd., E. P. 344454; abst. J. S. C. I. 1931, **50**, 541-B; British Plastics, 1931, **3**, #28, 181.
4. K. Maurer and W. Petsch, Ber. 1931, **64**-B, 2011; abst. J. S. C. I. 1931, **50**, 1275-A.
5. J. McCloud, I. E. C. 1931, **23**, 1334.
6. J. McLaurin, F. P. 711017; abst. Chem. Zentr. 1931, II, 3177.
7. J. McNally and S. Sheppard, J. Phys. Chem. 1931, **35**, 100; abst. C. A. 1931, **25**, 2623; J. S. C. I. 1931, **50**, 422-A.
8. J. McNally and W. Vanselow, J. A. C. S. 1930, **52**, 3846; abst. Eastman Kodak Co., Abridged Scientific Publ., 1930, **14**, 186.

Carbon papers may be trade-marked by applying a design to the supporting paper or tissue with a nitro- or acetyl-cellulose solution including ethyleneglycol monoethyl-ether acetate[1]. O. Merz[2] has described the acetylcelluloses with their solvents and plasticizers as especially applicable in paints for aircraft, and L. Meunier and G. Revillon[3] the solutions used for swelling acetate fibers and films. Method of preparing cyclohexanol lactate[4] has been patented. An ink for printing upon unexposed and undeveloped cellulose ester motion picture film[5] is formed of monoethyl-ethylene glycol, nigrosine base and a nitrocellulose thickener, the ink being insoluble in alcohol after application to the film.

When cellulose (cotton linters) is treated with 85-90% phosphoric acid at low temperature[6], and afterwards with acetic acid, the cellulose dissolves to a clear, transparent, heavy solution, suitable for film formation. Direct photographic positives are made by coating a translucent cellulose ester, as acetylcellulose film with a sensitive silver emulsion[7], exposing, developing the image, and reversing it by known chemical reversal processes. From experimental results confirmed by thermodynamic calculations, B. Moldavskii has shown[8] that the patent of H. Dreyfus for the synthesis of acetic acid from methane and carbon dioxide[9] is unworkable.

Cellulose oxalate (p. 646, n. 6)[10] is prepared by heating together cellulose 10, crystallized oxalic acid 8, con-

1. W. Mendel, U. S. P. 1828374; abst. C. A. 1932, **26**, 847.
2. Farben-Ztg. 1931, **36**, 2156; abst. C. A. 1931, **25**, 5999.
3. L. Meunier and G. Revillon, Chim. et Ind. 1932, **27**, 251.
4. W. Michael and W. Haag, U. S. P. 1831025; abst. C. A. 1932, **26**, 735.
5. E. Middleton, U. S. P. 1833086; abst. C. A. 1932, **26**, 931.
6. G. Miles and C. Dreyfus, U. S. P. 1787542; abst. J. S. C. I. 1931, **50**, 837-B.
7. Mimosa Akt-Ges., E. P. 349947. F. P. 685795; abst. Chem. Zentr. 1931, I, 1403.
8. B. Moldavskii, J. Applied Chem. (U. S. S. R.) 1931, **4**, 667; abst. C. A. 1932, **26**, 964. H. Dreyfus, E. P. 226248.
9. E. P. 226248; see p. 772, n. 2.
10. J. Montgomery, J. A. C. S. 1931, **53**, 2700; abst. C. A. 1931, **25**, 4221; J. S. C. I. 1931, **50**, 1034-A.

centrated HCl 10. W. Morgan[1] has detailed the history, manufacture and characteristics of laminated glass, and W. Moss[2] the uses of methylene chloride as an acetylcellulose solvent, it appearing that a mixture of it with *n*-butyl alcohol forms a solvent equal to that of acetone. His method of non-shattering glass manufacture[3] is to interpose a sheet of acetylcellulose between sheets of glass, and cause to adhere by a film containing an ethyltoluenesulfonamide-formaldehyde resin. Equilibrium in the system acetic acid-acetic anhydride-water has been studied[4].

Fine filaments of high strength, particularly wet strength[5], are obtained by stretch-spinning a cellulose reaction mixture containing 12% ester, into a solution of 40-60% sulfuric acid containing 1% formaldehyde, and optionally adding salts and solvents. A discussion of the chemistry and processes involved in the production of acetate yarns has been given by C. Mullin[6], including obtaining acetic acid by hardwood distillation[7].

Imitation linen, towels, handkerchiefs, serviettes, table cloths and sheets are made by pressing superposed layers of cellulose wadding impregnated with acetylcellulose[8]. Methods have been given for determining the acetyl value of acetylated compounds by a modification of the Eberstadt method[9], and for the analysis of acetylcellulose with a re-

1. I. E. C. 1931, **23**, 505; abst. Jour. Chem. Ed. 1931, **8**, 2456.
2. U. S. P. 1844365.
3. W. Moss and C. Dreyfus, Can. P. 317726; abst. C. A. 1932, **26**, 1409.
4. W. Muehlhaeusser and M. Trautz, Z. physikal. Chem. 1931, 319; abst. J. S. C. I. 1931, **50**, 1234-A.
5. G. Mueller, E. P. 358501; abst. J. S. C. I. 1932, **51**, 17-B; Textile Mfr. 1932, **58**, #687, 119.
6. Textile Colorist, 1931, **53**, 48; abst. Jour. Chem. Ed. 1931, **8**, #5, 983.
7. C. Mullin and H. Hunter, Cellulose, 1931, **1**, 171, 215, 287; abst. C. A. 1931, **25**, 4696, 5768. Chem. Markets, 1931, **28**, 597; **29**, 44, 268, 380, 482.
8. E. Munktell, E. P. 338224. Refer to E. P. 252719, 252720.
9. T. Murray, C. Staud and H. Gray, I. E. C. Anal. Ed. 1931, **3**, 269; abst. C. A. 1931, **25**, 4701; J. S. C. I. 1931, **50**, 876-B; British Plastics, 1931, **3**, #28, 61; #29, p. 73.

duction of the saponification time from 24 to ½ hr. Acetic or butyric-acetic anhydride is obtained by heating "monobasic" aliphatic acids in admixture with monoketones as acetone[1], or *iso*propyl alcohol, *sec*-butyl alcohol or propylene oxide, at about 600-700°.

Substantially anhydrous formic acid is obtainable by once distilling 85% acid at 12 mm. pressure with orthophosphoric acid[2]. T. Nakashima[3] has reported on the oxidation products of biosan acetate, and C. Nash in 1931 first published his molding mixture formula of acetylcellulose, urea-formaldehyde type of resin, and dialkyl phthalate[4]. Highly polymerized lower cellulose aliphatic acid esters are formed by separating the esters from the original acetylation mixture, transferring to a solvent as acetone, and adding an organic base as pyridine with a halogen phosphorous compound (oxychloride, trichloride, sulfochloride, pentachloride) or an organic phosphorous compound (such as phenylchlorphosphine, diethylaminochlorphosphine, phenylphosphoryl dichloride), the products being suitable for artificial silk formation[5]. In the waterproofing of paper[6], the latter is treated with anhydrides, acid chlorides or other esterification-inducing derivatives of high fatty acids as stearic anhydride, the cellulose being superficially esterified to a cellulose stearate, which remains waterproof after extraction with volatile solvents. Textiles, as cotton, are esterified with a higher fatty acid (stearic or palmitic

1. Naamlooze Vennootschap de Bataafsche Petroleum Maats, E. P. 338507; abst. J. S. C. I. 1931, **50**, 237-B; C. A. 1931, **25**, 2440; Chem. Zentr. 1931, I, 1167. Can. P. 312630.

2. N. V. de Bataafsche Petroleum Maats., E. P. 339045; abst. C. A. 1931, **25**, 2440; J. S. C. I. 1931, **50**, 289-B. F. P. 683088; abst. C. A. 1930, **24**, 4522; Chem. Zentr. 1930, II, 1441. Dutch P. 23586; abst. C. A. 1931, **25**, 3360. See N. V. Drya, Maatschappiji tot Exploitatie van Kunstzijdefabrieken, Swiss P. 145979; abst. Chem. Zentr. 1931, II, 2808.

3. J. S. C. I. (Japan), 1931, **34**, 414; abst. J. S. C. I. 1932, **51**, 149-A.

4. C. Nash and Bakelite Corp., Can. P. 321191.

5. A. Nathansohn, E. P. 340651; abst. C. A. 1931, **25**, 5030. F. P. 683251; abst. Chem. Zentr. 1930, II, 1633.

6. *Ibid.* E. P. 356277; abst. J. S. C. I. 1931, **50**, 1045-B. F. P. 697149; abst. Chem. Zentr. 1931, I, 2956.

acids) until such condition that little or no alkali or condensing agent is required[1], the textiles being rendered decidedly water-repellent.

In the manufacture of laminated glass and wood (nonshatterable glass and acetylcellulose)[2], alternating sheets of glass or veneer are assembled in a mixture of ethyl and butyl lactates and methylene chloride, and after removal are consolidated by compression at 300 lb. per sq. inch at 90-130°. In the dyeing and printing of acetylcellulose[3], there is applied to the fiber a solution of an ester salt of leuco vat dye, followed by drying and steaming in order to fix the ester salt as such on the fiber, the dyeing being then developed by oxidation. When the methyl (or ethyl, propyl, butyl or benzyl) ether of ethylene glycol is heated with mercuric fluoborate or fluosilicate and acetylene passed into the mixture, acetals from alcohol, substituted with more than one other group are formed[4], useful as cellulose ester solvents.

Liquid acetaldehyde may be oxidized to acetic acid with oxygen in the presence of catalysts[5], when the upper portion of the cylindrical reaction vessel is filled with nitrogen or other inert gas under pressure, especially when manganese acetate is used as catalyst and a gas pressure of 5-6 atms. is used[6]. In measurements made with an Ostwald-Auerbach overflow viscometer[7], acetylcellulose in benzyl alcohol and

1. A. Nathansohn, E. P. 356878; abst. J. S. C. I. 1931, **50**, 1090-B; Textile Mfr. 1932, **58**, #687, 116. Heberlein & Co., A.-G., E. P. 313616; abst. J. S. C. I. 1930, **49**, 815-B. Can. P. 308284. D. R. P. 535283; abst. C. A. 1932, **26**, 1136.

2. Newtex Safety Glass Co., Ltd., and W. Dougan, E. P. 355604; abst. J. S. C. I. 1931, **50**, 972-B.

3. G. de Niederhaeusern, U. S. P. 1816766; abst. C. A. 1931, **25**, 5578. E. P. 274094; abst. Chem. Zentr. 1927, II, 2574. Cites D. R. P. 415937, 433146.

4. J. Nieuwland, U. S. P. 1824963. See W. Lawson, U. S. P. 1824961.

5. Nihon Tisso Hiryo K. K. and H. Hasimoto, Jap. P. 91019; abst. C. A. 1932, **26**, 1301.

6. Nippon Chissohiryo Kabushiki Kaisha, E. P. 359878; abst. J. S. C. I. 1932, **51**, 221-B.

7. Y. Nisizawa, Kolloid-Z., 1931, **56**, 59, 317; abst. C. A. 1931, **25**, 5554, 5982.

in ethyl alcohol-benzene shows structure viscosity effects which increase with increase of cellulose ester concentration. A duplex waterproof foil may be prepared by waterproofing nitrocellulose by inclusion of Japan wax, lanolin or paraffin[1], with a glycerol-phthalic anhydride resin, superimposed on an acetylcellulose film. In order to produce curved or flat compound sheets[2], two glass sheets, one of which is about 0.01 inch thick, is cemented to the other sheet with an interposed celluloid or acetylcellulose sheet of 0.015 inch in thickness. F. Ohl[3] has given a patent review with comments of the innovations in the artificial silk industry, primarily in connection with cellulose acetate.

As a backing for sheets as artificial mother-of-pearl[4], a composition of acetylcellulose 7, ethyl lactate 25, methyl alcohol 50, ethyl acetate 25, pigment 7, has been patented, upon which to apply the nacreous mixture. In delustering acetate filaments[5], particularly dry-spun, by the action of hot water or moist steam, the delustering action may be prevented by the presence of such salts as sodium or ammonium sulfates of 5% strength. E. Partridge[6] has given a general view of the acetic industry of the United States and of the cellulose acetate industry as it affects the con-

1. Non-Inflammable Film Co., Ltd., and G. Staley, E. P. 356146; abst. J. S. C. I. 1931, **50**, 1045-B.

2. J. Nye and W. Stainer, E. P. 364277; abst. J. S. C. I. 1932, **51**, 262-B.

3. Kunstoffe, 1931, **21**, 198, 347; abst. C. A. 1931, **25**, 1774, 5762. Metallborse, 1932, **22**, 49; abst. C. A. 1932, **26**, 1773. Textilber. 1931, **12**, 200. Farbe. u. Lack, 1931, 51, 64; abst. C. A. 1931, **25**, 1989; J. S. C. I. 1931, **50**, 340-B. Kunstseide, 1931, **13**, 43; abst. C. A. 1931, **25**, 4132. Textilber. 1931, **12**, 647; abst. J. S. C. I. 1931, **50**, 1088-B; Chem. Zentr. 1931, II, 3175. Rayon and Synthetic Yarn Journal, 1931, **12**, #6, 12; Am. Dyestuff Rept. 1931, **20**, 475. Rayon Record, 1931, **5**, 443; abst. C. A. 1931, **25**, 5285. Russa 1931, **6**, 1097; abst. C. A. 1931, **25**, 5555. Seide 1931, **36**, 320; abst. Chem. Zentr. 1931, II, 3285.

4. J. Paisseau, U. S. P. 1808372; abst. C. A. 1931, **25**, 4372. F. P. 649019; abst. Chem. Zentr. 1930, I, 462. See also D. Othmer, Chem. Met. Eng. 1932, **39**, 136.

5. C. Palmer and S. Fulton, U. S. P. 1808061; abst. Chemicals, 1931, **36**, 27. See also U. S. P. 1554801.

6. I. E. C. 1931, **23**, 482; abst. J. S. C. I. 1931, **50**, 620-B; British Plastics, 1931, **3**, #30, 268.

sumption of acetic acid, and W. Pease[1] his patented method for the manufacture of acetylcellulose films, in which the ester dissolved in methylethyl ketone with a plasticizer, is allowed to evaporate in a closed chamber at 30-75° with a humidity of 50-75%.

In discussing the problems of safety glass manufacture[2], T. Pesch has pointed out that acetylcellulose has been found the most satisfactory material, the synthetic resins for the intermediate layer, while giving brilliance, transparency and good adhesion, has a resistance lying within narrow limits of temperature, and C. Peters[3] the production of acetylcellulose and lacquers therefrom in Russia. Formic and acetic acids may be separated by distillation[4], after addition to the mixture of a liquid which is miscible with acetic acid but immiscible with formic acid and which forms an azeotropic mixture with the latter, suitable liquids being trichlorethylene, carbon tetrachloride, benzene and benzine.

In the printing of union fabrics (acetylcellulose with cotton, linen, silk or wool)[5], certain aminoanthraquinones (1-amino-2-methyl-, 1-methylamino-, 1-amino-4-hydroxy-, 1.4-diamino-, 1.4.5.8-tetramino-, 1.4-diaminodimethyl-anthraquinone and dinitrodiphenylamine) when printed upon such composite fabrics will react differently during the course of the fixing, giving differential dyeing effects (see p. 879, n. 4). In the manufacture of filaments from difficultly tractable animal fibers as horsehair, mohair, goat hair and the lower grades of wool, which have a tendency to become displaced and form free ends in yarns and fabrics[6], the material is impregnated with the following composition:

1. W. Pease, E. P. 357079; abst. J. S. C. I. 1931, **50**, 1089-B.
2. Chem. Ztg. 1931, **55**, 730; abst. J. S. C. I. 1931, **50**, 1049-B.
3. Kunstoffe, 1931, **21**, 85; abst. C. A. 1931, **25**, 3162.
4. I. Petersen and C. Angelbrecht, U. S. P. 1813636; abst. C. A. 1931, **25**, 5178. D. R. P. 513024; abst. C. A. 1931, **25**, 1263. E. P. 305594; abst. Chem. Zentr. 1929, II, 650.
5. R. Petitdidier and F. Feynier, U. S. P. 1847697.
6. H. Pike, E. P. 353429; abst. Brit. Plastics, 1932, **3**, #32, 104; Textile Mfr. 1932, **58**, #685, 36.

acetylcellulose 5, triacetin 5.2, ethyl alcohol 20, benzene 24, acetone 45 and triphenyl phosphate 0.8. R. Pinault[1] has discussed, illustrated and diagrammed the three general processes for safe ironing acetate textiles.

In order to avoid creasing of fabrics made from cellulose acetate or propionate[2], the fabric to be dyed is first subjected to a surface saponification, and then dyed on a winch in the usual manner. A tinting fluid for the identification of acetate yarns comprises a fugitive dyestuff, a non-drying oil and a sulfonated oil[3]. According to H. Price[4], if natural luster of acetylcellulose fiber is to be preserved, temperatures in wet-processing should not exceed 82°, and strong alkalis should be avoided. Satins, twills and failles are dyed in the jig; flat or warp knit fabrics on reels; voiles and ninons in open hanks; and Celanese velvets in the Star dyeing machine. *a*- and *b*-Alloamylosan have been described[5]. Ethylsulfuric acid (sulfovinic acid) may be converted by direct catalytic action to acetic acid[6]. Ramie tripalmitate fibers in swollen and unswollen state have been photomicrographically reproduced[7].

Traffic signals on road surfaces are made by means of a concentrated volatile solvent and a cellulose ester preferably loaded with barium sulfate or lithopone[8], the composition being introduced into cavities in the road surface. Anhydrous acetic acid is obtainable from its solutions[9] by

1. Textile World, 1931, **80**, 132; abst. C. A. 1931, **25**, 5037.
2. H. Platt, U. S. P. 1802956; abst. C. A. 1931, **25**, 3848. E. P. 339429; abst. Chem. Zentr. 1931, II, 1355.
3. H. Platt, W. Whitehead and F. Williams, U. S. P. 1840290, 1840291; abst. C. A. 1932, **26**, 1455. Can. P. 305265; abst. C. A. 1931, **25**, 827.
4. Proc. Am. Assoc. Textile Chem. Colorists, 1931, 17; Am. Dyestuff Reptr. 1931, **20**, 19; abst. C. A. 1931, **25**, 1087.
5. H. Pringsheim, A. Weidinger and P. Ohlmeyer, Ber. 1931, **64**-B, 2125; abst. J. S. C. I. 1931, **50**, 1277-A.
6. Procedes et Produits Chimiques, F. P. 705662; abst. C. A. 1932, **26**, 152.
7. B. Rabinowitsch, Kolloid-Z., 1931, **57**, 203; abst. C. A. 1932, **26**, 1116.
8. Reimann-Bauasphalt G. m. b. H., D. R. P. 533046; abst. C. A. 1932, **26**, 577.
9. E. Ricard and H. Guinot, U. S. P. 1839894; abst. C. A. 1932, **26**, 1301. Can. P. 319137.

distilling with a liquid of higher boiling point than the acid with which it will not form an azeotropic mixture as amyl acetate, and an auxiliary entraining liquid as ethyl acetate, which with water will produce a mixture having a low minimum boiling point so as to remove the water, the dehydrated mixture of acid and solvent being then distilled. The final distillation may be in the presence of gasoline, b. pt. 114-116°[1]. A foam for cellular concrete manufacture has been evolved[2], involving the use of a foaming agent as ammonium caseinate, mixed with acetylcellulose as stabilizing solution. The solution is converted into a foam upon adding formaldehyde.

A non-waterproof paper towel has been described (see p. 209, n. 4)[3] obtained by uniformly incorporating cellulose ester as the acetate or nitrate throughout a non-sized paper towel web, and then regenerating the cellulose within the web by a saponification treatment. The chemical analysis of rayons and acetate filaments has been exhaustively treated by P. Ridge, H. Parsons and M. Corner[4] and the changes in voscisity of acetylcellulose-acetone solutions by C. Rittenhouse and C. Staud[5], who found the viscosity increased faster than the concentration,—an indication of a colloid system.

Acetylene may be hydrated to acetaldehyde by the use of mixed mercuric and ferric sulfates as catalyst[6], the concentration of iron salt being maintained sufficiently high to avoid reduction of $HgSO_4$ to Hg. In producing esters as methyl acetate[7], acetic acid and methyl alcohol are caused

1. E. Ricard and H. Guinot, U. S. P. 1839932; abst. C. A. 1932, **26**, 1301.
2. J. Rice, U. S. P. 1807810; abst. C. A. 1931, **25**, 4379; Chem. Zentr. 1931, II, 896.
3. G. Richter and M. Schur, Can. P. 315866.
4. J. Textile Inst. 1931, **22**, 117-T; abst. C. A. 1931, **25**, 5036; J. S. C. I. 1931, **50**, 581-B.
5. C. Rittenhouse and C. Staud, Paint, Oil & Chem. Rev. 1931, **91**, #9, 9; abst. C. A. 1931, **25**, 1989.
6. R. Riley and Imperial Chem. Industries, E. P. 346883; abst. J. S. C. I. 1931, **50**, 710-B; Chem. Zentr. 1931, II, 630.
7. K. Roka and O. Fuchs, U. S. P. 1800319; abst. C. A. 1931, **25**, 3359. D. R. P. 507205; abst. Chem. Zentr. 1930, II, 2958. See also U. S. P. 1791238.

to react together at a temperature of 100-250° under sufficient pressure to maintain the materials in the liquid phase, the ester formed being continually removed from the reaction mixture. The properties and dyeing of acetate silk have been dealt with by J. Rolland[1], and the degree of purity of raw materials used in the rayon industry by K. Roos[2].

According to the E. Roth method[3], cellulose to be acetylated is first treated with an acetylation mixture until the mass has become capable of being pumped, and is then passed repeatedly through nozzles to obtain an intimate mixture. The technics of acetylcellulose were reviewed in 1931 by H. Rudy[4], in which the Ruth-Aldo Co.[5] described their process for cellulose acetation, comprising the use of a mixed catalyst of sulfuric acid with an oxidizing agent (manganese sulfate or acetate, chromic acid, monopersulfuric acid) capable of liberating a definite amount of oxygen. The acetylation may be completed in another bath at 25-40° by a reagent capable of reducing the catalytic power of the sulfuric acid[6]. Their method of producing acetate filaments is to extrude the ester solution into a setting bath composed of a polyhydric alcohol and a hydrocarbon boiling above 80°, which will extract acetone from the threads but is a non-solvent for the acetylcellulose[7]. Yarns made from such filaments are adapted for weaving and knitting[8], when sized with a mixture of calcium resinate and a fatty

1. Tiba, 1931, **9**, 387; abst. C. A. 1931, **25**, 5567.
2. Russa, 1931, **6**, 1507; abst. C. A. 1932, **26**, 1774.
3. E. Roth, E. P. 345069; abst. C. A. 1932, **26**, 304; J. S. C. I. 1931, **50**, 533-B; Silk J. and Rayon World, 1931, **8**, #86, 54; British Plastics, 1931, **3**, #28, 179. E. Roth-Schmidt, D. R. P. 527770; abst. C. A. 1931, **25**, 5286; Chem. Zentr. 1931, II, 1373.
4. Am. Dyestuff Rept. 1931, **20**, 505.
5. Ruth-Aldo Co., F. P. 722719. Ruth-Aldo Co., Inc., and H. Barthelemy, Can. P. 308741.
6. Ruth-Aldo Co., Inc., and H. Barthelemy, Can. P. 308743, 308744.
7. *Ibid.* Can. P. 315965.
8. C. Ryley and G. Awcock, U. S. P. 1807755; abst. C. A. 1931, **25**, 4414.

lubricating agent as lard, which may also be mixed with zinc oleate and benzene or xylene.

With increasing purification of the fiber before acetylation[1], the apparent viscosity of the cellulose acetate solutions diminishes together with a strongly-marked anomaly with regard to the law of outflow. The viscosimetric properties appear to be the result of fiber purification and de-organization, during which foreign matter with a great influence on the viscosity is removed, rather than of the existence of a large number of chemical individuals with differing molecular weight. In cellulose acetylation, with increase in sulfuric acid as catalyst, the viscosity of the acetate greatly diminishes, the effect being rather due to the decomposing action of the acid on a substance accompanying cellulose in the fibers rather than to acetolytic degradation of cellulose.

In the swelling of cellulose acetate[2], it is considered that, besides the attraction between the dipoles of this substance and the liquid mols, the diffusion pressure of the liquid is quite important, otherwise it is difficult to explain why so much liquid is sometimes absorbed by the cellulose acetate (e.g., 1 mol. of the latter takes up 43 mols. chloroform and 12 of ethyl acetate), whereas, when little swelling occurs, only a small amount of liquid is absorbed. Cellulose acetylated for a long time, and hence depolymerized to a greater extent, swells less and gives a much less viscous solution in chloroform than that less drastically treated; hence high viscosity corresponds with great swelling. Since heat is evolved during swelling, rise of temperature should be accompanied by decreased swelling, but the reverse is often the case. Cellulose may be acetylated in the presence of sodium perchlorate and sulfuric acid as catalyst[3],

1. I. Sakurada and K. Hess, Ber. 1931, **64-B**, 1174; abst. C. A. 1932, **26**, 1114; J. S. C. I. 1931, **50**, 828-A.
2. I. Sakurada and S. Suzuki, J. S. C. I. (Japan) 1931, **34**, 490-B; abst. J. S. C. I. 1932, **51**, 255-B.
3. Schering-Kahlbaum A.-G., D. R. P. 531276; abst. C. A. 1931, **25**, 5433; Nitrocellulose, 1931, **2**, #8, 166; Chem. Zentr. 1931, II, 2536.

perchloric acid being liberated. As the culmination of X-ray examinations, G. Schick[1] has come to the conclusion that photographic emulsions are just as stable on acetyl- as on nitro-cellulose films.

In dehydrating vapor mixtures containing acetic anhydride and water[2], there is added a solvent (benzene, toluene, chloroform, trichlorethylene) indifferent to acetic anhydride and having a b. pt. about that of water, the water with added solvent being removed by fractionation. In the molding of acetylcellulose[3], designs are produced by applying the ester by means of a roller to the surface of a glass plate provided with a design composed of two or more depths of engraving, a solvent of the cellulose ester being interposed between the ester sheet and the plate. The surface of the glass plate may be initially smooth or rough, and the design formed by cutting or etching. The plate, covered with the acetylcellulose sheet, is heated to accelerate the evaporation of solvent and dry the material, which is then peeled from the plate. H. Schmidt[4] has given formulas for the preparation of cellulose nitrolaurate, nitrooleate, nitrobenzoate and nitroacetate, the latter[5] containing 0.01-10% N., and methods for the use of wire netting as a support for acetylcellulose films with the difficulties encountered[6].

Light-sensitive films are made from a mixture of organic dye components as diazo compounds and solutions of cellulose esters[7], which are mixed with boron trifluoride compound of diazotized 4-amino-1-monoethylamino-2-tol-

1. G. Schick, Nitrocellulose, 1931, **2**, 199; abst. C. A. 1932, **26**, 930.
2. F. Schleicher, G. Schwaebel and K. Briesewitz, U. S. P. 1815802; abst. C. A. 1931, **25**, 5436. F. P. 652820; abst. Chem. Zentr. 1929, I, 2693. See p. 667, n. 2.
3. R. Schlochoff, E. P. 359072; abst. British Plastics, 1932, **3**, #34, 482.
4. Nitrocellulose, 1931, **2**, 4; abst. C. A. 1931, **25**, 2282.
5. Nitrocellulose, 1931, **2**, 91.
6. Kunstoffe, 1931, **21**, 217; abst. C. A. 1932, **26**, 818.
7. M. Schmidt and W. Krieger, D. R. P. 535913; abst. C. A. 1932, **26**, 931; Chem. Zentr. 1931, II, 3424.

uene, resorcinol, tartaric acid and alcohol. The mixture is rolled out in a layer, dried and exposed under a positive. On developing with gaseous ammonia, a yellowish-brown positive is obtained. To coat fabrics with acetylcellulose[1], the ester is spread on a rigid surface as glass or metal and the solvent evaporated to form a film. The fabric to be coated is wetted with a dilute solution of the cellulose ester and the wetted fabric pressed against the film, the united film and fabric being then removed from the support. The E. Schnitzler adhesive strip[2] comprises paper or cloth coated on one side with a rubber composition and on the other with cellulose laurate, to facilitate unwinding when in rolls.

Hollow artificial silk produced by dry spinning at the usual temperature of an acetylcellulose solution containing a suitable amount of non-solvent for the acetate[3], gives a product (density 0.8) having greater covering power than ordinary acetate (1.3), viscose (1.5) or hollow viscose (1.37) filaments. Although its normal luster is slightly less than that of ordinary acetate silk, the conditions of spinning may be so adjusted that it is perfectly opaque and white, this latter mat appearance resisting scouring, bleaching and dyeing processes. 100 denier of this silk has a covering power in textiles equal to 150 denier yarn of ordinary acetate silk, and is much warmer to handle. The tensile strength is 1.2-1.3 gm. per denier, and suffers a loss of 25-30% in strength when wetted. It is used principally in crepe and plush materials. A process for cellulose pretreatment for esterification[4] comprises submitting to a very gentle nitration (less than 1% nitration) which is said to greatly increase its receptivity for esterification.

1. G. Schneider, U. S. P. 1824690; abst. C. A. 1932, **26**, 319; Chem. Zentr. 1931, II, 3416.
2. U. S. P. 1837680; abst. C. A. 1932, **26**, 1405.
3. H. Schupp, Kunstseide, 1931, **13**, 424; abst. J. S. C. I. 1932, **51**, 177-B.
4. M. Schur and B. Hoos, U. S. P. 1848553. Cites U. S. P. 1701543. E. P. 233367. M. Schur, B. Hoos and T. Morris, Can. P. 319044.

The G. Seymour coating composition[1] comprises cellulose acetate 10, formal-glycerol synthetic resin 1-20, acetone 50, benzene 25, ethyl alcohol 25 and diacetone alcohol 20, mixed to a transparent solution. Our knowledge of the saponification of acetylcellulose by ammonia has been presented in thesis form by G. Shahid[2]. Bromoil prints are made on acetylcellulose supports sensitized with a silver halide gelatin emulsion[3], to which a hardening agent has been added before coating.

In the precipitation of acetylcellulose in solution by the addition of water thereto accompanied by agitation (p. 644, n. 5), if a blast of air be concurrently applied[4], especially in the presence of zinc chloride, sodium acetate or sulfate, the porosity is greatly increased, admitting of ready removal of dilute acetic acid from the reacting mixture with but little effort. In film production[5], it is advocated to spread the ester solution on a smooth surface, coagulate by immersion in a liquid or vapor as steam, followed by stripping the film while still wet, the film being subjected to the swollen condition to a stretching operation under tension to avoid shrinkage. The kinetics of sorption of water vapor by cellulose acetate in film form[6] has been detailed by S. Sheppard and P. Newsome.

Cellulose acetate may be precipitated in the form of a porous, coherent, easily washed ribbon by gradually diluting the reaction mixture after hydrolysis to the acetone-soluble stage, with 50-75% of that quantity of water which would be required to cause the appearance of a permanent precipitate of acetylcellulose, and feeding the resulting mixture between wet rollers into a precipitating bath. If the dilution is insufficient a yellow, translucent

1. Can. P. 317117; abst. C. A. 1932, **26**, 1460.
2. Thesis, Berlin, 44 pp., abst. C. A. 1931, **25**, 3831.
3. F. Shephard and F. Renwick, E. P. 341924.
4. S. Sheppard and L. Eberlin, U. S. P. 1844717.
5. S. Sheppard and J. McNally, E. P. 344170; abst. C. A. 1932, **26**, 303; Chem. Zentr. 1931, II, 3566. See also U. S. P. 1784758.
6. J. Phys. Chem. 1930, **34**, 1158; abst. Eastman Kodak Company Abridged Scien. Publ. 1930, **14**, 138.

ribbon is obtained which sticks to the rollers and is difficult to wash; if too great, the coherence of the ribbon is impaired. The process is advantageously combined with recovery of acetic acid in which the reaction mixture, after addition of sufficient sodium acetate to neutralize the sulfuric acid catalyst, is distilled *in vacuo*, preferably at a gradually rising temperature not above 70° and with continuous agitation, until 40-50% acetic acid is recovered[1]. R. Simmonds[2] has dealt in a general way with the technology of molding cellulose acetate.

For modifying the luster and covering power of acetylcellulose silk[3], finely divided inert pigments are incorporated in the ester solution before spinning, then filtered to remove the larger particles and increase the homogeneity. Paraffin oil may be added[4]. J. Sisley[5] has reviewed the various dyes and processes which have been proposed for dyeing acetate silk black.

As a plasticizer which may be used in approximately equal weight with cellulose acetate the alkylesters of carbamic acids have been proposed[6], as methyl, methylmethyl, ethyl, ethylethyl carbamates, dissolved in acetone and with the addition of high boilers (amyl acetate, ethyl lactate) if desired. In the separation of aliphatic anhydrides from their aqueous solutions (see p. 716, n. 1; 830, n. 4), for propionic acid the solvent may be amyl propionate, the entrainer ethyl propionate, and the accessory liquid (if any) a petroleum of b. pt. 138-140°. For formic acid, amy[1] for-

1. O. Silberrad and H. Bleasdale, E. P. 357552; abst. J. S. C. I. 1931, **50**, 1135-B. Can. P. 308445, 316009.

2. Plastics, 1931, **7**, #9, 502; abst. Nitrocellulose, 1931, **2**, #10, 199; Chem. Zentr. 1931, II, 2806.

3. J. Singmaster, E. P. 339603; abst. C. A. 1931, **25**, 2849. F. P. 680492; abst. Chem. Zentr. 1930, II, 656. Can. P. 310803. Compare E. P. 274054, 290263, 290693, 297364.

4. *Ibid.* E. P. 342743; abst. C. A. 1931, **25**, 5559; Silk J. and Rayon World, 1931, **8**, #85, 53. Cites E. P. 243350, 339603.

5. Tiba, 1931, **9**, 17; abst. C. A. 1931, **25**, 1677. Russa, 1931, **6**, 643; abst. C. A. 1931, **25**, 5567.

6. H. Smith, U. S. P. 1836687; abst. C. A. 1932, **26**, 1120.

mate for solvent, propyl formate the entrainer, and accessory liquid (if any), *n*-heptane[1].

For the fabrication of designs on mixed fabrics containing acetate silk[2], or immunized cotton in association with cotton, wool or natural silk, the fabrics are dyed or printed with dyes which color both acetylcellulose and immunized cotton and have no affinity for the other fibers, or give with the other fibers readily dischargeable dyes. The fabrics are then steamed, washed, treated with discharging agents, if necessary, and then treated with dyes having no affinity for cellulose acetate and immunized cotton. Acesil is the trade-marked name for cellulose acetate yarns[3]. 2.5-Dimethoxy-1-aminobenzene, soluble in ethyl acetate, dyes cellulose acetate a fast red[4]. Dyestuffs having good affinity for acetylcellulose[5], and giving yellow to brown tints fast to light, washing and scrubbing, are obtained by coupling non-sulfonated nitrodiazo compounds,—other than those having an oxy group ortho to the diazo group—with monosulfonic acids capable of being coupled.

When alkalicellulose is treated with a solution of a heterocyclic compound containing one or more N:C. Halogen groups (cyanuric chloride, dichlorquinazoline, tribrompyrimidine), substitution takes place, the product being immunized to direct cotton dyes, but showing affinity for acetylcellulose dyes[6]. Cellulose may be partly acylated by means of acetic anhydride in the presence of a basic agent (alkali

1. Soc. Anon. des Distilleries des Deux-Sevres, E. P. 348282, Addn. to 296974; abst. J. S. C. I. 1931, **50**, 796-B. F. P. Addn. 37269 to F. P. 651528; abst. Chem. Zentr. 1931, I, 685.
2. Soc. Anon. des Establissements Petitdidier (Ancienne Maison Jolly-Belin), D. R. P. 536068; abst. C. A. 1932, **26**, 1134. E. P. 256238 (p. 641, n. 1), 258562 (p. 641, n. 2), 261399, 268327, 270657 (p. 716, n. 5).
3. Societa Anonima Italiana, Trade-Mark, Sept. 9, 1931.
4. Society of Chemical Industry in Basle, F. P. 709779; abst. Chem. Zentr. 1931, II, 3400. D. R. P. 534566; abst. C. A. 1932, **26**, 1128. E. P. 343016; abst. Chem. Zentr. 1931, I, 2941. F. P. 682841.
5. *Ibid.* E. P. 220303; abst. Soc. Dyers & Col. 1926, **42**, 64.
6. *Ibid.* E. P. 342167; abst. J. S. C. I. 1931, **50**, 343-B; Chem. Zentr. 1931, II, 3287. F. P. 687301; abst. Chem. Zentr. 1930, II, 2979. Swiss P. 146541; abst. C. A. 1932, **26**, 303. Belg. P. 377253.

hydroxide, pyridine, sodium acetate)[1], and afterwards esterified in the usual manner. When a non-sulfonated *o*-aminophenol *o*-arylsulfonate is diazotized and coupled with a non-sulfonated phenol or arylamine of the benzene series, pigments result suitable for acetate silk dyeing; e.g. *o*-aminophenyl toluene-*p*-sulfonate + aniline, hydrolyzed and acetylated (greenish-yellow); or with phenol, hydrolyzed and ethylated (greenish-yellow)[2].

Diazo compounds coupled in the 3-position with 4-hydroxy-1-naphthoic esters give, according to the first component used, pigments for acetate silk. Examples of diazo components are: aniline (red), *p*-aminoacetanilid (bluish-red), *m*-aminobenzyl alcohol (red-orange), 4-chlor-*o*-aminophenol-6-sulfonic acid (chrome-red-violet), sulfanilic acid (red-orange), and *b*-naphthylamine -1-sulfonic acid (red barium lake)[3]. Acylated 1.5.8-triamino-4-anilinoanthraquinone dyes acetate silk blue[4], and 1.5.8-triamino-4-*p*-anisidinoanthraquinone (green-blue).

Cellulose esters free from sulfur are formed by treating cellulose xanthate or cellulose xanthic acid with an organic acid anhydride in presence or absence of a solvent and catalyst[5]. When a leuco-*a*-hydroxyanthraquinone is condensed with ammonia or an alkylamine in presence of boric acid[6], acetate silk dyes are formed, *b*-sulfonic groups being eliminated during the reaction. 4.8-Diaminoanthrarufin-2.6-disulfonic acid with boric acid and ammonia gives 4.5.8-triamino-1-hydroxyanthraquinone (blue on acetate silk). 1.8-Diamino-5-methylamino-4-hydroxyanthraquinone

1. Society of Chemical Industry in Basle, E. P. 343889; abst. C. A. 1932, **26**, 303; J. S. C. I. 1931, **50**, 480-B; British Plastics, 1931, **3**, #28, 179; Chem. Zentr. 1931, II, 2951. F. P. 705309; abst. C. A. 1931, **25**, 5288; Chem. Zentr. 1931, II, 2951.
2. *Ibid.* E. P. 343006; abst. J. S. C. I. 1931, **50**, 580-B. F. P. 683955; abst. Chem. Zentr. 1930, II, 2835.
3. *Ibid.* E. P. 343016; abst. J. S. C. I. 1931, **50**, 580-B; Chem. Zentr. 1931, II, 2941.
4. *Ibid.* E. P. 344117; abst. J. S. C. I. 1931, **50**, 623-B. F. P. 687299; abst. Chem. Zentr. 1930, II, 3858.
5. *Ibid.* E. P. 349322; abst. Textile Mfr. 1931, **57**, #682, 381.
6. *Ibid.* E. P. 353932; abst. J. S. C. I. 1931, **50**, 1133-B; Chem. Zentr. 1931, II, 3161.

(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).

When acetylated fibers obtained without degradation of the cellulose from which they are derived (see p. 299, n. 3) are treated with a swelling agent (acetic acid, pyridine, ammonium thiocyanate) and then stretched up to 150%, the resulting fibers show increased softness and tensile strength (up to 50%), both in the dry and wet condition[1]. In the manufacture of acetic anhydride or acetyl chloride from aliphatic salts and sulfuryl chloride or sulfur dioxide and chlorine[2], alkaline earth salts may be used provided they are diluted with sand or other inert matter. Improvements in the preparation of cellulose acetobutyrate (see p. 578, n. 2) have been described[3].

Cellulose acetate may be prepared by acetylating cellulose with acetic anhydride in the presence of methanesulfonic acid in amounts of 80-100% of the weight of the cellulose, and should contain in the catalyst less than 5% of its weight of sulfuric acid[4]. Surfaces of glass that are to be united by means of acetylcellulose, are first coated with a light layer of gelatin and celluloid, and the sheets assembled at slight pressure in a bath of acetate solvent (ethyl lactate or alcohol-water) only when hot, the whole being then heated in an autoclave containing gas under pressure[5].

In the production of moldable materials, cellulose acetate is vigorously stirred with plasticizers (camphor, ethyl phthalate) in suspension in water, fillers and coloring matters added if desired, and the suspended mixture mechanically separated into very fine particles, being molded in this

1. Soc. Chemical Industry in Basle, E. P. 363284; abst. J. S. C. I. 1932, **51**, 258-B.
2. Soc. Des Brevets Etrangers Lefranc & Cie, E. P. 344116; abst. J. S. C. I. 1931, **50**, 621-B; Chem. Zentr. 1931, II, 125.
3. Soc. des Usines Chimiques Rhone-Poulenc, D. R. P. Anm. S-94825, Addn. to D. R. P. 505610; abst. Nitrocellulose, 1931, **2**, #10, p. 204.
4. *Ibid.* F. P. 705546; abst. C. A. 1931, **25**, 5287; Chem. Zentr. 1931, II, 2951. Can. P. 308568.
5. *Ibid.* E. P. 339872; abst. C. A. 1931, **25**, 2827; British Plastics, 1931, **2**, #23, 530; Chem. Zentr. 1931, I, 1809.

condition[1]. Cellulose butyrates soluble in methyl alcohol result when cellulose tributyrate dissolved in a solvent containing water[2], is saponified by water until the desired methyl alcohol solubility has been reached. The ester is soluble in hot methyl alcohol, insoluble in cold. As an acetylcellulose plasticizer, there has been recommended a mixture of triacetin and toluenesulfonethylamide[3], to which benzyl alcohol may be added.

Acetic acid is produced by submitting methyl alcohol to the action of oxygen or air under pressure, the acid as produced being fixed with ammonia[4]. By the action of H on formamide[5] at 200-500°, acetamide and glycocoll are prepared. The action of HCN on methyl chloride, or the direct action of a mixture of CO, ammonia and methyl chloride[6], result in the formation of acetic acid, acetamide and acetonitrile, and acetone forms when acetylene and steam are caused to react at high temperature in the presence of heavy metal oxides under 5 atms. pressure[7].

For the supply, delivery and storage of acetylcellulose solutions[8], use is made of endless conduits, the supply to each vat being controlled by a "distributor," so that after the valve has been closed, the solution below runs down into the vat, any stagnation of any part of the solution being avoided. In the preparation of cellulose esters containing

1. Soc. des Usines Chimiques Rhone-Poulenc, E. P. 351390; abst. J. S. C. I. 1931, **50**, 853-B; British Plastics, 1931, **3**, #30, 268. F. P. 707593; abst. C. A. 1932, **26**, 815; Chem. Zentr. 1931, II, 2243.

2. *Ibid.* Can. P. 313825.

3. *Ibid.* Swiss P. 143654; abst. Nitrocellulose, 1931, **2**, #8, 167.

4. Soc. Francaise de Catalyse Generalisee, F. P. 706216; abst. C. A. 1932, **26**, 154; Chem. Zentr. 1931, II, 1489. Belg. P. 378258.

5. *Ibid.* F. P. 708084; abst. C. A. 1932, **26**, 995; Chem. Zentr. 1931, II, 1922.

6. *Ibid.* F. P. 708111; abst. C. A. 1932, **26**, 1301; Chem. Zentr. 1931, II, 1922. See also E. P. 342283.

7. Soc. Industrielle des Derives de l'Acetylene, F. P. 712967; abst. C. A. 1932, **26**, 1624.

8. Soc. Industrie de Moy, E. P. 356182; abst. Textile Mfr. 1932, **51**, #686, 79. See Societe Kodak-Pathe, F. P. Addn. 40228 to 702116; abst. Chem. Zentr. 1931, II, 3061.

insoluble pigments[1], the latter are suspended in a "homogenizing liquor" (e.g., a solvent mixture containing a small amount of cellulose acetate) and forced under pressure and at high speeds (50-300 meters per second) through one or more narrow orifices, further quantities of cellulose acetate being subsequently added for conversion of the intermediates into varnishes, films or lacquers.

Crepe effects are obtained by incorporating substances which have a high affinity for water in cellulose acetate[2], making cloth from the highly twisted threads, and then treating the cloth obtained with water or an aqueous solution of calcium chloride, nitrate or lactate. In the coloring of granules of crushed rock[3], the particles are enveloped in a thin film of a cellulose ester containing a waterproof coloring matter as pigments. H. Stadlinger[4] has detailed the steps in cellulose acetate filament manufacture which have recently been simplified or combined, and W. Stahl[5] discussed the delustering of acetate silk in hot baths containing sodium, potassium or ammonium hydroxides, sodium carbonate and hydrochloric, sulfuric, acetic and tartaric acids in various concentrations and at 20°, 40°, 75° and 100°. It is shown that delustering in all cases becomes apparent at about 70° and increases up to the boiling point of the solution. Although the luster is destroyed by boiling in distilled water, there is no evidence of hydrolysis, no relation being found to exist between the degree of hydrolysis and loss of luster. Photomicrographs of lustrous and delustered acetate silk indicate that the latter is permeated with bubbles. Increase in acetyl content above the usual 53-57% improves resistance to delustering, but at the expense of tenacity and elasticity. An acetate silk nitrated

1. Soc. Pour la Fabr. de la Soie "Rhodiaseta," E. P. 356740; abst. J. S. C. I. 1931, **50**, 1062-B. F. P. 707330; abst. C. A. 1932, **26**, 843; Chem. Zentr. 1931, II, 2537. Belg. P. 375731.
2. *Ibid.* F. P. 715047; abst. C. A. 1932, **26**, 1803.
3. I. Sproat and R. Vanderbilt Co., U. S. P. 1830489; abst. C. A. 1932, **26**, 825.
4. Kunstseide, 1931, **13**, 181; abst. C. A. 1931, **25**, 4400.
5. Seide, 1931, **36**, 358; abst. C. A. 1932, **26**, 1792.

to contain 1-2% N as nitrate is stable towards hot solutions while retaining the properties of normal acetate fiber. Stretch spinning produces alignment of micelles with fewer and smaller intermicellar spaces, and hence less tendency for delustering. The addition of swelling agents (phenol, cyclohexanol, tetrachlorethane) to water baths produces stronger delustering and at lower temperatures.

In operations such as the manufacture of high-tension cables and electric condensers[1], 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 impregnation. Cellulose acetate solutions are used as impregnating media. By introducing nitrogen dioxide or tetroxide in the hydrolysis of cellulose acetate after acetylation, bleaching takes place simultaneously with saponification[2], an undegraded product being formed. Cellulose formate, propionate or butyrate may be similarly treated, and ethyl or amyl nitrite, guanidine nitrite or nitrous acid used.

In producing films and sheet material having the property of flatness in an unusual degree[3], they may be formed by the use of acetylcellulose having a precipitation value of at least 90% in a solution consisting of 40% water and 60% acetone at 20°, together with a plasticizer. When cellulose acetylation is conducted in the presence of selenic acid[4], the acetylated cellulose does not pass into solution but remains in the fibrous condition. If cellulose is preliminarily treated with sodium perborate in the presence of

1. Standard Telephones & Cables, Ltd., T. Scott and T. Riley, E. P. 339990; abst. C. A. 1931, **25**, 2787.

2. C. Staud and C. Webber, U. S. P. 1813685; abst. C. A. 1931, **25**, 5288; Plastics, 1932, **8**, #1, 43. Cites U. S. P. 1683347. E. P. 345235; abst. C. A. 1932, **26**, 303; J. S. C. I. 1931, **50**, 582-B; Silk J. and Rayon World, 1931, **8**, #87, 52. Refer to E. P. 29991, 1909.

3. A. Sulzer, U. S. P. 1833136; abst. C. A. 1932, **26**, 1120; Plastics, 1932, **8**, #3, 131. See also U. S. P. 1826335.

4. C. Staud and R. Van Dyke, U. S. P. 1836689; abst. C. A. 1932, **26**, 1119.

a small amount of boric, citric or tartaric acids[1], acetylation may then be conducted at lower temperatures and with less liability of degradation of the cellulose.

In the sizing of acetate filaments[2], casein 50-80, dextrinized flour 40-10 and corn sugar (glucose) 10 are dissolved in an ammoniacal liquor, together with a small proportion of a neutral, soluble oil and applied to the filaments at 60-70°. The W. Stelkens adhesive comprises cellulose acetate, a filler of low-viscosity nitrocellulose and a solvent (acetone, ethyl acetate, methyl glycol), which may be used in the form of a film[3]. J. Sterling has given methods for relustering acetate fabrics with special reference to crepeback satins[4], and shown how skillful dyeing and finishing may counteract defects in acetate textiles[5].

In order to increase the resistability of photographic emulsion layers[6], the film, after the photograph has been finished, is swollen by treatment with concentrated acetic acid containing ammonia, and a cellulose ester incorporated in the swollen film. The dry film shows increased resistance to wear. In forming threads or bands from cellulose ester solutions[7], the spinning liquid with oil admixed therein is first filtered and deaerated, then extruded into filament form. In producing formic acid by the interaction of equivalent parts of calcium formate and sulfuric acid[8], an improvement consists in introducing 0.6-1 part formic acid per part of calcium formate before distilling.

In the concentration of acetic acid[9], the dilute acid is

1. C. Staud and J. Fuess, U. S. P. 1844718.
2. Stein, Hall & Co., Inc., E. P. 359802; abst. J. S. C. I. 1932, **51**, 19-B.
3. E. P. 361317; abst. J. S. C. I. 1932, **51**, 121-B.
4. Textile World, 1931, **80**, 1202; abst. C. A. 1931, **25**, 5995; Chem. Zentr. 1931, II, 2948.
5. Textile World, 1932, **81**, 856.
6. J. Stock, U. S. P. 1801375; abst. J. S. C. I. 1931, **50**, 1155-B; Chem. Zentr. 1931, II, 371.
7. W. Stokes and Courtaulds, Ltd., U. S. P. 1823769; abst. C. A. 1932, **26**, 307. E. P. 290693; abst. Chem. Zentr. 1928, II, 1282.
8. D. Strauss and R. Uhsemann, U. S. P. 1848504.
9. H. Suida, U. S. P. 1795977; abst. C. A. 1931, **25**, 2440. Aust. P. 121251; abst. Chem. Zentr. 1931, I, 2673.

subjected to extraction with anthracene oil or quinoline as solvent, and the acid and extractant separated by distillation, or methyl, ethyl, butyl or dihexyl naphthenates or *o*-phthalates may be used for the same purpose[1]. J. Sussmuth[2] has explained various preferred sizing operations in the beam sizing of acetate yarns. In producing fine threads[3], acetylcellulose filaments are stretched 300-900% during or after passage through a bath containing a swelling agent which has but a slight solvent action on the ester (methylene chloride, chloroform, tetrachlorethane) in admixture with an organic liquid (carbon tetrachloride, trichlorethylene, benzene) which is neither a swelling agent nor a solvent for cellulose acetate and will repress the solvent action of the admixed swelling agent. The individual stretched filaments may be reduced to 0.5-2 denier, and give up to 100% increase in wet and dry strength. Methods have been published for the production of sodium, zinc, calcium and copper butylglyceryl phthalates and zinc *iso*amylglyceryl phthalate, useful for acetylcellulose plasticizing agents[4].

Cellulose acetate is readily dispersable in liquid ammonia[5], and sols containing 60 or more of the acetate in 100 of the medium have been obtained. Two types of gels, one heat-reversible and the other heat-irreversible, have been obtained. The gels form more rapidly and are firmer in structure at an optimum concentration of water, but in absence of water precipitation takes place. Acetaldehyde and acetic acid are formable in the usual manner[6], if a catalyst is used formed by mixing equivalent proportions of

1. H. Suida, U. S. P. 1796059; abst. C. A. 1931, **25**, 2440. F. P. 639112; abst. Chem. Zentr. 1928, II, 1150.
2. Rayon and Synthetic Yarn Journal, 1931, **12**, #1, 14.
3. H. Suter, E. P. 358512; abst. J. S. C. I. 1932, **51**, 17-B.
4. L. Swallen and W. Bannister, U. S. P. 1835915; abst. C. A. 1932, **26**, 994.
5. R. Taft and J. Stareck, J. Physical Chem. 1931, **35**, 578; abst. J. S. C. I. 1931, **50**, 562-A.
6. C. Tanner and Imperial Chemical Industries, Ltd., E. P. 344638; abst. C. A. 1931, **25**, 4559; J. S. C. I. 1931, **50**, 621-B; Chem. Zentr. 1931, II, 312.

solutions of ammonium molybdate and bismuth nitrate and adding ammonia, the bismuth molybdenum molybdate being dried and formed into pellets. H. Tatu has critically reviewed the methods for identification of various artificial filaments[1], with methods used for decreasing the luster[2]. The million dollar Tennessee Eastman Corporation acetylcellulose film and filament plant was described and illustrated in 1931[3].

The inflammability of nitro- and acetyl-cellulose solutions may be diminished by the addition thereto of carbon tetrachloride, which liberates acid on storage only with difficulty[4]. Celluloid-like masses are produced from acetylcellulose by combining the ester 75, with acetone 33, benzene 52 and ethyl alcohol 14, to which 25 parts of plasticizer may be added[5], coloring matters being incorporated if desired[6]. Formylcellulose fibers are formed by extrusion of a formic acid solutions of cellulose diformate[7], but because of the high boiling point of formic acid, the process should be carried out under a vacuum, the filaments being pure cellulose, stronger and more resistant to water than regenerated cellulose (Cellophane). No glycerol is required. Incorporation of casein increases both plasticity and fragility. Cellulose diformate is highly stable in dry air, but in ordinary air begins to decompose after some weeks, decomposition being retarded by immersion in water or other neutral liquid[8]. It is readily soluble in phosphoric acid, zinc chloride, formic acid, thiocyanates and pyridine.

1. Russa, 1931, **6**, 175; abst. C. A. 1931, **25**, 2571.
2. Russa, 1931, **6**, 11; abst. C. A. 1931, **25**, 5570.
3. Tennessee Eastman Corp., Manuf. Record, 1931, **100**, 23.
4. M. Thau, U. S. P. 1793726. Cites Swiss P. 66509. Griesheim Elektron, Chemical Review, 1906, 56.
5. M. Theumann, U. S. P. 1818108; abst. C. A. 1931, **25**, 5558. Cites U. S. P. 1015155.
6. M. Theumann, Chemicals, 1931, **35**, 30.
7. G. Tocco, Giorn. chim. ind. applicata, 1931, **13**, 414; abst. C. A. 1932, **26**, 1116; J. S. C. I. 1931, **50**, 1087-B.
8. G. Tocco and A. Nyssens, Giorn. chim. ind. applicata, 1931, **13**, 325; abst. C. A. 1932, **26**, 591; J. S. C. I. 1931, **50**, 876-B; Nitrocellulose, 1931, **2**, #10, 199. See p. 914, n. 2.

The amorphous films of acetylcellulose consist partly of truly amorphous material and partly of crystallites having no definite orientation[1], the greater the degree of esterification, the more complete is the orientation of the crystallites. In the manufacture of decalcomania paper, with a design thereon[2], in addition to the cellulose ester coating there is combined an ester gum, plasticizer (dibutyl phthalate), solvent(ethyl oxybutyrate) and pigments. In protecting cellulose acetate fibers from friction[3], they are lubricated to form a protective coating during the weaving and knitting operations, by the use of an inert mineral oil and "mahogany" sulfonates obtained by refining mineral oils with oleum, which are used as dispersing agents[4]. A. Ullrich[5] has reviewed the patents for acetaldehyde manufacture.

Organic cellulose esters may be dissolved or dispersed in liquid sulfur dioxide (see p. 566, n. 4; 620, n. 8; 669, n. 5; 877, n. 6; 915, n. 3), the liquid mass being then discharged into a precipitating medium so that the SO_2 is suddenly gasified, causing disruption of the precipitated ester to a light, fluffy product[6]. By the use of liquid SO_2, acetic anhydride may be obtained from sodium or calcium acetates, the solution of anhydride in SO_2 being readily filtered and fractionated[7]. In cellulose acetylation[8], the reaction temperature may be controlled by conducting the acylation in

1. J. Trillat, J. phys. radium, 1931, (7), **2**, 65; abst. C. A. 1931, **25**, 4701.
2. R. Tull, U. S. P. 1826228; abst. C. A. 1932, **26**, 569.
3. Twitchell Process Co., E. P. 349962; abst. Textil. Mfr., 1931, **57**, #683, 419; Chem. Zentr. 1931, II, 3689.
4. *Ibid.* E. P. 354326; abst. J. S. C. I. 1931, **50**, 922-B. Compare E. P. 127159.
5. Metallboerse, 1931, **21**, 315; abst. C. A. 1931, **25**, 1810.
6. U. S. Industrial Alcohol Co., E. P. 346430, Addn. to E. P. 306531; abst. J. S. C. I. 1931, **50**, 671-B; Silk J. and Rayon World, 1931, **8**, #88, 54. F. P. 686491; abst. Chem. Zentr. 1931, II, 2241. Can. P. 312218. E. P. 346824; abst. J. S. C. I. 1931, **50**, 626-B. F. P. 686492; abst. Chem. Zentr. 1931, II, 2241. Can. P. 312219. E. P. 356956; abst. J. S. C. I. 1931, **50**, 1135-B. Can. P. 307761.
7. *Ibid.* E. P. 353381; abst. J. S. C. I. 1931, **50**, 1085-B; Chem. Zentr. 1931, II, 2514. F. P. 713602; abst. C A. 1932, **26**, 1623.
8. *Ibid.* E. P. 355382; abst. J. S. C. I. 1931, **50**, 1005-B. F. P. 702446; abst. C. A. 1931, **25**, 4401; Chem. Zentr. 1931, II, 3417.

a closed vessel and incorporating liquid SO_2, the regulated volatilization of which is used to absorb heat. Thus, by using a closed reaction vessel fitted with reflux condenser cooled from a refrigerating plant and also a heating coil, it is possible by using a thermostat to maintain a constant reaction temperature, or to vary the temperature in any predetermined manner. Valette[1] has given an outline of the chemical and tinctorial properties of fibers which give trouble to dyers and cleaners, including acetate silk, acetylated wool, "immunized" cotton, "passive" cotton, and "amido" cotton.

Acetone-soluble cellulose acetonitrate is made by preheating cellulose in a bath containing acetic acid and a catalyst[2], and subsequently acetylating the preheated material with a mixture of acetic anhydride partially saturated with an oxide of nitrogen, catalyst and acetic acid. In an investigation of the action of acetic-sulfuric acid mixtures on cellulose and oxidized cellulose[3], it has been determined that the yield of oxidized cellulose is an inverse function of the severity of the oxidizing solutions employed, the more vigorously oxidized cellulose giving products with the smallest acetyl content. The results indicate that 1 OH group per $C_{24}H_{40}O_{20}$ in cellulose behaves differently from the other 11. A process for neutralizing precipitated acetylcellulose from the original acetylation mixture has been patented[4]. Acetic acid contained in aqueous or salt solutions may be concentrated by extraction with ethyl acetate[5], the operation being carried out by pulverization (or formation of fog) of

1. Tiba 1931, **99**, 141; abst. C. A. 1931, **25**, 2570.
2. R. Van Dyke, C. Webber and C. Staud, Can. P. 315902; abst. C. A. 1932, **26**, 1439.
3. R. Van Dyke, C. Staud and H. Gray, J. A. C. S. 1931, **53**, 2725; abst. C. A. 1931, **25**, 4398; J. S. C. I. 1931, **50**, 1041-A; I. E. C., Analyt. Ed., 1931, **3**, 269.
4. Verein fur Chemische Industrie, A.-G., D. R. P. Anm. V-59130; abst. Nitrocellulose, 1931, **2**, #10, 204. Verein fur Chemische Industrie, A.-G., and K. Werner, D. R. P. 535724; abst. C. A. 1932, **26**, 1119; Nitrocellulose, 1931, **2**, #10, 204.
5. Verein fur Chemische Industrie, A.-G., F. P. 710879; abst. C. A. 1932, **26**, 1622; Chem. Zentr. 1931, II, 3156.

one of the liquids in the other, after which the liquids are separated in the usual manner.

The luster of cellulose acetate may be diminished by dissolving in a volatile solvent as acetone[1], which is then spun into an atmosphere in which has been introduced a proportion of water admitted from the outside of the spinning cell, the proportion of water used determining the degree of delustering. The alleged novelty in cellulose acetylation of S. Vles and L. de Hoop[2] resides in allowing a mixture of acetic anhydride and glacial acetic acid to stand for several hours until the water in the acid has combined with the anhydride, adding catalyst and allowing to stand for several hours further, then proceeding with the acetylation in the usual manner. In reducing the denier of acetate filaments by a drawing operation[3], the ester before spinning is dissolved in a mixture of alcohol and an ethylene derivative which is non-miscible, and wet-spun. By boiling sodium ethylate and ethyl acetate[4] a 94% yield of ethyl acetoacetate is obtained, the alcohol formed during the reaction being removed during the reaction.

In the formation of metallized cellulose acetate plastics[5], a fused metallic spray of high melting point is directed against a suitable hard and firm cellulose ester until the desired thickness is obtained, then removing the built up article from the form. If it is desired to produce a non-conducting surface[6], a cellulose acetate surface is coated with a metallic salt as silver nitrate and a powdered metallic precipitate of the same metal, which is subjected to the action of a reducing agent as formaldehyde, and then dried. On account of the fact that 1.4-dioxan is a solvent

1. S. Vles, U. S. P. 1838121; abst. C. A. 1932, **26**, 1440.
2. U. S. P. 1794126; abst. C. A. 1931, **25**, 2288; Plastics, 1931, **7**, #5, 300. E. P. 263771; abst. Chem. Zentr. 1927, I, 2253.
3. A. Wacker Gesellschaft fur Elektrochemische Industrie, G. m. b. H., Can. P. 320447. Swed. P. 72604.
4. *Ibid.* D. R. P. 526691; abst. C. A. 1931, **25**, 4891. E. P. 311707; abst. Chem. Zentr. 1929, II, 1590.
5. J. Walsh, B. Andersen and Celluloid Corp., Can. P. 321218.
6. A. Warren and British Metallising Co., U. S. P. 1834812; abst. C. A. 1932, **26**, 1079.

both for cellulose triacetate (chloroform-soluble) and hydrolyzed acetate (acetone-soluble), it has been proposed as a solvent in the hydrolysis of primary acetylcellulose[1].

In the benzoylation of cellulose (pp. 495, 553, 621, 700, 868) a relatively lower temperature may be used, if the esterification is carried out in the presence of BB′-dichlordiethyl ester (see p. 801, n. 1)[2], in a bath containing benzoyl chloride and pyridine, the BB′-dichlordiethyl ether acting as a solvent for the cellulose benzoate at all ordinarily employed reaction temperatures. The ester is soluble in ethylene chloride, chloroform, ethylene chloride-alcohol, chloroform-alcohol and benzene-alcohol.

In the production of multiple esters of cellulose, especially those containing three different acid groups attached to the cellulose molecule (cellulose aceto-propio-butyrate being an example)[3], a practically unlimited range of solubility may be attained by selection of the substituent acid radicals. Mixed esters of cellulose may be esterified still further by organic acids by merely dissolving the cellulose mixed ester in a bath containing an organic acid, which has a higher activity than one of the acid groups in the cellulose, or by treating a single ester of cellulose in a bath containing one or more organic acids, all of which have an activity greater than the acid group which is combined with the cellulose. Di-esters result from substituting in cellulose acetate, such acids as tartaric, racemic, malic, glycollic, pyruvic, α-ketobutyric, α-ketovaleric, α-ketocaproic, levulinic, toluic, benzoic and mandelic, as each of these acids have an ionization constant greater than that of acetic acid. Methods for the formation of cellulose acetyl-pyruvyl-lactate, m. pt. 232-250°, soluble in acetone and methyl alcohol, have been described, as well as tri-ester of the above 12 acids with cellulose acetolactate, an example being cel-

1. C. Webber and C. Staud, U. S. P. 1826335; abst. C. A. 1932, **26**, 598. See also U. S. P. 1823359.
2. *Ibid.* U. S. P. 1831274; abst. C. A. 1932, **26**, 844.
3. *Ibid.* U. S. P. 1836695; abst. C. A. 1932, **26**, 1439. E. P. 360417; abst. J. S. C. I. 1932, **51**, 256-B. E. P. 360058. See p. 918, n. 1.

lulose acetolactyl-tartrate (acetotartryl-lactate, lactotartryl-acetate). Acetic acid may be dehydrated by treatment with sulfur dioxide and nitrogen dioxide until nitrosyl sulfuric acid is formed[1].

In making variegated rods from artificial horn[2], irregular-surfaced layers of the material of varying colors and shapes are charged into a mold, and the interstitial spaces filled with a liquid or pasty cellulose acetate binder, the solvent removed and the article removed from the cast. It has been found that a mixture of sodium boroformate and salicylic acid liberates formic acid gradually when moistened[3]. A non-curling photographic support has been described[4] comprising a support of cellulose acetate and an intermediate backing of the same ester of low precipitation value in conjunction with a color backing.

It has been shown that the delustering of acetate silk may take place without saponification[5], skeins boiled-off in de-aerated distilled water under reduced pressure at various temperatures deluster as much as when air is present, from which it is contended that delustering takes place only in swollen fiber. Treatment in the cold with weak phenol solutions induces a different type of delustering—a sort of surface emulsification.

In a patented method of precipitation of cellulose acetate solutions[6], separate streams of the former and of the precipitating liquid, either of which may contain a bleaching agent, flow into each other through a centrifugal pump placed at their point of union, by which they are conveyed onwards in very intimate admixture. W. Werring[7] has made a survey of the uses of acetylcellulose plastics in the

1. C. Webber and C. Staud, Can. P. 321229.
2. E. Weber, D. R. P. 538065; abst. C. A. 1932, **26**, 1732.
3. H. Weitz, E. P. 360299; abst. J. S. C. I. 1932, **51**, 221-B.
4. J. Wells, Can. P. 315907.
5. W. Weltzien and A. Brunner, Seide, 1931, **36**, 399; abst. C. A. 1932, **26**, 1448.
6. K. Werner, E. P. 338214; abst. C. A. 1931, **25**, 2288; J. S. C. I. 1931, **50**, 108-B.
7. Bell. Lab. Record, 1931, **9**, 470.

telephone industry, and N. White[1] formulas for dyeing and cross-dyeing of acetate silks. Dyes may be readily extracted from cellulose acetate[2] by treatment with a solution of benzene containing 2% acetone, which is a swelling agent for the ester and a solvent of the dyes.

In the lubrication of acetate yarns and other cellulose acetate textiles[3], high-boiling polyhydric alcohols are recommended as glycerol (b. pt. 290°), ethylene glycol (197.5°), diethylene glycol (250°), and propylene glycol, or their mono- or di-ethers. When ethyl alcohol, steam and air are passed over copper at 220-240°, silver at 450-500°, or silver vanadate or copper nitrate at 360-400°, acetaldehyde in nearly theoretical amount is produced[4]. Formic acid may be concentrated by adding formamide to the solution[5], and decomposing with sulfuric or hydrochloric acids, the formic acid being then separated from the resulting ammonium salt of the inorganic acid by filtration and distillation.

Directions have been given for the preparation of lantern slides using acetylcellulose film[6], and for the production of filaments, films and foils from aqueous cellulose ester solutions[7]. In the latter, the precipitating bath comprises sulfuric acid and methyl alcohol, together with sufficient water to form a polyhydrate of methyl alcohol. The loss in weight at 80° of a known acetylcellulose plasticizer and "Hydropalat CY," alone and when incorporated into cellulose acetate films has been observed[8], it being demon-

1. Cotton, 1931, **95**, 385; abst. C. A. 1931, **25**, 3840.
2. W. Whitehead, U. S. P. 1839819; abst. C. A. 1932, **26**, 1454.
3. *Ibid.* U. S. P. 1852891.
4. K. Wiesler, A. Peake and British Industrial Solvents, Ltd., E. P. 353071; abst. J. S. C. I. 1931, **50**, 1085-B; Chem. Zentr. 1931, II, 2932.
5. R. Wietzel and M. Herbst, U. S. P. 1843434; abst. C. A. 1932, **26**, 1622. D. R. P. 542254.
6. J. Wilson, Jour. Chem. Education, 1931, **8**, 2212.
7. Wolff & Co. Komm. Ges. auf Akt. and R. Weingand, E. P. 360688; abst. J. S. C. I. 1932, **51**, 141-B.
8. H. Wolff and I. Rabinowicz, Farben-Ztg. 1932, **37**, 585; abst. J. S. C. I. 1932, **51**, 271-B.

strated that the behavior of a plasticizer in a lacquer film should not be drawn from observations on the plasticizer alone. Recent methods of cellulose acetate manufacture have been classified by V. Yarsley[1], while W. Young[2] has outlined the procedure to be followed in dyeing acetylcellulose yarn, with particular reference to the preparation and handling of the skeins.

The properties and methods of preparation of *b*-glucosan triacetate, *a*-1-chlor(or brom)-2.3.4-triacetyl-*d*-glucose, 1-chloracetylgentiobiose, acetobromcellobiose, 1-chlor(or brom)-6.*b*-cellobiosidoglucose deca-acetate[3] were published in 1931. The A. Zetter lacquer[4] suitable for forming capsules on stoppered bottles, is prepared by dipping, a viscous cellulose acetate solution being employed, and treated with a fatty oil until coagulation begins, then diluted with solvent until the precipitate just dissolves. Products such as films adapted to pass ultra-violet rays in the region biologically most beneficial[5], are formed by evaporating a thin solution of acetylcellulose and a plasticizer as diethyl phthalate. The material has sufficient resistance to the weather to serve as a commercially satisfactory substitute for glass (see p. 389, n. 4; 741, n. 5).

In the application of acetylcellulose to the field of plastics[6], and the manufacture of acetate threads and fabrics of acetate silk[7], the latter are steeped in cold or warm (40-50°) aqueous solutions containing 15-35% formaldehyde and 10-30% methyl, ethyl or butyl alcohol capable of forming an

1. British Plastics and Molded Products, 1932, **3**, #32, 344.
2. Textile World, 1931, **79**, 1312; abst. C. A. 1931, **25**, 4711.
3. G. Zemplen, A. Gerecs and J. Erdelyi, Ber., 1931, **64-B**, 1545; abst. J. S. C. I. 1931, **50**, 1039-A.
4. A. Zetter, D. R. P. 526467; abst. C. A. 1931, **23**, 4420; Chem. Zentr. 1931, II, 1065.
5. A. Zimmerli, U. S. P. 1842640; abst. C. A. 1932, **26**, 1781. Cites Journal of Amer. Medical Assoc. 1927, **88**, #4, 245. U. S. P. 1613073.
6. R. Ball and B. Andersen, J. S. C. I. 1932, **51**, 371-C. & I.
7. K. Beck, E. P. 361200; abst. J. S. C. I. 1932, **51**, 226-B. F. P. 710299; abst. C. A. 1932, **26**, 1136. See F. Bayer & Co., Ital. P. 167228.

acetal-like compound with the formaldehyde, then washed and dried, whereby they become softer, more lustrous and more voluminous, although shrinking occurs. Dyes suitable for coloring cellulose acetate are formed by dissolving 50 parts 1-phthalimidoanthraquinone in 500 of 97% sulfuric acid, maintaining the temperature of about 10°, adding 100 each of 80% nitric acid and 97% sulfuric acid, maintaining the temperature at 15-20° for 1-2 hrs., and pouring the melt into water and washing it[1].

In the dyeing of acetylcellulose[2], a hydrogenated carbocyclic base having a benzene or naphthalene nucleus as hexahydro-aniline, -methylaniline, -ethylaniline, -toluidines, -xylidines, -naphthalenediamines, is added to 1-amino-4-hexahydroanilidoanthraquinone, Orange II, Benzo brown G, Rhodulin orange NO and similar dyes, the addition of the base facilitating penetration of the dyestuff. A method suggested for the maximum recovery of acetylation components[3] comprises treating the acetylated mass after ripening to the desired degree, first with solid sodium acetate to neutralize the catalyst (H_2SO_4), then distilling under high vacuum at 70° while maintained in agitation in order to remove and recover acetic acid. The hot distillation residue is then treated with sufficient water to nearly initiate precipitation, then cooled and precipitation completed by means of water or dilute acetic acid. E. Bleibler[4] has described a process for obtaining films of acetylcellulose of high extensibility, and L. Blumer[5] a lacquer composed of cellulose acetate mixed with a phenol-aldehyde condensation product of the novolak type, a mixture of acetone and ethyl alcohol being the solvent medium employed, which is harmonious to both the resin and the ester.

1. E. Beckett and J. Thomas, U. S. P. 1838523; abst. C. A. 1932, **26**, 1452.
2. H. Berthold and P. Rabe, U. S. P. 1855278. Cites D. R. P. 81963.
3. H. Bleasdale and Apex (British) Artificial Silk, Ltd., E. P. 365710; abst. J. S. C. I. 1932, **51**, 335-B.
4. Belg. P. 379818.
5. D. R. P. 536372; abst. C. A. 1932, **26**, 1142.

Acetic anhydride, acetic acid and water may be separated[1] by cooling the mixture to —20° to —40° whereby solid acetic acid and water are removed, leaving acetic anhydride and acetic acid of concentration suitable for cellulose acetylation. A non-aqueous solvent of low freezing point as toluene may be present[2], and may be separated from the acetic anhydride by distillation. A cellulose acetate especially suitable for filament formation[3] is obtained by acetylating cellulose at 20-25° using as catalyst a halogen, halogen halide, or halogenated fatty acid, sufficient acetic acid being added to partially at least, retain the original fibrous structure of the cellulose acetylated. The resulting primary cellulose triacetate is dissolved by chloroform-ethyl alcohol or methylene chloride-ethyl alcohol mixtures and spun into filaments in the usual manner.

Materials containing non-lignified cellulose as peat, young reeds or green straw[4] have the water content raised to about 100% by the addition of water, and are then treated in different steps by means of alkali, the liquid being separated by centrifugalization after each alkali treatment. The products obtained are acetylated and said to produce a satisfactory grade of filament. K. Bratring[5] has compared the mechanical properties of acetylcellulose photographic support for resistance to wear and damage, which is considered by him as inferior to nitrocellulose for motion picture purposes.

In the concentration of acetic acid in an acetylation reaction mixture[6], the latter is atomized into a chamber containing heated air at a temperature not exceeding 80°,

1. C. Boehringer & Soehne, G. m. b. H., E. P. 358831; abst. J. S. C. I. 1932, **51**, 172-B.
2. *Ibid.* E. P. 360330; abst. J. S. C. I. 1932, **51**, 221-B. F. P. 709150; abst. C. A. 1932, **26**, 999.
3. *Ibid.* E. P. 363700; abst. J. S. C. I. 1932, **51**, 256-B. F. P. 713576; abst. C. A. 1932, **26**, 1783.
4. A. Bosse, A. Seidel and H. Sedlacek, F. P. 712856; abst. C. A. 1932, **26**, 1783. See H. Bohme, A. G., Belg. P. 380154, 380155.
5. Kinotechnik, 1931, **13**, 237.
6. K. Bratring and E. Roth-Schmidt, E. P. 349016; abst. C. A. 1932, **26**, 2053.

the cellulose acetate being deposited in flakes and may be recovered by filtration from the air current, the acetic acid being obtained by condensation. An insulating material has been described[1], comprising a strip with a plurality of terminals held in spaced relation with a front portion of cellulose acetate.

J. Calladine[2] has published methods and formulas for printing bright fast shades on cotton-acetylcellulose fabrics with indigosol colors (except indigosol R, OR, yellow indigosol HCG, violet indigosol AZB and green indigosol IB) without steaming, little or no caustic alkali being used; and H. Calmels[3] a description of the properties of the raw materials and of the production of lacquers from cellulose derivatives on a small manufacturing scale. Acetic acid may be concentrated by means of solvent extraction with *iso*propyl ether[4].

Intermediate material for plastic formation has been patented[5], comprising mixing cellulose esters or ethers, as cellulose acetate, with a limited amount of solvent, passing the doughy mass formed through a restricted heated area which intumesces the mass and permits of rapid dissemination of volatile solvent, the mass on cooling being in a puffed up and friable condition. J. Walsh[6] has described a composition of low inflammability comprising acetylcellulose 100, aromatic phosphate and tartaric acid ester, each 12-17. Or[7], a mixed solvent of triphenyl phosphate 10-15 and diethyl phthalate 10-15 may be used. E. Charles[8] has reported upon the technical analysis of glacial acetic acid; while a stable preparation evolving formic acid slowly on

1. R. Burns, Can. P. 321492.
2. Russa, 1931, **6**, 1543; abst. C. A. 1932, **26**, 1791.
3. Rev. gen. mat. plastiques, 1931, **7**, 579; abst. C. A. 1932, **26**, 1807.
4. Carbide & Carbon Chemicals Corp., Belg. P. 381412.
5. Celanese Corp. and A. Eichengrun, Can. P. 305428.
6. Celluloid Corp. and J. Walsh, Can. P. 315656.
7. Celluloid Corp., J. Walsh and K. Flynn, Can. P. 314577.
8. Ann. chim. anal. chim. appl. 1932, **14**, 5; abst. C. A. 1932, **26**, 1215.

moistening a boroformate or borosalicylate[1] has been described.

A series of double cellulose esters has been patented (see p. 139, n. 6; 621, n. 9; 622, n. 1; 758, n. 3; 906, n. 3; 942, n. 3), containing small amounts of unsaturated acyl groups, prepared by heating cellulose in a bath containing the unsaturated acid and a solvent which lowers the boiling point of the mixture below the temperature at which harmful degradation of the cellulose occurs. Details have been given for the production of cellulose crotonates and acetocrotonates, and of mixed cellulose esters as crotono-stearate (stearocrotonate) or acetic acid with propionic, *n*-butyric, *iso*-butyric, *n*-valeric, *iso*-valeric, *n*-caproic, *n*-heptylic, caprylic, pelargonic, capric, lauric, myristic, palmitic, stearic, crotonic, cinnamic, cyclohexane-carboxylic, benzoic, *o*-methoxybenzoic, *o*-chlorbenzoic, acetylsalicylic, phenylacetic and hydrocinnamic acids[2]. Cellulose acetohydrocinnamate would be an example.

In a process of color photography in which images in relief are formed by hardening to a variable degree, by the action of light or by a chemical reaction, on layers of colloidal substances, there is used as support for the image in relief a sheet of regenerated cellulose superficially covered with cellulose acetate[3]. An investigation on the partial alkaline hydrolysis of acetyl silk as a pretreatment for dyeing has been made[4], and it was found that treatment of the acetylcellulose fibers in dilute NaOH and sodium acetate at 60° and 70° under standard conditions, attained maximum effects that depended primarily on the alkali concentration.

1. Chemische Fabrik Apotheker Weitz, G. m. b. H., F. P. 710451; abst. C. A. 1932, **26**, 1622. D. R. P. 538856; abst. C. A. 1932, **26**, 2279.

2. H. Clarke and C. Malm, U. S. P. 1739210; abst. C. A. 1930, **24**, 962; J. S. C. I. 1930, **49**, 943-B; Brit. Plastics, 1930, **2**, #18, 278.

3. Colour Photographs (British & Foreign), Ltd., F. P. 708638; abst. C. A. 1932, **26**, 931.

4. W. Coltof, H. Waterman and I. Wolf, Z. angew. Chem. 1931, **44**, 163; abst. C. A. 1932, **26**, 1446. See p. 944, n. 4.

Methods for the production of acid anhydrides from vinyl esters and carboxylic acids have been patented[1].

In the production of mixed cellulose esters derived both from nitric acid and a fatty acid[2], nitrocellulose containing NO_2 groups equivalent to at least cellulose dinitrate (10.5-12.5% N) is treated with a fatty acid preferably containing 2-5% water, and a reagent capable of converting fatty acids into acid chlorides, i.e., sulfuryl chloride. If 100 of nitrocellulose (11.1% N) are dissolved in 400 of acetic acid containing 2.5% water and treated with 200 of sulfuryl chloride, the temperature being raised to 50-60° and maintained until evolution of gas ceases, there results a cellulose mononitroacetate (5.2% N, 41% combined acetic acid), which is precipitated in white flocks. The cellulose suffers little degradation owing to low solubility of HCl in glacial acetic acid. In preparing concentrated acetic acid by esterifying and saponifying a dilute solution of the acid[3], the vaporized intermediate product containing the ester, especially ethyl acetate, when heated to 500-700° in the presence of silver or copper catalyzers, causes splitting into acetic acid and unsaturated hydrocarbons as ethylene.

Loss of strength in acetate silk by wetting is diminished by treating with an acid chloride (phosphorous oxychloride, phosphorous trichloride, benzoyl chloride, stearyl chloride) in the presence of an organic base (pyridine, quinoline)[4]. The recommended compound solvent for acetylcellulose by H. Dreyfus[5] comprises acetone, diacetone alcohol and diethylene glycol. In order to augment the clearness of cellulose acetate solutions, especially when used for films in non-shatterable glass manufacture, it is recom-

1. H. Deutsch, W. Herrmann and Consortium fur Elektrochem. Ind., G. m. b. H., D. R. P. 537363; abst. C. A. 1932, **26**, 999. See D. R. P. 503131, 526795.
2. Deutsche Celluloid-Fabr., E. P. 360311; abst. J. S. C. I. 1932, **51**, 224-B. F. P. 710004; abst. C. A. 1932, **26**, 1438.
3. Deutsche Gold- und Silber-Scheideanstalt vormals Roessler, D. R. P. 539867; Addn. to D. R. P. 459604; abst. C. A. 1932, **26**, 2201.
4. Deutsche Kunstseiden-Studienges, G. m. b. H., D. R. P. 541097; abst. C. A. 1932, **26**, 2067.
5. C. Dreyfus, Belg. P. 361494. See Belg. P. 361636, 362600.

mended to submit the ester to repeated extraction with a liquid which dissolves the lower acetylated celluloses, iodoform, dichlorethane, or other chlorinated hydrocarbons being particularly applicable (p. 953, n. 5)[1].

In producing acetylcellulose molded articles[2], it is advised to heat the cellulose ester with *p*-toluenesulfonamide, *p*-toluenesulfonimide, diethyl phthalate and rosin accompanied by pressure, in the formation of such plastics as phonograph records. C. Avery and H. Kress[3] have described the details of a plant designed and developed for coating textile insulated wire with a film of cellulose acetate, the wire being treated at a speed of 240 feet per minute. Acetone is the solvent used, an 85% recovery being obtained with carbon absorbers.

Artificial bristles and straw of subdued luster are produced by the union of a plurality of acetylcellulose filaments by means of a mixture of acetone and xylene in such proportions that the mixture is a solvent for the cellulose acetate, but upon evaporation of some of the acetone, the higher boiling xylene predominates, resulting in a non-solvent combination, and inducing incipient gelatinization[4].

Alkoxyaliphatic acids, especially methoxyacetic acid[5], are converted into anhydrides by passing the vapors with or without diluent gases, preferably with carbon oxides, through a copper, silica or fire-clay tube at 500-800°, which may contain a dehydrating catalyst as carrier. Water is absorbed from the resulting mixture by passing over cal-

1. C. Dreyfus, F. P. Addn. 39061 to F. P. 689134; abst. C. A. 1932, **26**, 1781. Can. P. 309984.

2. C. Dreyfus, W. Cameron and G. Schneider, U. S. P. 1843214; abst. C. A. 1932, **26**, 1731. See Ital. P. 263103, 263590.

3. Chem. & Met. 1932, **39**, 273.

4. C. Dreyfus and W. Whitehead, Can. P. 318759; abst. C. A. 1932, **26**, 2053. See R. Payne and R. Roberts, Can. P. 303277, 303278. C. Cross and C. Dreyfus, Ital. P. 159935. H. Dreyfus, Belg. P. 286147, 356349, Addn. to 354320. H. Dreyfus, Belg. P. 357096, 361055, 361056, 361057. Can. P. 282961. Compare also Can. P. 293049, 293733, 301344, 321172, 321527, 321528, 321529, 321534, 321536. E. P. 256664.

5. H. Dreyfus, E. P. 317342; abst. C. A. 1930, **24**, 2144; J. S. C. I. 1929, **48**, 888-B; Chem. Zentr. 1929, II, 2936. F. P. 672149.

cium chloride at 250-800°. Aliphatic acids or their esters may be prepared by the reaction of alkyl ethers with CO in presence of non-acid catalysts capable of favoring the synthesis of aliphatic acids from the corresponding alcohols. Copper, tin, zinc or lead oxides; copper or zinc acetals; copper, aluminum or tin methylates may be used as catalysts, the reaction being carried out in the presence of steam. Thus, acetic acid is prepared from methyl ether and CO, preferably at 200-300° and under pressures of 50-300 kgm[1].

It is recommended to spin acetylcellulose solutions into an evaporative medium which is evacuated by aspiration in such a manner that the whole or a definite part of the medium is caused to pass through the immediate neighborhood of the spinning nozzles[2]. In making acetylated celluloses (see p. 773, n. 1; 866, n. 8), a part at least of the esterification is carried out in the presence of an iron catalyst containing a greater amount of ferric radical than that equivalent to the acid radical present[3]. Thus, the catalyst may contain ferric chloride and ferric oxide or hydroxide.

Carboxylic acid esters (acetylcellulose) are prepared by treating cellulose while avoiding disaggregation[4], with HCl, HBr or HI in amount less than 2% of the weight of the cellulose, and then esterifying in the usual manner. The cellulose may also be treated simultaneously or separately with acetic acid and/or iron, tin, nickel, manganese or copper chlorides, bromides or iodides. Or[5], the cellulose may be treated with acetic anhydride and the product then hydrolyzed as with steam. Aliphatic acids, particularly acetic acid[6], are extracted from their aqueous solutions by means of a phenol ether (*a*-naphtholmethyl ether, phenetol, ani-

1. H. Dreyfus, F. P. Addn. 38770, 38900 to F. P. 637763; abst. C. A. 1932, **26**, 1622. Ital. P. 265691, 266431, 268755.
2. *Ibid.* F. P. Addn. 39394 to 654062; abst. C. A. 1932, **26**, 2318. See also F. P. 713184, 713847; abst. C. A. 1932, **26**, 1785.
3. *Ibid.* F. Addn. 39344 to 660623; abst. C. A. 1932, **26**, 2317.
4. H. Dreyfus, F. P. Addn. 39019 to 666896; abst. C. A. 1932, **26**, 303, 1781. (See p. 773, n. 1; 866, n. 8.)
5. H. Dreyfus, F. P. 710640; abst. C. A. 1932, **26**, 1781.
6. *Ibid.* F. P. 711295; abst. C. A. 1931, **25**, 3360; 1932, **26**, 1622.

sole, *b*-naphtholethyl ether, or *o*-, *m*- or *p*-tolyl ether). In the partial saponification of acetylcellulose filaments, threads and ribbons, in order to obtain differential dyeing effects thereon[1], they are saponified by distributing the alkali reagent on the material in movement and drying immediately afterwards by heat.

Aliphatic ketones are prepared by submitting acetylene, aliphatic alcohols or their derivatives (aldehydes or esters) to a reaction with steam in the presence of a catalyst[2], the latter being prepared by heating a mixture of one or more alkaline earth oxides with silica, so as to form a product having hydraulic properties, afterwards treating with water to cause it to set and transform to a *cement*. Acetic acid or methyl acetate results by the action of CO on methyl alcohol in the presence of a catalyst composed of one or more phosphoric acids or acid phosphates[3], the degree of hydration of the acids being maintained throughout the reaction. Or[4], acetic acid to be concentrated may be reduced to acetaldehyde, which may then be transformed into glacial acetic acid.

A. Drinberg[5] has reported that the specific degree of solvation of cellulose acetate sols decreases with increase in

1. H. Dreyfus, F. P. 713184; abst. C. A. 1932, **26**, 1784.

2. *Ibid.* F. P. 713845; abst. C. A. 1932, **26**, 1616. Can. P. 321724.

3. *Ibid.* F. P. 713342, 714767; abst. C. A. 1932, **26**, 1622, 1623. F. P. 715549; abst. C. A. 1932, **26**, 1946. See also F. P. 714062; abst. C. A. 1932, **26**, 1623. F. P. 716448, 722851; abst. C. A. 1932, **26**, 2201. Ital. P. 228903, 263350, 263381, 263777, 265296. Swiss P. 95042; abst. C. Zent., 1922, IV, 1062. Belg. P. 286147.

4. H. Dreyfus, U. S. P. 1851664.

5. J. Appl. Chem. Russ. 1931, **4**, 87; abst. J. S. C. I. 1932, **51**, 225-A. It was found that the relative length of mol. chains decreases with increase in depolymerization, while increase in mol. volume of peptizing agents increases the viscosity and degree of solvation. Sols having ethyl alcohol have smaller viscosity and degree of solvation the higher the ethyl alcohol concentration and the molecular weight of peptizing agents. Increase in molecular weight of acid radicals of esters used as peptizing agents increases the viscosity of sols. The viscosity and degree of solvation with a homologous series of peptizing agents increase with the molecular polarization, dipole moment and ethyl alcohol coagulation value. Higher temperatures

concentration, the total volume of the hydrated phase increasing inversely with increase in depolymerization. It appears that cellulose acetate in acetone or cellulose triacetate in tetrachlorethane-ethyl alcohol have no measurable permanent rigidity, although the viscosity of some of these solutions is 10^7 times that of water[1]. For example, the time of relaxation of cellulose nitrate in nitrobenzene is 170 seconds. A process for the manufacture of acetic and butyric acids from marine algae has been patented[2].

An interesting 3-sheet bulletin on Du Pont cellulose acetate of low and medium viscosity has been published, setting forth the physical constants, chemical properties and methods of testing of this ester, made in the United States under patents of the Societe Chimique des Usines du Rhone[3]. As a hydrolyzing agent for primary cellulose acetate[4], ethylene chloride in conjunction with a mineral acid catalyst and water has been proposed, the ester being applicable for the production of an adhesive tape comprising a support with an adhesive coated on one side, and a cellulose acetate composition disposed on the other[5]. Acetic anhydride is producible in nearly theoretical quantity[6] when mixtures of acetic acid and ketones are caused to react at elevated temperature in the presence of catalytically acting bodies.

In the coloring of cellulose acetate[7], hydrocyanaphthoic arylide dyes are used in which the arylide is applied before

decrease viscosity and degree of polymerization of sols with the same peptizing agent, and of sols for which the ratio of the coagulating agent to peptizing agent is less than the peptizing volume, when this ratio lies between the peptizing and coagulating values, coagulation takes place as the temperature is raised.

1. J. Duclaux and F. Hirata, J. Chim. Phys. 1931, **28**, 537; abst. J. S. C. I. 1932, **51**, 122-A.
2. L. Dupont, U. S. P. 1371611.
3. E. I. DuPont de Nemours & Co., Bull. #653, Apr. 28, 1930. See H. Dreyfus, F. P. 723016. Ital. P. 162996, 163599, 212623.
4. H. Gray, C. Staud and C. Webber, U. S. P. 1857190. Can. P. 322076.
5. E. Dow, Can. P. 322078.
6. H. Elkington, New Zeal. P. 65392.
7. G. Ellis, H. Olpin and E. Walker, U. S. P. 1844350; abst. C. A. 1932, **26**, 2065.

diazotization takes place, in the free state in the form of a dispersion. The volatile aliphatic acid concentration process of A. Gorhan[1] involves treatment of the dilute acid with salts capable of forming with the acids to be concentrated, double salts which can be separated in solid form, using, for instance, potassium acetate. If it is desired to produce acetaldehyde from acetylene[2], as in the process patented by A. Guyot, acetylene and mercury sulfate are submitted in a continuous manner, to the action of a vacuum, the hydration to acetaldehyde being continuous, and the latter being eliminated from the system as formed. The dissociation constant of acetic acid from 0° to 35° has been determined[3].

R. Herzog and A. Deripasko[4] have fractionally precipitated solutions of cellulose acetate (51.9% acetic content) in acetone, with increasing quantities of water or petroleum ether, and determined the viscosity of the fractions obtained. There is no change in acetic acid content of the fractions, although ash accumulates in the first fraction. Molecular weight determinations yielded values for different fractions between 22,500 and 74,000, the initial acetylcellulose value being 45,000-50,000. The National Nacelan group of dyestuffs for acetate silk has been reported upon[5], formulas being submitted for dyeing Nut beige, Radiance red, Mosque purple, Castalan, Rhum, Malaga red, Cannes blue, Burnt coffee, Arbor green, Martinique brown, Guardsman blue and Shadomist.

Acetaldehyde results when one molecular proportion of acetylene and 6 of water vapor is led at 300° over a catalyst

1. U. S. P. 1858150, 1858151. In this connection, see Feldmuhle, Papier und Zellstoffewerke, Ital. P. 269226, 269227. Firminy Societe Anonyme des Acieries & Forges, Ital. P. 171810, 171811, 171812. Foltran, Ital. P. 266346, 266443.

2. U. S. P. 1343715, F. P. 425057, 475183. D. R. P. 171900. See Guillumette, Belg. P. 380373. Gutehoffnungshutte Oberhausen, Belg. 381676.

3. H. Harned and R. Ehlers, J. A. C. S. 1932, **54**, 1357. See W. Herrmann and H. Deutsch, U. S. P. 1856251.

4. Cellulosechem. 1932, **13**, 25; abst. C. A. 1932, **26**, 2313; J. S. C. I. 1932, **51**, 223-B.

5. W. Holst, Jr., Rayon & Syn. Yarn J. 1932, **13**, #2, 35; #3, 16.

prepared by impregnating pieces of clay with silico-tungstic acid, at a speed of about 250 liters per hour per liter of reaction space. By a single passage over this catalyst 20-30% of the acetylene is converted into acetaldehyde[1].

As a preferred application to metal and other surfaces[2], especially useful for airplane coatings, 3 parts acetylcellulose to 2 parts nitrocellulose with tolyl phosphate as plasticizer has been advocated. If it is leather that it is desired to coat[3], a composition comprising cellulose ester (nitrate or acetate), a wax and suitable volatile solvents with ethyl alcohol as diluent, is worked into the leather until the effect desired has been obtained.

A cellulose ester useful as a molding composition is claimed to result when wood is treated with dimethylaniline and benzoyl chloride, which are warmed together and allowed to stand for an hour. The base is then removed, and the product dried, heated and pressed into molds[4]. A photographic film has been described[5] consisting wholly or in part of sensitized acetylcellulose, an image then produced thereon by changes in the physical or chemical properties of the ester, as swelling power, solubility or coloring capacity. The support may comprise a layer of cellulose acetate and one of nitrocellulose[6], or a rubber layer may be incorporated between them.

In working up crude cellulose ester solutions[7], after neutralizing the catalyst, water is stirred in and the volatile solvents distilled off in azeotropic mixture with water, the

1. Horst-Dietrich v. d. Horst & R. Wietzel, U. S. P. 1856639. See H. Specht, D. R. P. 535355; abst. C. A. 1932, **26**, 2281. Holzverkohlungs-Ind. A. G., E. P. 347695; abst. C. A. 1932, **26**, 1624. Holzverkohlungs-Ind. A. G., E. P. 359430; abst. J. S. C. I. 1932, **51**, 172-B. G. Horsley, Can. P. 320359.
2. Imperial Chem. Ind., Ltd., E. P. 353589; abst. Brit. Plast. 1932, **3**, 102.
3. *Ibid.* E. P. 365338; abst. J. S. C. I. 1932, **51**, 274-B. See Belg. P. 358066, 358067, 362860. Can. P. 321241. Belg. P. 364702, 379824, 379898, 380481. Ital. P. 266370.
4. I. G. Farbenind. A.-G., E. P. 326502.
5. *Ibid.* E. P. 354274.
6. *Ibid.* E. P. 357817.
7. *Ibid.* E. P. 358979; abst. J. S. C. I. 1932, **51**, 225-B.

quantity of water added being such that the residue after distillation, consists of a solution of the cellulose ester in 40-70% aqueous acetic acid, from which the ester is then recovered in the usual manner by precipitation with water. Or[1], the crude esterification solution may be treated with sodium acetate to neutralize the acid catalyst, and heated to 60-100° until a stable product is obtained, sufficient water being added before heating so that the solubility properties of the cellulose ester remain unaltered. If it is desired to eliminate the use of acetic anhydride or acetyl chloride in the esterification of cellulose[2], the latter is treated with liquid sulfur dioxide in the presence of free fatty acid only. If it is desired to produce mixed esters as cellulose acetonitrate, metallic nitrates are introduced into the acetylating bath during the course of esterification[3]. Formic acid is prepared by the action of sulfuric acid on calcium formate to which one or more sodium salts as sodium sulfate has been added[4].

Envelopes which are impermeable to gases may be prepared by building up a plurality of coats of cellulose acetate, between which are sandwiched an albuminous substance of high degree of polymerization[5], softening agents and fillers being added. L. Rosenthal has described the manufacture of lacquers utilizing cellulose acetopropionate[6], and F. Jaehn[7] combinations of tar oils as "carbolineum" mixed with cellulose esters and a solution of natural or synthetic resin for the impregnation of wood and the painting of metal surfaces.

Low viscosity cellulose acetate may be prepared by pre-

1. I. G. Farbenind. A.-G., E. P. 362489; abst. J. S. C. I. 1932, **51**, 224-B.
2. *Ibid.* F. P. Addn. 34916, 38819 to 664459; abst. C. A. 1932, **26**, 1781, 2317. Ital. P. 262605. Norw. P. 47185.
3. *Ibid.* F. P. Addn. 39276 to 681143; abst. C. A. 1932, **26**, 2317. Ital. P. 262738. See p. 783.
4. *Ibid.* F. P. 710822; abst. C. A. 1932, **26**, 1622.
5. *Ibid.* F. P. 715130; abst. C. A. 1932, **26**, 1783. See P. Baumann and R. Stadler, D. R. P. 542225; abst. C. A. 1932, **26**, 2201.
6. D. R. P. 541167; abst. C. A. 1932, **26**, 2071.
7. D. R. P. 536429; abst. C. A. 1932, **26**, 1092. Jardin, Ital. P. 267547.

treating cellulose with acetic acid and a catalyst containing phosphoric acid at 38° for about 4 hrs.[1], adding 85% acetic anhydride and conducting the acetylation at 49-65.5°, —the higher the temperature the lower the viscosity of the ester formed. In the preparation of photographic films[2], the acetylcellulose base is coated on the back with cellulose acetate of lower "precipitation value" before the anti-halation backing is applied. The precipitation value is derived from a prescribed determination of the percentage of acetate precipitated from 5% acetone solution, when an acetone-water mixture is added to produce a total of 40% water. The presence of this intermediate layer facilitates the bleaching or washing out of the color backing during the subsequent processing. A protective layer of cellulose acetate and resins may be applied[3].

In the hydrolysis of acetylated cellulose, one method is to hydrate at a temperature below 45° until a test portion withdrawn gives the lowering of viscosity desired[4]. If cellulose acetate silk is steeped at 20° for 5-45 minutes in an aqueous solution of calcium thiocyanate (sp. gr. 1.115-1.21) and then washed, partial delustering takes place, and there is simultaneously acquired 50-80% increased affinity for dyes, 5-10% increase in tensile strength, and 20-30% increased extensibility[5]. It is alleged that treatment of dried acetylcellulose with ozone gas considerably lowers the viscosity in the same solvent in the same proportions, accompanied by well marked bleaching[6]. Nitrated cellulose and cellulose ethers are likewise similarly affected. The kinetics of esterification of acetic anhydride in ethyl alcohol solu-

1. C. Malm and A. Andersen, E. P. 364749; abst. J. S. C. I. 1932, **51**, 303-B.
2. J. Wells, E. P. 366380; abst. J. S. C. I. 1932, **51**, 369-B.
3. Kodak-Pathe, F. P. 715538; abst. C. A. 1932, **26**, 2070.
4. Algemeene Kunstzijde Unie N. V., Holl. P. 24805; abst. C. A. 1932, **26**, 2053. See L. Lilienfeld, Span. P. 122122, Belg. P. 361531, 361532. Ital. P. 238535, 238536, 238537, 242879.
5. Lyons Piece Dye Works, E. P. 361418; abst. J. S. C. I. 1932, **51**, 226-B. Cf. Lonza Elektrizitats-Werke & Chemische Fabriken, A. G., Belg. P. 381464.
6. C. Malm and A. Andersen, U. S. P. 1857562.

tion has been investigated[1], and its velocity coefficient determined. A mixed solvent for acetylcellulose has been patented[2], comprising methylene chloride and a relatively non-volatile alcohol or ether boiling above 100°, as ethylene glycol or its monomethyl ether.

Rubber and other insulating materials, especially on electrical apparatus[3] are protected against air, oxygen and ultraviolet light by a coating containing an organic derivative of cellulose as cellulose acetate, together with an aromatic sulfonamide (xylenesulfonmethylamide) and dibutyl tartrate as plasticizer.

F. Ohl[4] has investigated the resistance of acetate silk to hot solutions, and its relation to other properties of the thread, and finds that water above 70° and alkali solutions at correspondingly lower temperatures reduce luster, decrease strength, increase crimping and tendency to felt. The resistance of acetate silk toward hot solutions and the corresponding properties of the thread, depend upon the chemical nature of the ester and on the spinning process. Up to a certain degree, the resistance may be enhanced by controlling conditions of the acetylcellulose and the filaments produced therefrom. Increased resistance is obtained by high acetic acid content, low sulfuric acid and ash values, and by high titer, dense cross section, freedom from entrapped air, geometrical arrangement of the filament crystals parallel to the filament axis, and high twist of the filaments themselves.

Acetylcellulose may be plasticized and dispersed by mixing a plastifier and water into the ester by a malaxation treatment, incorporating a hydrophilic colloid into the mass,

1. E. Moelwyn-Hughes and A. Rolfe, J. C. S. 1932, **138**, 241; abst. J. S. C. I. 1932, **51**, 233-A.
2. W. Moss, U. S. P. 1844365; abst. C. A. 1932, **26**, 2053.
3. *Ibid.* E. P. 362480, 362481; abst. J. S. C. I. 1932, **51**, 235-B, 237-B.
4. Seide. 1931, **36**, 239; abst. C. A. 1932, **26**, 2323. Orioli, Ital. P. 268372. Compare N. V. Fabriek Van Chemische Producten, Belg. P. 363154. For mfr. of masses of cellulose acetate see, N. V. Nederlandsche Kunstijde-fabriek, Holl. P. 20522.

gradually manipulating water thereinto until a change of phase takes place and the plastic mass disperses as fine particles into the aqueous medium[1]. Acetylene may be hydrated to acetaldehyde[2] by circulating an acid liquor containing iron in solution through a hydration vessel containing acetylene, oxidizing therein ferrous to ferric condition with pure oxygen, and withdrawing aldehyde as formed.

The non-inflammable composition of R. Roland[3] comprises acetylcellulose and methyl or ethyl alcohol 25 each, and chlorbenzene, tetrachlorethane, benzyl benzoate, triacetin, and dichlorhydrin, 10 each, the mass being heated to 75° until the cellulose acetate dissolves, when excess solvent is evaporated off until the desired plasticity and total solids have been obtained. Mixtures of liquids which taken separately have not a high solvent action for cellulose butyrate[4], may be used as solvents when combined, for producing lacquers, films and plastic materials, an example being a mixture of alcohol and benzene.

A process has been described for saccharifying cellulose, cellulose waste and wood which seems too expensive for commercial application[5], the cellulose being first formed into formylcellulose by treatment with concentrated formic acid in the presence of a catalyst, the resulting mass then being hydrolyzed by addition of water or dilute mineral acid. Cellulose butyrates and mixed butyric esters (acetobutyrate) may be simultaneously deodorized and homogenized by the action of steam under pressure[6]. In order

1. W. Pratt and R. Halstead, Can. P. 321427. W. Peterson and E. Fred, U. S. P. 1856425. Compare J. Perl, U. S. P. 1828982.
2. R. Riley, Can. P. 319059.
3. R. Roland, N. Zeal. P. 62198. Refer to S. Rowson, Kinemat. Weekly, 1931, **176**, 27.
4. O. Kohorn & Co. and H. Schupp, F. P. 710304; abst. C. A. 1932, **26**, 1120.
5. E. Ricard and H. Guinot, D. R. P. 534621; abst. C. A. 1932, **26**, 1438.
6. Soc. Des. Brevets Étrangers Lefranc et Cie; F. P. 716317; abst. C. A. 1932, **26**, 2316. See Societe Pour L'Ind. Chim. a Bale, Belg. P. 380211, 380961.

to increase the normal receptivity of acetylcellulose for dyes[1], 5-10% of nitrocellulose is added before spinning, and the formed filament submitted to a bath containing 10-12% sodium hydrosulfide and 0.6-1.2% magnesium chloride at 65° to denitrate the nitric ester. The assumption appears to be that the regenerated cellulose from the denitrated nitrocellulose is sufficient so that substantive dyes may be used advantageously. In a recent process for concentration of acetic acid by solvent extraction[2], dimethyl, diethyl, dibutyl or dihexyl phthalates or the corresponding benzoates are specified.

The superficial production of cellulose maleate on vegetable fibers for the purpose of immunizing to direct dyeing dyestuffs[3], results by treating with maleic anhydride, in the presence of a catalyst and/or diluent. Fused maleic anhydride is used. Details of the Eastman cellulose acetate filament plant at Kingsport, Tenn., have been published[4]. When finely divided fillers and adjuvants as pigments and plastifiants are added to acetylated cellulose followed by the incorporation of a precipitating agent in amounts sufficient to throw the dissolved components out of solution[5], the mass after removal of moisture therefrom, may be directly pressed into thermoplastic forms.

When vaporized ethylidene diacetate is led over calcium phosphate deposited on pumice as catalyst[6] at about 300°, both acetaldehyde and acetic anhydride result. The electrolytic purification of acetic acid solutions[7], especially acetylating mixtures, may be accomplished, only electrolytes containing ions having a high mobility and ions having

1. F. Straub, U. S. P. 1856033.
2. H. Suida, U. S. P. 1855072, Ital. P. 262012. See U. S. P. 1624810, 1624811.
3. Soc. of Chemical Industry in Basle, E. P. 315434.
4. Rayon & Syn. Yarn J. 1931, **12**, #10, 12.
5. M. Theumann, U. S. P. 1845821; abst. C. A. 1932, **26**, 2316. Refer to Soc. Anon. des Usines De Melle, Belg. P. 379845. Verein. f. Chem. Ind., Belg. P. 363810.
6. H. Walter, D. R. P. 541471; abst. C. A. 1932, **26**, 1946.
7. C. Webber, C. Staud and H. Gray, U. S. P. 1857224.

mobility being used, the acid impurities and metallic ions being first removed, and the remaining acetic acid concentrated by distillation. Comparative determination of the viscosity of celluloses and the acetylcelluloses prepared from them in connection with the progress of acetylation, have been made by K. Werner[1], results obtained indicating that the viscosity of acetylcellulose solutions (with the same acetic content) has no relation to the viscosity of the cellulose from which it is prepared, viscosity values in acetone and formic acid bearing no relation to one another. Treatment with 2% KOH in methyl alcohol gives cellulose with a very low, approximately constant viscosity in cuprammonium hydroxide solution, independent of the viscosity of the acetylcellulose saponified.

Ethyl alcohol may be nearly quantitatively converted into acetaldehyde[2] by contacting the alcohol vapor in admixture with air or other gaseous oxygen containing medium at 420-450° with copper as catalyst. The evaporation rate of a plasticizer is not necessarily indicative of its efficiency[3]. Although plasticizer I (unnamed) evaporated less rapidly from a Petrie dish than II (hydropalat CY), it evaporated more rapidly from cellulose acetate films. The effect on the tensile strength and elongation of the films varied accordingly.

Artificial silk velvet fabric consisting of a cotton backing and a cellulose acetate silk pile may be printed or padded with a solution of regenerated cellulose (viscose) in 8-12% NaOH, neutralized with acetic acid, and then dyed with direct colors, the luster of the pile not being dulled[4]. Several anonymous papers appeared during this year, on the stripping of dyed cellulose acetate, the dry cleansing of

1. Cellulosechem., 1931, **12**, 320; abst. J. S. C. I. 1932, **51**, 302-B.
2. K. Wiesler, K. Bodensee and A. Peake, Can. P. 320355.
3. H. Wolff and J. Rabinowicz, Farben.-Ztg. 1932, **37**, 855; abst. C. A. 1932, **26**, 2069.
4. J. & J. M. Worrall, Ltd., H. Livesey and G. Holden, E. P. 365132; abst. J. S. C. I. 1932, **51**, 337-B. See E. P. 297607.

acetate fabrics[1], utilization of acetylcellulose sheets[2], recovery of acetic acid from cellulose acetylating baths[3], details of Celloda Syndicate acetylcellulose plant[4], degumming of real silk fabrics containing cellulose acetate silk[5], light refraction of acetylcellulose filaments[6], and desizing and dyeing of cellulose acetate fabrics[7].

H. Smith has described a series of new cellulose acetate compositions, utilizing as plasticizing bodies guaiacol acetate[8], salicylaldehyde[9] and ethyl acetylglycollate[10]. J. Duclaux and F. Hirata[11] have examined various solutions of cellulose, nitrocellulose and acetocellulose by the method of F. Michaud[12] and by horizontal displacement for the existence of permanent rigidity. Results by both methods showed that none of the solutions possessed a permanent rigidity although the viscosity was very great, attaining in one instance 130,000 poises. The time of relaxation of a solution of 6% nitrocellulose in nitrobenzene was 170 seconds.

It has been found[13] that the solubility of cellulose acetate in ethyl acetate, ethyl acetoglycollate, methylbenzyl ether, methyl phthalate, diacetone alcohol, cyclohexanone and benzyl alcohol at 25° varies with the amount of solid phase used. The curves connecting solubility with the amount of solid phase do not show a pronounced maximum,

1. American Dyestuff Reporter, 1931, **20**, 573, 604. Amer. Silk J. 1931, **50**, #9, 50.
2. Brit. Plastics, 1931, **2**, 496.
3. Ind. Chem. 1931, **7**, 147.
4. Celloda Syndicate, Ltd., Kinemat. Weekly, 1930, **166**, 15.
5. Kunstseide, 1931, **13**, 434; abst. J. S. C. I. 1932, **51**, 176-B.
6. Silk J. & Rayon World, 1931, **7**, #82, 37; **8**, #89, 47; #90, 54. Syn. Org. Chem. 1931, **4**; abst. J. Chem. Ed. 1931, **8**, 1878.
7. Anon., Textilber. 1932, **13**, 26; abst. J. S. C. I. 1932, **51**, 178-B. Textile Colorist, 1931, **53**, 407. Textile Mfr. 1931, **57**, 299.
8. H. Smith, U. S. P. 1858285.
9. *Ibid.* U. S. P. 1858286.
10. *Ibid.* U. S. P. 1858287.
11. J. Chim. Phys. 1931, **28**, 537; abst. C. A. 1932, **26**, 2587.
12. Compt. rend. 1922, **175**, 1196. Ann. phys. 1923, **19**, 63.
13. W. Ostwald and H. Ortloff, Kolloid-Z. 1932, **58**, 215; abst. J. S. C. I. 1932, **51**, 336-A.

as is observed in adsorption or dissolution peptization, but are linear, convex or concave, according to the solvent. The solid-phase rule also holds in certain binary mixtures of the above solvents, in which case the curves are concave to the axis representing the amount of solid phase. The solid-phase relation is ascribed to the mixed nature of cellulose acetate. The injection molding process for acetylcellulose has been historically treated as to priority of conception[1], and D. Othmer[2] has given a general survey of the performance of corrosion-resistant materials as wood, rubber, and metals in the handling of acetic acid solutions.

L. Meunier and G. Revillon[3] have reported upon experiments on the swelling of cellulose acetate in aqueous solutions of aniline, pyridine, acetone, triethanolamine and ammonium and calcium thiocyanates; T. Truax[4] upon the development of wood adhesives containing cellulose esters and gluing technic; and S. Sheppard and S. Sweet[5] have reported on the amount of substances required to precipitate cellulose acetate from an acetone solution from a number of members of each of the series, *n*-aliphatic hydrocarbon, alcohols, *sym*-ether, aldehydes, ketones, acids and acid esters, alkyl chlorides, methyl and ethyl esters of acetic, lactic, succinic, oxalic, and tartaric acids. Also for *iso*-, and *ter*-butyl alcohol, butyl acetate, amyl alcohol, and for benzene, toluene, *m*-xylene, mesitylene, phenylethane, cumene, cymene, phenol, cyclohexane and cyclohexanol. The precipitating power is proportional to the molecular weight for the higher members of each series, and is lowered by branching of the carbon chain, and by unsaturation in the benzene series. It is markedly affected by the presence of OH and carboxyl groups. The solvent power of acetone is

1. H. Stadlinger, Brit. Plas. 1932, **3**, 520.
2. Chem. Met. Eng. 1932, **39**, 136; abst. C. A. 1932, **26**, 2351.
3. Chimie & Ind. 1932, **27**, 251; abst. C. A. 1932, **26**, 2600.
4. Trans. Am. Soc. Mech. Engrs. (Wood Ind.) 1932, **54**, 1; abst. C. A. 1932, **26**, 2616.
5. J. Phys. Chem. 1932, **36**, 819; abst. C. A. 1932, **26**, 2362.

increased by the addition of water to a maximum value, then decreased, the effect varying with the precipitant used.

In attempts to spin acetylcellulose direct from the acetylation mixture[1], acetylation may be conducted in two phases; i.e., in the first, chlorine is used as catalyst, and in the second, very small quantities of sulfuric acid, which, with the HCl derived from the Cl in the first phase, are sufficient to complete the reaction in a short time. When acetylation is finished, the viscosity is reduced by addition of acetic acid, excess of acetic anhydride hydrolyzed by aqueous formaldehyde, and the solution spun in water or salt solutions. Spinning of the triacetate solution is difficult owing to its corrosive action on the apparatus and to the large contraction on drying of the threads, which, although elastic, are quite brittle. The triacetate yarn differs from the acetone-soluble acetate in its resistance to boiling water, soap solutions, and dilute alkali without loss of luster or partial saponification, and also in its dyeing properties.

Organic Cellulose Esters Advancement in 1932. *Cellulose Formate.* Acetone-soluble formylcelluloses contain more than 7 formyl groups per C_{24} cellulose by formylation with a mixture of 85% formic acid and chloracetic anhydride[2]. Mixed esters as cellulose acetoformate, propioformate, butyroformate, caproformate, lauroformate, myristoformate, palmitoformate and stearoformate may be similarly prepared. G. Tocco[3] has reviewed the applications of cellulose formate in the plastics industry. For producing the anhydrous acid[4], the aqueous acid is treated with phthalic anhydride or pyroboric acid equivalent to the water present and the formic acid isolated by distillation. Phosphoric acid may be used for the same purpose[5].

1. A. Lautenberg, Ind. Chem. 1932, **8**, 50; abst. J. S. C. I. 1932, **51**, 379-B.
2. H. Clarke and C. Malm, U. S. P. 1880420.
3. Brit. Plastics, 1931, **3**, 298.
4. K. Rohde, U. S. P. 1848664; abst. C. A. 1932, **26**, 2751.
5. Naam. Vennootschap de Bataafsche Petroleum-Maatschappij and A. v. Peski, D. R. P. 543554; abst. C. A. 1932, **26**, 3264.

Acetic Acid. Acetic acid may be extracted and concentrated by means of ether[1], by propyl oxide[2], by a mixture of propyl oxide and ethyl acetate[3], or by means of a liquid dissolving acetic acid and at the same time having a low solvent power for water[4]. An acetate or dilute acetic acid may be concentrated to glacial by heating to 300-320°, care being taken to ensure uniform heating and to avoid local superheating[5]. By subjecting a gaseous mixture of H and CO to action of a phosphoric acid catalyst[6], methyl acetate results which may be saponified into acetic acid. Boric, arsenic or phosphomolybdic acids may also be used[7]. A mixture of dimethyl ether 5 and CO 3 parts at 100-200 atms. and 300-400° with zinc oxide catalyst[8], also yields methyl acetate.

By adding to oxidized paraffin slaked lime and distilling the calcium salt[9], acetic and higher acids are obtained, or sodium acetate may be distilled under 25 mm. pressure to remove the water, and then decomposed by means of an organic acid[10]. Or an aqueous solution of the dilute acetic acid may be concentrated by extraction with ethyl acetate[11], butyl acetate[12] or amyl acetate[13]. Acetic acid may be prepared by the thermic decomposition of acetaldehyde in the presence of silica-gel as catalyzer[14], or by oxidizing ace-

1. J. Coahran, U. S. P. 1865887; abst. C. A. 1932, **26**, 4466. U. S. P. 1870834; abst. C. A. 1932, **26**, 5576.
2. J. Davidson and J. Schaeffer, E. P. 370771; abst. J. S. C. I. 1932, **51**, 763-B.
3. E. Badger & Sons Co., E. P. 371554; abst. J. S. C. I. 1932, **51**, 792-B.
4. H. Dreyfus, Can. P. 322981.
5. Deutsche Gold- und Silber-Scheideanstaldt vorm. Roessler and A. Gorhan, D. R. P. 546826; abst. C. A. 1932, **26**, 3518. D. R. P. 552425; abst. C. A. 1932, **26**, 4346. See U. S. P. 1858150, 1858151.
6. H. Dreyfus and W. Bader, U. S. P. 1864531; abst. C. A. 1932, **26**, 4346.
7. *Ibid.* U. S. P. 1864643; abst. C. A. 1932, **26**, 4346.
8. H. Dreyfus, U. S. P. 1879606.
9. H. Franzen and M. Luther, U. S. P. 1864058.
10. W. Haworth, U. S. P. 1867943; abst. C. A. 1932, **26**, 5104.
11. E. Ricard and H. Guinot, U. S. P. 1860553.
12. *Ibid.* U. S. P. 1860512. D. R. P. 548204; abst. C. A. 1932, **26**, 3518.
13. *Ibid.* D. R. P. 546660; abst. C. A. 1932, **26**, 3518.
14. J. Kathol, D. R. P. 547641; abst. C. A. 1932, **26**, 3521.

tylene by air and nitrogen oxides as catalyzer[1]. Mercury vapor may replace the nitrogen oxides[2]. A mixture of formamide vapor and hydrogen[3], with or without steam, is led through a tube at 250-300° filled with pumice or copper powder and exposed to ultraviolet ray radiation, acetic acid and acetamide being formed. Or[4], acetylene and steam may be passed through molten zinc chloride, with or without a solid catalyst as barium sulfate and zinc oxide, acetaldehyde being formed.

Dilute acid may be concentrated to 40% strength in two operations by cooling to —2° and flowing through a heat exchanger so that free ice crystals are carried forward to a separating vessel, deposition of ice crusts being avoided[5]. Or[6], the crude acid may be fed through a column into a boiler, the vapors from which, and from the bottom of the column pass into a second reflux condenser, from which glacial acid is collected. In the preparation of absolute acetic acid from acetaldehyde with manganese acetate[7] as catalyst, air is passed at 1.3-2 atms. pressure through acetaldehyde at 30-40°[8]. The acid may be simultaneously purified and concentrated by adding it to a ternary mixture of acetic acid, sulfuric acid and water within the range of compositions in which, at the b. pt., the concentration of the acetic acid in the vapor phase is greater than the ratio of acetic acid to water in the liquid phase[9].

1. Gutehoffnungshütte Oberhausen, A.-G., E. P. 376045; abst. J. S. C. I. 1932, **51**, 972-B. F. P. 720683; abst. C. A. 1932, **26**, 3807.
2. E. Eberhardt, D. R. P. 544691; abst. C. A. 1932, **26**, 3521. D. R. P. 554784; abst. C. A. 1932, **26**, 5971.
3. Soc. Franc. de Catalyse Generalisee, E. P. 371555; abst. J. S. C. I. 1932, **51**, 792-B.
4. Consort. f. Elektrochem. Ind. G. m. b. H., E. P. 373893; abst. J. S. C. I. 1932, **51**, 832-B.
5. Distillers Co., Ltd., H. Langwell and R. Gilmour, E. P. 378463; abst. J. S. C. I. 1932, **51**, 1071-B.
6. Soc. des Etabl. Barbet, E. P. 372507; abst. J. S. C. I. 1932, **51**, 792-B.
7. British Celanese, Ltd., E. Thomas, W. Groombridge and H. Oxley, E. P. 367863; abst. J. S. C. I. 1932, **51**, 590-B.
8. L. Christensen and W. McCutchan, U. S. P. 1875368.
9. J. Schulze, U. S. P. 1863698; abst. C. A. 1932, **26**, 4346.

E. Poste[1] has given details of the Suida process for acetic acid recovery including description of two 80-cord plants, and D. Othmer[2] has reviewed problems in the piping of acetic acid.

Acetic Anhydride. When acetic acid is treated with phosgene (carbonyl chloride) in presence of aluminum chloride[3], which is soluble in heated acetic acid, and at a temperature of about 100°, acetic anhydride results. When *aa'*-dichlordiethyl ether is heated with glacial acetic acid and benzene[4], *aa'*-diacetodiethyl ether results, and this heated with zinc or stannous chlorides decomposes into 2 mols. acetaldehyde and 1 mol. acetic anhydride. A copper-silver alloy reaction vessel containing 6-30% silver is recommended[5]. Acetic acid and acetaldehyde may be separated by adding sodium, potassium or calcium acetates together with toluene or other acetic anhydride solvent[6], and the anhydride distilled off the solid double acetate, from which the acetic acid may be recovered by distillation or extraction.

E. Berl[7] passes acetic acid and acetone over vanadium pentoxide at 675°, or the acetone is first converted by the pentoxide into ketene, which is then led into the vapors of condensate produced from acetic acid at 730° in contact with pumice. Or[8], brine may be added to the distillate and the acetic anhydride extracted with benzene, or water-insoluble alcohols, ethers or esters. Acetic anhydride may also be prepared by the catalytic dehydration of acetic acid,

1. Ind. Eng. Chem. 1932, **24**, 722; abst. C. A. 1932, **26**, 4463; J. S. C. I. 1932, **51**, 791-B.
2. Heating, Piping, Air Conditioning, 1932, **4**, 346; abst. C. A. 1932, **26**, 3857. J. Carlin and N. Krass, Can. P. 326232. E. Badger & Sons Co. and G. Lunt, Can. P. 327224.
3. E. Winter and A. Grimm, U. S. P. 1865405; abst. C. A. 1932, **26**, 4347.
4. R. Müller and F. Voeller, U. S. P. 1859786. D. R. P. 553605; abst. C. A. 1932, **26**, 5577.
5. R. Müller and E. Rabald, D. R. P. 548369; abst. C. A. 1932, **26**, 3520.
6. C. Boehringer & Söhne, E. P. 372434; abst. J. S. C. I. 1932, **51**, 782-B.
7. E. P. 377442; abst. J. S. C. I. 1932, **51**, 972-B.
8. E. Berl, E. P. 379042; abst. J. S. C. I. 1932, **51**, 1071-B.

the acid vapors being carried by a liquid capable of forming an azeotropic mixture with water (as crystallizable benzene, thiophene-free)[1]. The water vapor is immediately separated by passing the mixture into a dephlegmator at about the b. pt. of the azeotropic mixture. Or the anhydride may be prepared by heating under reduced pressure dry heavy metal acetates, the oxides of which do not promote the formation of acetone. Copper or chromium acetates heated to 150-250° under 12 mm. pressure give an especially high yield[2].

In producing acetic anhydride[3], acetic acid vapor is subjected to pyrogenetic decomposition while being passed through a heated zone containing at least one metal, the oxide of which is reducible by a reducing gas such as H, being passed through the reaction zone of the acetic vapor, and is then condensed. The anhydride may be dissolved by *b*-naphtholmethyl ether, *a*- or *b*-naphtholethyl ether, phenol-phenyl ether, phenyl-*b*-naphthyl ether, cresoltolyl ether or benzyl-*b*-naphthyl ether[4]. To avoid oxidation[5], it is advised to effect the thermal decomposition in presence of CO. Acetic anhydride results by passing acetic acid vapor and carbonyl chloride through a packed tube[6] at 280-310°.

W. Tale[7] prepares acetic anhydride by mixing acetic acid with chloracetyl chloride and cuprous chloride, and the material warmed to drive off halogen halide. The mixed anhydride is heated substantially to the b. pt. of the simple acid anhydride, to liberate and vaporize the latter. As catalysts suitable for acetic anhydride production, boron phosphate is used with an alkali metal salt such as sodium

1. J. Campardou, F. P. 724803; abst. C. A. 1932, **26**, 4829.
2. R. Meingast and M. Mugdan, U. S. P. 1878593. D. R. P. 556247; abst. C. A. 1932, **26**, 5577.
3. H. Dreyfus, U. S. P. 1872914; abst. C. A. 1932, **26**, 5971. U. S. P. 1884627. Can. P. 325646, 325647.
4. *Ibid.* F. P. 39763, Addn. to F. P. 633856; abst. C. A. 1932, **26**, 4829.
5. *Ibid.* U. S. P. 1884626. Can. P. 325645.
6. British Celanese, Ltd., S. Green and T. Dee, E. P. 371946; abst. J. S. C. I. 1932, **51**, 792-B. Can. P. 325859.
7. U. S. P. 1863788; abst. C. A. 1932, **26**, 4347.

ammonium hydrogen phosphate[1], or a mixture of boron, zinc and lead phosphates[2], or a mixture of alkali and alkaline earth phosphates[3], or by heating acetyl chloride continuously with glacial acetic acid in approximately stoichiometric proportions at temperatures near the b. pt. of acetic anhydride[4]. In another process[5], dry alkaline earth salts of the acids are treated with sulfuryl chloride, or a water-free mixture of sulfur dioxide and chlorine at low temperatures and in the presence of a solid, inorganic diluent as dry sand. Anhydride formation is facilitated by reducing the pressure. Or[6], the anhydrous salt may be suspended in liquid sulfur dioxide and treated with sulfuryl chloride.

In producing methoxyacetic anhydride[7], vapors of an alkoxy-aliphatic acid as methoxyacetic acid are subjected to thermal decomposition at 300-1200°, suitably in the presence of sodium pyrosulfate. Propionic anhydride results from reacting upon propionic acid in the presence of a phosphoric acid catalyst[8], or HCl as catalyst[9]. Propionic or butyric acid may be rendered anhydrous[10] by treatment with di- or tri-chlorethylene at about 200°, and then subjecting to fractionation. A process of acetic anhydride production has been described[11], consisting in heating ethylidene diacetate vapor to 300-450°.

1. A. Dierichs, U. S. P. 1870357; abst. C. A. 1932, **26**, 5577.
2. I. G. Farbenindustrie, A.-G., E. P. 370438; abst. J. S. C. I. 1932, **51**, 763-B. F. P. 39574, Addn. to F. P. 698907; abst. C. A. 1932, **26**, 4829.
3. *Ibid.* F. P. 717152; abst. C. A. 1932, **26**, 2751.
4. F. Henle, V. Lanz, G. Meder and F. Privinsky, D. R. P. 546511; abst. C. A. 1932, **26**, 3520.
5. Brevets Etrangers Lefranc & Cie., D. R. P. 552833; abst. C. A. 1932, **26**, 5577.
6. B. Herstein, U. S. P. 1860542. U. S. Industrial Alcohol Co., E. P. 353381; abst. C. A. 1932, **26**, 5314.
7. H. Dreyfus, U. S. P. 1865177; abst. C. A. 1932, **26**, 4347.
8. *Ibid.* U. S. P. 1872029; abst. C. A. 1932, **26**, 5971.
9. *Ibid.* U. S. P. 1872030; abst. C. A. 1932, **26**, 5971.
10. W. Walter, E. Hartmann and H. Tegtmeyer, U. S. P. 1854568; abst C. A. 1932, **26**, 3265.
11. Canadian Electro Products Co., Ltd., and H. Matheson, Can. P. 327242.

Pretreatment of Cellulose. In the treatment of cellulose preparatory to esterification[1], the cellulose is mixed with acetic acid of such strength that the acid crystallizes when cooled, and the mixture is then further cooled to effect crystallization throughout the mass. E. Worden[2] has described an *α*-cellulose obtained from Musa and hemp fibers, claimed to produce unusually high tensile strength esters and ethers. *α*-Cellulose pulp suitable for acetylation results from digesting undercooked sulfite pulp in a rotary boiler with 15 times its weight of a liquor containing 1.5% each NaOH and sodium sulfite at a temperature rising to 133° in 2.75 hrs.[3]. Kodak-Pathe[4] recommends to treat cellulose in a bath of sulfuric, phosphoric or nitric acids diluted in an organic acid, which transforms it to hydrocellulose, the nitric acid being removed by washing before esterifying.

By treatment of cellulose with a small amount of formic acid[5], it is said to be more readily susceptible to esterification[6]. 80% strength formic acid is specified in a similar process[7]. To condition the pulp preliminary to esterification or etherification[8], it is shredded while wet and containing 40-70% bone-dry celluloe, and then directly dried. A two stage method of preparing cellulose for etherification has been described[9], comprising first treating with an organic acid and then with an organic acid anhydride.

Properties of the Cellulose Organic Esters. J. Katz

1. H. Dreyfus, U. S. P. 1857183; abst. C. A. 1932, **26**, 3919.
2. U. S. P. 1866917; abst. C. A. 1932, **26**, 4717.
3. C. Blodgett and H. Hanson, U. S. P. 1831435; abst. J. S. C. I. 1932, **51**, 837-B.
4. F. P. 728504; abst. C. A. 1932, **26**, 5753.
5. H. Dreyfus, Belg. P. 344888, 361052.
6. L. Christensen, U. S. P. 1875688.
7. I. G. Farbenindustrie, A.-G., E. P. 305601; abst. C. A. 1929, **23**, 4819; J. S. C. I. 1929, **48**, 280-B.
8. M. Schur and B. Hoos, U. S. P. 1880052.
9. C. Dreyfus, H. Martin, J. Elder and L. Rogers, Can. P. 327930.

and A. Weidinger[1] believe intumescence is the cause of the characteristic lack of sharpness in the Röntgen spectrum of cellulose acetate I, prepared from ramie fiber by acetylating with acetic anhydride in benzene (in order to obtain a fibrous product) and a trace of sulfuric acid. The sharpness of the spectrum is destroyed on washing with water. It is suggested that benzene, acetic anhydride or acetic acid mols form part of the lattice; on their removal, the regularity of the structure is destroyed. A 42-45% yield of cellulose may be obtained from bamboo meal by extraction with glycol containing a small percentage of mineral acid. Upon acetylation and dissolving[2], solutions are obtained inversely varying in viscosity with the pentosan content. The solutions have a yellowish color, notwithstanding preliminary bleaching of the cellulose.

F. Ohl[3] has fractionally precipitated several varieties of acetylcellulose and studied the properties of the different fractions obtained, finding a close relationship existing between the quality of the cellulose acetate and the properties of the different fractions. He has discussed the principles of efficient acetylation and plant requirements for large scale production[4]. According to I. Sakurada[5], the acetylation of natural and regenerated cellulose by heating with acetic acid or acetic anhydride is irregular and progresses in stages, a view to which we do not subscribe. He finds that if the cellulose is pre-treated with NaOH the acetylation is regular. The methylation and acetylation of glycogen and various starches have been studied in detail[6].

1. Rec. Trav. chim. 1932, **51**, 847; abst. J. S. C. I. 1932, **51**, 904-A.
2. B. Rassow and A. Reckeler, Nitrocellulose, 1932, **3**, 17, 41, 60; abst. C. A. 1932, **26**, 3374.
3. Kunstseide, 1932, **14**, 3; abst. C. A. 1932, **26**, 2861.
4. Chem. Fabr. 1932, **5**, 233; abst. J. S. C. I. 1932, **51**, 745-B; C. A. 1932, **26**, 4710.
5. J. Soc. Chem. Ind. Japan, 1932, **35**, 123; abst. C. A. 1932, **26**, 3662; J. S. C. I. 1932, **51**, 498-B. J. Soc. Chem. Ind. Japan, 1932, **35**, 283; abst. J. S. C. I. 1932, **51**, 880-B.
6. G. Hughes, A. Macbeth and F. Winzor, J. Chem. Soc. 1932, **135**, 2026; abst. C. A. 1932, **26**, 5079.

It appears that the presence of casein or ovalbumin endows a cellulose acetate membrane with marked adsorptive power for dyes from dilute sulfuric acid solution[1], the effect running parallel with the ratio protein:cellulose. A similar phenomenon is observed with cellulose acetate:casein membranes in bismuth trichloride solution. The rate of diffusion of 2-20% acetylcellulose in benzyl alcohol when brought in contact with methyl or ethyl alcohols has been measured[2], and the diffusion coefficient D, and the effective pore radius R calculated[3]. The law of diffusion is said to be valid for this system. The high values of D are inconsistent with a solid solution. The entire behavior is what would be predicted by the liquid-solid theory of gel structure[4].

In an investigation of the osmotic pressure of cellulose acetate solutions (see p. 855, n. 1)[5], at 20° the apparent molecular weight of 2 samples of cellulose acetate determined by the osmotic pressure of acetone solutions, varies inversely with the concentration (0.5-4.4%) and directly with the relative viscosity. The mol. wt. curves intersect at a concentration of 3% where $M = 23{,}000$-$34{,}000$. Fractionation experiments (using acetone:water mixtures) have been carried out on commercial cellulose acetates[6] and the properties of the various fractions determined, especially stress-strain curves from different fractions being plotted.

A method for measuring the dielectric polarization constant has been described[7], and the polarization of acetylcellulose in simple and mixed solvents determined. In gen-

1. J. Loiseleur and P. Morel, Compt. rend. Soc. Biol. 1931, **108**, 484; Chem. Zentr. 1932, I, 1885; abst. J. S. C. I. 1932, **51**, 1085-A.
2. K. Klemm and L. Friedman, J. Am. Chem. Soc. 1932, **54**, 2637; abst. C. A. 1932, **26**, 4523; J. S. C. I. 1932, **51**, 995-A.
3. L. Friedman, J. A. C. S. 1930, **52**, 1305; abst. J. S. C. I. 1930, **49**, 693-A.
4. Aladin, Plastics, 1932, **8**, 15; abst. Chem. Zentr. 1932, I, 2913.
5. J. Grard, J. Chim. Phys. 1932, **29**, 287; abst. C. A. 1932, **26**, 5477.
6. R. Herzog and A. Deripasko, Cellulosechemie, 1932, **13**, 25.
7. W. Haller and H. Ortloff, Kolloid Zts. 1932, **59**, 137; abst. J. S. C. I. 1932, **51**, 692-A.

eral, the value increases with increasing concentration and varies with the solution activity of the solvent approaching a limiting value 0.66 in weakly active liquids. The value in mixtures is equal to that of the liquid of greater activity, suggesting that the solution-active liquid is preferentially adsorbed. The dielectric constant of pure, dispersed cellulose acetate is 17.25 (obtained by extrapolation), which is considerably higher than the value for the material in mass. Cellulose acetate solutions have been studied by the methods of Michaud and by horizontal spreading to detect evidence of permanent rigidity[1], no evidence of any permanent rigidity having been found. The time of relaxation of a 6% nitrocellulose solution in nitrobenzene was found to be 170 seconds.

H. Clarke and H. Gillespie[2] report that potato starch yields a continuous series of amorphous acetates, the acetic acid content of which increases with time of treatment and reaches a limit with the introduction of 3 acetyl groups for each glucose residue. Specimens of acetylcellulose containing 53-55% acetic acid have been dissolved in acetone, acetophenone and benzyl alcohol and the osmotic pressures measured[3]. A semi-permeable membrane of partially denitrated nitrocellulose was used. Measurements at 40° and 60° indicate that the osmotic pressure is proportional to the concentration, while at 0° or 20°, the pressure increases more rapidly than the concentration. An increase of 20° raises the osmotic pressure by about 7%. The samples had an average mol. wt. of about 35,000. T. Tomonari[4] finds that the refractometric method, together with röntgenographic experiments, is useful for the study of the action of organic substances upon cellulose esters, and that it permits of the determination of equivalent relationships of resulting compounds, when one excludes certain disturbing experimental factors which are specified. H. Pringsheim

1. J. Duclaux and F. Hirata, J. Chim. phys. 1931, **28**, 537.
2. J. A. C. S. 1932, **54**, 2083; abst. J. S. C. I. 1932, **51**, 722-A.
3. E. Büchner and P. Samwel, Proc. Sci. Amsterdam, 1931, **33**, 749; abst. C. A. 1932, **26**, 2635.
4. Cellulosechemie, 1932, **13**, 101; abst. C. A. 1932, **26**, 6123.

and K. Ward[1] have described a new degradation product of cellulose acetate.

According to K. Werner[2], acetylation of cellulose and viscosity determinations show that decrease in viscosity due to acetylation is not greater than in case of nitration; wood and cellulose are identical, and viscosity of solutions of acetylcellulose has no relationship to the viscosity of the cellulose used in their preparation. No relationships exist between viscosity of acetylcelluloses in formic acid and acetone solutions; and viscosity of copperammonia solutions of regenerated celluloses is low after treatment of the acetylcelluloses with 2% KOH in methyl alcohol, and probably is a function of particle size. The viscosity of cellulose acetate may be reduced by bringing an acid gas in contact at room temperatures[3]. The effect of various substances on the viscosities of cellulose acetate in acetone and benzyl alcohol have been studied[4]. Water increases the viscosity accompanied with an increase of the structure region and later causes coagulation. Addition of benzene results in gelating systems, the resulting gels exhibiting synaresis. The liquid obtained through synaresis also shows structure viscosity, indicating in this case that synaresis does not cause separation of pure dispersion medium. Acetic acid causes a decrease in the viscosity as well as the structure viscosity, while triphenyl phosphate and camphor increase the structural viscosity at high concentrations[5]. R. Eisenschitz and B. Rabinowitsch[6] have determined the particle size of acetylcellulose in acetone from viscosity determinations. Decrease in viscosity and polymerization degree of nitrocellulose solutions is attributed to the influence of electrolytes[7].

1. Cellulosechem. 1932, **13**, 65; abst. J. S. C. I. 1932, **51**, 502-A.
2. Cellulosechem. 1932, **12**, 320; abst. C. A. 1932, **26**, 6121.
3. E. Reid, U. S. P. 1874350; abst. C. A. 1932, **26**, 6136.
4. Y. Nisizawa, Kolloid Zts, 1931, **56**, 317.
5. I. Sakurada, J. S. C. I. Japan, 1932, **35**, 78; abst. C. A. 1932, **26**, 3373; J. S. C. I. 1932, **51**, 416-B.
6. Ber. 1931, **64**, 2522.
7. A. Drinberg, J. App. Chem. Russia, 1931, **4**, 293; abst. J. S. C. I. 1932, **51**, 465-A.

The viscosity of cellulose acetate formed in the presence of a sulfur-containing catalyst[1] may be effected by passing a mixture of the ester and water through a heated passage at superatmospheric pressure, the pressure and heat being so adjusted that the process is continuous. The viscosity of cellulose acetate is also lowered by heating the finely divided solvent-free ester at 120-130°[2], or ozone may be passed into the cellulose acetate until the desired degree of viscosity reduction is obtained[3], the above three methods being equally applicable to the cellulose ethers.

In reducing the burning qualities of the organic cellulose esters and cellulose ethers, dichlornaphthalene[4], trichloracetamide[5], bromtoluene[6], and antimony trichloride in non-aqueous mixture[7] have been described. Bromphenyl acetate[32] has also been patented for addition to cellulose acetate for the purpose of diminishing the inflammability[9].

Manufacture of Organic Cellulose Esters. A fibrous cellulose acetate insoluble in chloroform, but soluble in *m*-cresol, aniline and tetrachlorethane has been described[10], obtained by pre-treatment of cellulose with acetic acid at 20° for 24-48 hrs., then with 95% acetic anhydride and a catalyst of phosphoric and sulfuric acids. Cellulose may also be acetylated in the presence of HCl as catalyst[11] and a reducing substance which buffers the HCl against autoxidation, such products being mannose, lactose, glucose, phenol, polyphenols, hydroquinone and aminophenols, particularly those with *o*- and *p*-linkages. Production of acetyl-

1. C. Dreyfus and G. Schneider, Can. P. 324000.
2. L. Branchen and C. Prachel, U. S. P. 1831795; abst. J. S. C. I. 1932, **51**, 767-B.
3. C. Malm and A. Andersen, U. S. P. 1857562.
4. I. G. Farbenindustrie, A.-G., Belg. P. 376461.
5. S. Carroll, U. S. P. 1870556; abst. C. A. 1932, **26**, 5754.
6. C. Dreyfus, Can. P. 322977; abst. C. A. 1932, **26**, 4172.
7. A. Arent, Can. P. 229124.
8. C. Dreyfus, Can. P. 325644; abst. C. A. 1932, **26**, 6136.
9. K. Micksch, Kunstseide, 1932, **14**, 64; abst. C. A. 1932, **26**, 2869.
10. C. Staud and H. Gray, U. S. P. 1870594.
11. S. Sheppard, U. S. P. 1878988.

cellulose has been proposed[1], using as catalyzer the reaction of sulfur dioxide and a nitrogen oxide. If acetylated cellulose be hydrolyzed in the presence of unsaturated monobasic carboxylic acids (acrylic, crotonic, angelic, tiglic) and such unsaturated dibasic acids as maleic or fumaric or their anhydrides, the acetone-soluble modification is readily formed.

To produce stable acetylcellulose solutions[2], a method has been detailed comprising adding magnesium acetate to the acylating bath which combines with the sulfuric acid employed as catalyst, afterwards crystallizing out the magnesium sulfate formed. C. Noller[3] prepares cellulose acetate with vaporized acetylating agents, the cotton, previously impregnated with 0.23% sulfuric acid is placed in a closed vessel with acetic anhydride, the air exhausted to 10 mm. pressure, the vessel heated to 60-65°, and kept at that temperature until acetylation is completed. The solubility may be changed by conducting the hydrolysis in the primary acetylated mixture[4], first at an accelerated rate, and then lowering the temperature prior to stopping the hydrolysis. Or[5], the cellulose acetate may be hydrolyzed from 44.8% to 40% acetyl by means of a hydrolyzing bath of acetic acid and water containing 0.2% sulfuric acid and 0.6% phosphoric acid.

If to the finished acetylcellulose in solution there is added 2 parts of 35% HCl diluted with 5 parts acetic acid at 20° for 0.5 hr., then precipitated into a 35-40% acetic acid bath, it will be found when the ester is dissolved in acetone with the usual plasticizers added[6], that such solutions are clear and sparkling, and free from traces of haze. Cellulose acetate may be prepared by subjecting cotton to a swelling treatment without substantial production of

1. C. Webber and C. Staud, U. S. P. 1866686; abst. C. A. 1932, **26**, 4718. U. S. P. 1880560.
2. E. Hubert and K. Weisbrod, U. S. P. 1860461; abst. Plastics, 1932, **8**, 388.
3. U. S. P. 1880466.
4. C. Malm, U. S. P. 1870635; abst. C. A. 1932, **26**, 5754.
5. *Ibid.* U. S. P. 1878953. 6. *Ibid.* U. S. P. 1878954.

hydrocellulose as by treatment with zinc chloride[1], and in this swollen condition is esterified in the usual way. J. Haskins[2] esterifies by heating 1.81 parts cellulose in a mixture of 5.8 parts pyridine, 0.12 part sulfuric acid and 3.9 parts butyric anhydride for cellulose butyrate production, or by treating cellulose 8, with acetic anhydride 25.5, pyridine 59 and 96% sulfuric acid 1.12 parts for acetylcellulose formation.

Where acetylation takes place with insufficient acetic acid to dissolve the cellulose[3], the addition of ethylene chloride to the esterizing bath after acetylation has progressed for some time, an ester is said to be obtained especially valuable for photographic film and to be particularly free from haze, grain and fiber. F. Bidaud[4] has described a cellulose esterifying apparatus in which a continuous rotary motion is imparted to the materials in such a manner as to cause continuous forward movement of the reacting mass during its entire reaction period, the speed of the mass being checked at different points. H. Barthelemy[5] esterifies by a series of five acetylation baths containing acetic anhydride diluted with acetic acid, the first bath containing sulfuric acid as catalyst, as a later bath containing a reagent capable of reducing the catalytic power of the sulfuric acid without destroying it, as sodium or potassium acetate, sodium lactate or benzoate, or neutral sodium or potassium sulfates.

The apparatus of J. Altwegg[6] for preparing cellulose acetate comprises treating the cellulose with an acetylating agent, and subjecting the reacting mass continuously and progressively to tearing, kneading and paddling operations. Cellulose triacetate may be partly hydrolyzed to products

1. G. Heberlein and A. Bodmer, U. S. P. 1858993; abst. C. A. 1932, **26**, 3918; Plastics, 1932, **8**, 388.
2. U. S. P. 1866532; abst. C. A. 1932, **26**, 4718. C. Graenacher, Can. P. 326986.
3. H. Gray, C. Staud and C. Webber, U. S. P. 1857190. H. Gray and C. Staud, U. S. P. 1866971; abst. C. A. 1932, **26**, 4718.
4. U. S. P. 1859579; abst. C. A. 1932, **26**, 3919.
5. U. S. P. 1880067. E. P. 358881; abst. C. A. 1932, **26**, 6136.
6. U. S. P. 1870980; abst. C. A. 1932, **26**, 5754.

suitable for the manufacture of films and filaments[1] by subjecting them, while swollen or dissolved by means of ethyl alcohol, methylene chloride or chloroform, to the action of ammonia or aliphatic amines. If acetylation be conducted under energetic conditions, sodium acetate[2] or potassium acetate[3] may be used, the temperature being then kept at the b. pt. of acetic anhydride.

In the W. Triggs process[4], cellulose after a preliminary softening with acetic anhydride vapor is acetylated in two stages; first with excess of acetic acid, acetic anhydride and a catalyst, and second, with excess of acid and anhydride and a reduced quantity of catalyst, the claim being made that a more uniform cellulose acetate results and one of exceptionally high stability. If it is desired to produce a cellulose acetate of low viscosity[5], the cellulose is first pretreated with acetic acid in presence of a catalyst at 38°, after which the required amount of acetic anhydride is added without cooling the mixture. The temperature is then allowed to rise to 50-66° until acetylation is complete. Finally the temperature is lowered to 38° again and there held until the mixture has become free from lumps.

Ripened viscose may be acetylated after spinning into a bath containing 40% potassium acetate and 20% acetic acid, drying and treating with acetic or propionic anhydrides for cellulose acetate or propionate formation. It is claimed the cellulose ester is of improved stability to boiling water and to ironing. In the case of cellulose bu^{t}yrate made as above, enhanced resistance to alkalis is claimed[6]. Cellulose acetate may be hydrolyzed in the presence of a

1. A. Wacker, Ges. für Elektrochemische Industrie G. m. b. H., E. P. 372241; abst. J. S. C. I. 1932, **51**, 595-B. F. P. 724957; abst. C. A. 1932, **26**, 4950. H. Dreyfus, Can. P. 328390.
2. Soc. Chem. Ind. in Basle, E. P. 380822; abst. J. S. C. I. 1932, **51**, 1074-B.
3. *Ibid.* E. P. 353978; abst. J. S. C. I. 1931, **50**, 921-B.
4. E. P. 372844; abst. J. S. C. I. 1932, **51**, 674-B.
5. C. Malm and A. Andersen, E. P. 364794; abst. Chem. Zentr. 1932, I, 2791.
6. Soc. Chem. Ind. in Basle, E. P. 367312; abst. J. S. C. I. 1932, **51**, 416-B.

solvent mixture of acetic acid and ethylene dichloride and containing a mineral acid catalyst[1], the acetone-soluble product being afterwards precipitated in hot water. Cellulose or hydrocellulose may be esterified by treatment with ketene and/or a fatty acid (C_3 or above), or an aromatic carboxylic acid or halide in liquid sulfur dioxide[2], with or without addition of a catalyst. The esters or mixed esters so produced are said to be very pure and do not require bleaching[3].

According to Courtaulds, Ltd., and R. Wormell[4], cellulose is first treated with 60% sulfuric acid in an organic liquid as ethyl acetate and the resulting cellulose sulfate, which remains undissolved, is separated and treated with acetic acid whereby the combined sulfuric acid is replaced by the acetic acid. The products contain up to 35% combined acetic acid, and may be further esterified with acetic anhydride in the presence of a catalyst. The British Celanese, Ltd.[5], pre-treat cellulose with lower aliphatic acids and then esterify with sulfuric acid as catalyst in the presence of a solvent or non-solvent for the cellulose ester. After precipitation or separation, the ester of high acetyl content, is heated with water under pressure whereby its sulfur is eliminated and the solubility and viscosity characteristics modified as desired.

The solubility of acetone-soluble acetylcellulose may be modified by treating with aqueous salt solutions capable of swelling but not dissolving the acetate[6], with the addition of a small quantity of mineral acid. Calcium or ammonium nitrate in the presence of nitric acid are recom-

1. H. Gray, C. Staud and C. Webber, E. P. 369215; abst. J. S. C. I. 1932, **51**, 500-B.
2. I. G. Farbenindustrie, A.-G., E. P. 378044; abst. J. S. C. I. 1932, **51**, 929-B. F. P. 717083; abst. C. A. 1932, **26**, 2862. Can. P. 328065.
3. British Celanese, Ltd., E. P. 362401; abst. Chem. Zentr. 1932, I, 2790.
4. E. P. 377795; abst. J. S. C. I. 1932, **51**, 929-B.
5. E. P. 377313; abst. J. S. C. I. 1932, **51**, 929-B.
6. Soc. des Usines Chimques Rhone-Poulenc, F. P. 727735; abst. C. A. 1932, **26**, 5753.

mended. To stabilize the acetylated cellulose[1], it is advised to neutralize the catalysts contained in the crude solution after termination of the esterification, and then heat the reaction mass to a high temperature. A method for purifying and hydrolyzing acetylcellulose has been patented[2], in which it is precipitated from its crude solutions in solvents insoluble in water with recovery of the solvent, by neutralizing the catalyst, partially de-acidifying the solution, and passing it in a very finely divided state into water which is kept at a temperature above the b. pt. of the azeotropic mixture solvent-water-acid. The mixture which distils is condensed and the solvent separated. Chlorinated hydrocarbons may be used as the water-insoluble acetylcellulose solvents[3]. A method for acetylation has been advanced[4] in which the cellulose is acetylated in the presence of an aldehyde until the product is soluble in acetone.

A low-viscosity acetylcellulose may be made by an acetylation step in which the reaction temperature is allowed to rise above normal[5], and then completed by lowering the temperature below that usually employed. Or the cotton, wood pulp or hemp is partially acetylated in a bath containing insufficient acetylating agent for complete acetylation and a non-solvent diluent for the product[6]. Crude cellulose ester solutions may be worked up (where they contain fatty acids and water-insoluble solvents)[7], by heating with water to cause the insoluble solvent to distil off as an azeotropic mixture. The cellulose ester remaining in the dilute solution of fatty acid is isolated by addition of water or other precipitating agent. Thus, a crude solution

1. I. G. Farbenindustrie, A.-G., F. P. 720027; abst. C. A. 1932, **26**, 3918.
2. *Ibid.* F. P. 718529; abst. C. A. 1932, **26**, 3376.
3. *Ibid.* F. P. 718472; abst. C. A. 1932, **26**, 3110.
4. Kodak-Pathe, F. P. 725699; abst. C. A. 1932, **26**, 4950. T. Murray, Jr., and H. Gray, Can. P. 322871; abst. C. A. 1932, **26**, 4173.
5. *Ibid.* F. P. 725908; abst. C. A. 1932, **26**, 4950.
6. *Ibid.* F. P. 728785; abst. C. A. 1932, **26**, 6135.
7. I. G. Farbenindustrie, A.-G., W. Walter, R. Hofmann and F. Oschatz, D. R. P. 554783; abst. C. A. 1932, **26**, 6135.

of acetylcellulose, acetic acid, water and ethylene dichloride is treated with a slight excess of sodium acetate to deaden the catalyst remaining in solution, water is added and the ethylene chloride distilled off. The cellulose acetate is then precipitated by addition of water.

Fatty acid cellulose esters are prepared by impregnating cellulose with concentrated solutions of neutral salts of strong acids which accelerate the acylation of the cellulose[1], drying, and then treating with acetic anhydride. Thus, cotton treated with potassium thiocyanate solution, dried and heated with acetic anhydride gives cellulose acetate. In order to increase the acid-resisting characteristics of acetylcellulose[2], it is recommended to form a cellulose chloracetate by suspending or dissolving the acetate in an indifferent medium as tetrachlorethane and chlorinating with phosphorous pentachloride[3]. Where cellulose is pretreated with formic acid, and then esterified with acetic acid, anhydride and a small amount of acetyl chloride[4], an unusually stable cellulose ester is said to result. *iso*-Propylnaphthalenesulfonic acid[5] has been added to the acetylating bath with sulfuric acid as catalyst. Nitrogen tetraoxide has also been claimed as a catalyst in cellulose acetylation[6].

C. Dreyfus[7] esterifies cellulose in the presence of a catalyst and *iso*propyl ether is added to precipitate the cellulose acetate. Or[8], the cellulose ester may be formed by a suspension method in the presence of sulfuric acid as catalyst, and is then treated with an aqueous liquid at superatmospheric pressure and at a temperature above 100°. The ester recovered is said to contain little or no sulfur

1. Soc. Anon. Pour L'Ind. Chim. A Bale, D. R. P. 554696; abst. C. A. 1932, **26**, 6135.
2. R. Kuhn, D. R. P. 535650; abst. C. A. 1932, **26**, 1438.
3. E. Hubert, D. R. P. 544777; abst. C. A. 1932, **26**, 3667.
4. I. G. Farbenindustrie, D. R. P. 546281; abst. C. A. 1932, **26**, 3376.
5. *Ibid.* Swiss P. 134626.
6. Kodak, A.-G., D. R. P. 554948; abst. C. A. 1932, **26**, 6134.
7. Can. P. 323382; abst. C. A. 1932, **26**, 4470.
8. C. Dreyfus and G. Schneider, Can. P. 323997; abst. C. A. 1932, **26**, 4717.

compound and to be partially soluble in acetone. No ripening is required[1]. Where the cellulose contains more than 8% water[2], it is esterified in presence of iron, cobalt, nickel, manganese or copper chloride. Ferric chloride is specifically recommended as catalyst[3]. The ripening of the acetate is stopped when the acetyl value of the finished ester is between 56-60%[4].

In a process as developed by H. Dreyfus[5], cellulose is esterified by the usual action of acetic acid, anhydride and sulfuric acid, and the product ripened until it shows a minimum viscosity in an anhydrous, water-miscible solvent as acetone, the ripening being thereafter continued until a product is obtained having in a solution of equal concentration in the solvent diluted with water, a lower viscosity than the minimum viscosity in the anhydrous solvent[6]. Three gram mols. of acetic anhydride are used as esterification medium for each gram mol. cellulose[7], together with a further quantity of acetic anhydride not less than 8 times the weight of the cellulose, together with sulfuric acid as catalyst, thus producing esters of very high viscosity. The cellulose acetate produced may be purified by extraction with chloroform or methylene chloride or other chlorinated hydrocarbon that is a solvent for those constituents that are not readily soluble in solvents for the main bulk of the cellulose acetate[8].

C. Jayme[9] first treats the cellulose with acetic acid to dissolve out impurities and render the cellulose active to the acetylating reaction, washing the cellulose with acetic acid to remove the impurities[10]. V. Yarsley[11] claims the

1. C. Dreyfus and G. Schneider, Can. P. 323998; abst. C. A. 1932, **26**, 4717.
2. H. Dreyfus, Can. P. 322980, 322982.
3. *Ibid.* Can. P. 322979.
4. C. Dreyfus, F. P. 728344; abst. C. A. 1932, **26**, 5754.
5. U. S. P. 1872701; abst. C. A. 1932, **26**, 6135.
6. H. Dreyfus, Can. P. 322574.
7. *Ibid.* U. S. P. 1862589; abst. C. A. 1932, **26**, 4173. U. S. P. 1872701. D. Mason, Can. P. 325396.
8. W. Whitehead, Can. P. 326249; abst. C. A. 1932, **26**, 6135.
9. Can. P. 327755. 10. H. Gray, Can. P. 327633.
11. Brit. Plastics, 1931, **3**, 284; 1932, **3**, 344.

major portion of the acetic acid normally employed in cellulose esterification may be replaced by liquid sulfur dioxide, which is removed from the acetylation mixture by simple distillation and recovered for further use by condensation, the cellulose acetate at the same time being precipitated as a white, fibrous mass. It also offers possibilities of control during acetylation in that the temperature of the reaction mixture may be reduced by allowing some of the sulfur dioxide to evaporate, and it has a favorable catalytic effect on the reaction[1]. F. Ohl[2] has discussed the recent trend in cellulose acetate preparation.

Preparation of Other Organic Cellulose Esters. Esters such as cellulose acetonitrate, propionitrate or butyronitrate may be prepared from usual pre-treated cellulose by acetylation in the presence of nitrogen dioxide, nitrogen tetroxide or nitric acid in the presence also of oxygen[3]. In another process[4], a partially de-esterified cellulose acetate, made in the usual manner, is treated in anhydrous solution with a nitrating agent. A cellulose acetonitrate has been described[5], containing but 0.01-0.02% N, obtained by acetylation in presence of urea or ammonium nitrate. The Kodak A. G.[6] have described cellulose acetonitrates prepared by adding at least 4% of nitrogen dioxide or tetroxide to the usual acetylation mixture during the esterification process. A cellulose aliphatic ester having free hydroxyl groups such as cellulose diacetate, dipropionate or dibutyrate[7], is treated with diacetyl-*o*-nitric acid and a dehydrating agent. F. Ohl[8] has reviewed and discussed the

1. C. Malm, Can. P. 325531.
2. Kunstoffe, 1932, **22**, 135; abst. C. A. 1932, **26**, 4170.
3. R. v. Dyke, C. Webber and C. Staud, E. P. 358436; abst. C. A. 1932, **26**, 6135.
4. C. Staud and C. Waring, U. S. P. 1884338.
5. W. Walter and L. Lock, U. S. P. 1819397. E. P. 344761, Addn. to E. P. 319285. F. P. 38797, Addn. to F. P. 681754; abst. Chem. Zentr. 1932, I, 1969.
6. D. R. P. 554697; abst. C. A. 1932, **26**, 6135.
7. Deutsche Celluloid-Fabrik, E. P. 354221; abst. C. A. 1932, **26**, 5419.
8. Kunstseide, 1931, **13**, 420; abst. C. A. 1932, **26**, 2861.

literature and patents on the preparation of the cellulose acetonitrates.

H. Clarke and C. Malm[1] have described a method for mixed cellulose ester formation of wide applicability, comprising mixing the aliphatic or aromatic acid with chloracetic anhydride and magnesium perchlorate for cotton esterification. In this manner cellulose aceto-propionate, -butyrate, -valerate, -caproate, -caprate, -laurate, -myristate, -palmitate, -benzoate, -*o*-methoxybenzoate, -crotonate, -*o*-chlorbenzoate, -acetylsalicylate, -phenylacetate, -hydrocinnamate, and -cinnamate may be produced, of widely varying solubility characteristics. In general, these mixed esters are soluble in acetone and chlorinated hydrocarbons. A new cellulose derivative has been described[2] obtained by heating cellulose with epichlorhydrin, and contains the group $O.CH_2.CH.CH_2ClOH$, in which the chlorine is interchangeable.

The solubility of the cellulose laurates may be increased by heating them at below 200° in a liquid medium with an acid agent, and in the absence of water[3]. Textile filaments or fabrics may be esterified by treatment with a higher fatty acid chloride in association with pyridine, the fibrous character of the initial material being preserved[4]. The increase in dry weight exceeds 30%. Cellulose derivatives having relatively little affinity for substantive and vat dyes are prepared by treating cellulose with a phosphonitrile halide as the chloride[5], in the presence of an acid-binding substance, and usually in the presence of a solvent.

Cellulose acetobutyrates are formed by treating cellulose with acetic acid[6], and then with butyric or *iso*butyric

1. U. S. P. 1880808. C. Webber and C. Staud, Can. P. 327630, 327631, 327632.
2. Soc. Anon. pour l'Ind. Chim. A Bale, Swiss P. 148481; abst. C. A. 1932, **26**, 4950.
3. I. G. Farbenindustrie, A.-G., Can. P. 294514.
4. R. Lant, Can. P. 322195.
5. Soc. Anon. pour L'Ind. Chim. A Bale, D. R. P. 553069; abst. C. A. 1932, **26**, 4717.
6. Societe des Usines Chimiques Rhone-Poulenc, D. R. P. 542868, Addn. to D. R. P. 505610; abst. C. A. 1932, **26**, 3110.

anhydrides in the presence of an esterifying catalyzer and a diluent. Thus, hydrocellulose is stirred with glacial acetic acid and treated with a bath containing butyric acid, butyric anhydride and zinc chloride. The product is a viscous solution from which cellulose acetobutyrate may be precipitated by water. Cellulose naphthenates have been described[1], prepared in the same general manner, and by the preliminary esterification with acetic acid, cellulose acetonaphthenates result. A photographic substratum has been described prepared from a "cellulose ester-stearin"[2].

Cellulose derivatives of varying composition have been described[3], obtained by partial double decomposition between the halides of oxyacids of phosphorus, and alcohols and phenols caused to react with the cellulose in the presence of tertiary bases. Thus, cotton is boiled with the dichloride of the triphenylcarbinol ester of phosphorous acid, giving a product which has a good affinity for basic dyes. Products like cellulose acetobutyrate, cellulose butyropropionate (propiobutyrate) and starch acetobutyrate may be made by treating cellulose or starch with acetic anhydride or propionic anhydride in quantity calculated to produce the triacidylate, together with another aliphatic acid component of different character such as butyric acid with or without a catalyst as sulfur dioxide, zinc chloride or sulfuric acid[4]. Artificial filaments from the above have been described[5].

K. Hess and F. Klages[6] have described water soluble dextrins obtained by the acetolysis of cellulose, and the products formed by their methylation, and L. Clement[7] a method for separating cellulose acetate and nitrocellulose

1. I. G. Farbenindustrie, A.-G., D. R. P. 551253, Addn. to D. R. P. 515106; abst. C. A. 1932, **26**, 4470.
2. Schering-Kahlbaum, A.-G., F. P. 704880.
3. Soc. Anon. Pour L'Ind. Chim. A Bale, F. P. 718257; abst. C. A. 1932, **26**, 3110.
4. I. G. Farbenindustrie, A.-G., E. P. 356665; abst. C. A. 1932, **26**, 5753.
5. *Ibid.* E. P. 351438; abst. C. A. 1932, **26**, 5419.
6. Ann. 1932, **497**, 234; abst. C. A. 1932, **26**, 5419.
7. U. S. P. 1866965; abst. C. A. 1932, **26**, 4718.

film scrap. In a study of the action of fluorosulfonic acid on cellulose[1], it was found that cellulose dissolves in 3-4 times its weight of fluorosulfonic acid to a clear, brown, viscous liquid which mixes in water to a clear solution, and appears to contain cellulose tri- and tetra-fluorosulfonate. H. Pringsheim, E. Lorand and K. Ward[2] have given detailed results on the higher fatty acid esters of cellulose.

Cellulose Ester Solvents. Dichlorethylene[3] or trichlorethylene[4] may be stabilized by adding a small quantity of paraffin oil, hydrogenated naphthalene, turpentine oil, phenol, quinone, hydroquinone, hexalene, colophony, coumarone resin, oleic acid, trimethylamine, triethylamine, pyridine or quinoline. Plasticizers have been described[5] composed of *bb*-di(*p*-hydroxyphenyl)propane or 1.1-di(*p*-hydroxyphenyl)cyclohexane, used in conjunction with phenyl or tolyl phosphate. When *bb'*-dichlordiethyl ether is heated with mercury, silver, lead or copper oxides, dioxane is formed[6]; *b*-chlorethyl ether gives glycolmethylene ether.

C. Dreyfus[7] has described the production of a plastic mass of organic cellulose derivatives and *p*-tolueneethylsulfonanilid[8], and Usines de Melle[9] methods for the production of diacetone alcohol by condensing acetone with KOH in alcohol until a reaction is obtained with cresol red but not with *o*-cresolphthalein. The solvent mixture of J. Walsh and A. Caprio for cellulose acetate[10] comprises a mixture of ethyl alcohol, ethyl acetate and water in such proportions

1. C. Möllering, J. pr. Chem. 1932, (ii), **134**, 209; abst. J. S. C. I. 1932, **51**, 1022-A.
2. Cellulosechemie, 1932, **13**, 119; abst. C. A. 1932, **26**, 6123; J. S. C. I. 1932, **51**, 836-A.
3. M. Mugdan and J. Sixt, D. R. P. 555373; abst. C. A. 1932, **26**, 5106. See F. P. 714995.
4. Consortium für Elektrochemische Industrie G. m. b. H., F. P. 726362; abst. C. A. 1932, **26**, 4829.
5. British Celanese, Ltd., and W. Moss, E. P. 372327; abst. J. S. C. I. 1932, **51**, 807-B.
6. H. Dreyfus, E. P. 374134; abst. J. S. C. I. 1932, **51**, 832-B.
7. C. Dreyfus and G. Schneider, Can. P. 323142.
8. C. Dreyfus, Can. P. 322977.
9. Usines de Melle (formerly Soc. anon. des distilleries des Deux-Sevres), E. P. 356609; abst. C. A. 1932, **26**, 5578.
10. U. S. P. 1867040; abst. C. A. 1932, **26**, 4718. Can. P. 312793.

that the solvent evaporates uniformly. F. Wittka has described the manufacture of glyceryl polyricinoleate[1], and K. Klemm and L. Friedman[2] a study of the structure of gels of cellulose acetate in benzyl alcohol by measuring diffusion into the gels.

The velocity of dissolution of cellulose acetate in cyclohexanone, ethyl acetate, methyl phthalate and diacetone alcohol follows a normal course[3], but the curves representing the velocity of dissolution in methylethyl ketone are complex and suggest "autopeptisation," increased swelling due to the peptising action of the substances already in solution. The solubility varies with the amount of solid phase present. In the fractional solution of acetone-soluble acetylcellulose[4], the addition of increasing amounts of carbon tetrachloride or benzene to acetone or methyl acetate, decreases their solvent power for acetylcellulose, the solubility being independent of the amount of solid present. The position and shape of the curve of solubility *vs:* percentage of methyl acetate vary with different acetylcelluloses but are practically the same with carbon tetrachloride or benzene added to the solvent. With acetone substituted for methyl acetate the position is different, but the form is the same. Five fractions of the ester dissolved by different benzene-methyl acetate mixtures had equal contents of acetic acid but varied in viscosity.

In a research upon the sorption of alcohol vapors by cellulose and cellulose acetate[5], it is found that the amount of alcohol adsorbed under the saturated vapor pressure at 30° increases, with the acetyl content of the primary acetates, which have a smaller adsorption capacity than secondary acetates. Higher alcohols are usually adsorbed

1. F. Wittka, Swiss P. 151317; abst. C. A. 1932, **26**, 4825.
2. J. A. C. S. 1932, **54**, 2637.
3. W. Ostwald and H. Ortloff, Kolloid Zts. 1932, **58**, 295; abst. C. A. 1932, **26**, 3172; J. S. C. I. 1932, **51**, 465-A.
4. I. Sakurada and M. Taniguchi, J. S. C. I. Japan, 1932, **35**, 249; abst. C. A. 1932, **26**, 4947; J. S. C. I. 1932, **51**, 766-B.
5. S. Sheppard and P. Newsome, J. Phys. Chem. 1932, **36**, 2306; abst. C. A. 1932, **26**, 5241.

and desorbed more slowly than lower alcohols. The number of mols. absorbed per gram of adsorbent, decreases with the mol. wt. of the alcohol, but is practically constant from butyl alcohol to octyl alcohol. A solvent mixture has been granted patent protection in France[1], especially applicable to esters such as cellulose malate, maleate, levulinate or pyruvate, comprising a mixture of ethylene chloride with a monohydroxy aliphatic alcohol containing 1-5 C-atoms (i.e. methyl alcohol to amyl alcohol).

D. Keyes[2] has detailed practical general methods for ester formation, including the preparation of methyl and ethyl acetates, ethyl lactate, ethyleneglycol diacetate, ethyl chloride, diethyl carbonate, and amyl acetate by alcoholysis. Processes for the manufacture of dichlorethylene[3], dihydroxyacetone[4], and acetone[5] have been published. The cellulose acetate mixed solvent of S. Carroll[6] is methyl acetate 50, ethyl acetate 40 and acetone 40-10 parts to form a solution containing 30% cellulose. Cellulose acetate moistened with ethyl lactate and then dissolved in ethyl phthalate[7] has been put forward as a lubricant.

Organic Cellulose Ester Filaments and Fabrics. In fabrics composed of real silk and cellulose acetate filaments[8], the silk may be degummed by treatment with an alkaline liquor having a *p*H value not exceeding 10.5. H. Dreyfus has described a stretching treatment for cellulose acetate threads, yarns or warps[9] in which the threads are stretched

1. Soc. Kodak Pathe (Soc. anon. Francaise), F. P. 692051; abst. C. A. 1932, **26**, 1379.
2. I. E. C. 1932, **24**, 1096.
3. A. Ruppert, W. Fischer, J. Voigt and B. Hennig, U. S. P. 1868077; abst. C. A. 1932, **26**, 5106.
4. W. Lenz, D. R. P. 554000; abst. C. A. 1932, **26**, 5578. See D. R. P. 539268.
5. L. Schlecht, D. R. P. 553786; abst. C. A. 1932, **26**, 5578. See F. P. 688074.
6. U. S. P. 1866964; abst. C. A. 1932, **26**, 4718.
7. C. Staud and J. Fuess, U. S. P. 1866732.
8. G. Ellis, U. S. P. 1867660. C. Dreyfus, Can. P. 322978.
9. British Celanese, Ltd., and W. Taylor, E. P. 371910; abst. J. S. C. I. 1932, **51**, 595-B. H. Dreyfus, E. P. 378074; abst. J. S. C. I. 1932, **51**, 930-B. F. P. 725266; abst. C. A. 1932, **26**, 4965. See also A. Wacker Ges. für Elektrochemische Industrie G. m. b. H., F. P.

between two points between which a swelling or solvent agent is applied, which is afterwards removed either by evaporation or washing. For softening acetate filaments, treatment with a fatty material and lecithin is recommended[1], or by applying to the filament or fabric a finish containing glyceryl monoöleate, diethyleneglycol and a soap[2]. Cellulose acetate threads may also be made more supple and resistant during textile operations[3] by treating them with a 2-10% solution of magnesium or calcium chlorides in water or an alcohol[4]. To fuse cellulose into a compact mass without substantial decomposition[5], heating the ester with water under a pressure exceeding 100 lb. per sq. in., will substantially liquefy it[6].

For the partial saponification of cellulose ester material as cellulose acetate[7], C. Dreyfus and H. Platt treat the cellulose ester with aqueous solutions of sodium or potassium hydroxides, carbonates, silicates or sulfides of 3-7% strength. As softening agents for cellulose ester filaments or fabrics[8], water-soluble salts of aliphatic primary or secondary aminocarboxylic acids substituted by higher fatty acid residues as the nitrogen are used, examples being stearylsarcosine, or the condensation product of stearyl chloride and sodium butylaminoacetate and palmitylsarcosine. Or[9], the acetylcellulose textile may be treated with a mixture of a water-insoluble fatty acid amide (except *N*-hydroxyalkyl derivative) and a sulfonated higher alcohol, examples being the use of palmitamide with sulfonated dichlorhydroxy-hard paraffin C_{24}-C_{27}; stearamide with

725003; abst. C. A. 1932, **26**, 4952. D. R. P. 542891; abst. C. A. 1932, **26**, 3111. Can. P. 324207.

1. C. Dreyfus and W. Whitehead, Can. P. 325613; abst. C. A. 1932, **26**, 5771.
2. *Ibid.* Can. P. 325614; abst. C. A. 1932, **26**, 5771.
3. H. Dreyfus, F. P. 723856; abst. C. A. 1932, **26**, 4953.
4. R. Parkinson and F. Reeson, Can. P. 325862.
5. C. Dreyfus and G. Schneider, Can. P. 323999.
6. B. Borzykowski, E. P. 347241; abst. C. A. 1932, **26**, 2863.
7. C. Dreyfus and H. Platt, U. S. P. 1884623. Can. P. 324413.
8. E. Glietenberg, D. R. P. 550905; abst. C. A. 1932, **26**, 4965.
9. I. G. Farbenindustrie, A.-G., E. P. 374029; abst. J. S. C. I. 1932, **51**, 839-B.

lauryl hydrogen sulfate; palmitamide with sulfonated cetyl or oleyl alcohols, or by the use of a sulfonated oleamide.

In producing very fine threads as by spinning an acetone solution of cellulose acetate[1], there is employed in the spinning bath concentrated aqueous solutions of polyhydroxy compounds, which are readily soluble in or miscible with water, so that viscous "oily" solutions of 30-60% can be obtained. There may be used carbohydrates such as grape sugar, sucrose, invert sugar, concentrated beet juice, molasses, vinasse, sulfite waste liquor, glycol or glycerol, in connection with ammonium thiocyanate, ammonium chloride or calcium chloride. To produce coherent structures from textile filaments and fabrics[2], the cellulose material of the fabric is partially converted into cellulose fatty acid esters without destroying the physical structure of the material, by esterification with a relatively concentrated solution of higher fatty acid chlorides in pyridine, but without any other diluent.

Cellulose acetate silk may be improved by treatment with swelling baths containing halogenated hydrocarbons and stretching the swollen threads. Deleterious effects of the baths on the threads may be obviated by the addition to the baths of small quantities of unsaturated organic substances such as butylene, olein, olive oil, linseed oil or linolic acid[3]. The properties of cellulose ester threads are said to be improved by drawing the threads in the presence of swelling agents[4]. Thus, viscose rayon is acetylated, washed and dried, and then drawn in a 40% aqueous solution of pyridine[5]. In producing voluminous rayon[6], in order to facilitate gas formation in the spinning solution,

1. I.G.Farbenind., A.-G., E. P. 347144; abst. C.A. 1932, **26**, 2863.
2. R. Lant, E. P. 376295; abst. J. S. C. I. 1932, **51**, 932-B.
3. H. Suter, E. P. 363929; abst. The Textile Mfr. 1932, **58**, #690, 249.
4. Soc. anon. Pour L'Ind. Chim. A Bale, F. P. 717998; abst. C. A. 1932, **26**, 2863.
5. Soc. pour L'Industrie Chim. Basle, Belg. P. 378385.
6. A. de Wilde, Holl. P. 26910; abst. C. A. 1932, **26**, 4718.

naphthalene, nitronaphthalene, anthracene, camphor or diphenylamine (less than .01%) is added to the spinning bath.

In the dry spinning of solutions of organic derivatives of cellulose[1], a greater degree of stretching is made possible and therefore a considerably stronger filament is obtained, if, immediately after the extrusion of the filament, the solvent is replaced by a swelling liquid. To effect this, the upper part of the spinning cell is partioned off as a swelling chamber and is fitted internally with a spiral gutter in which a continuous flow of the swelling agent is maintained. For the scouring of fabrics mixed with acetate silk[2], the addition of pine oil to the scouring soap solution and the emulsification of the mixture at 90° is suggested for increasing the fastness to boiling. The scouring takes place at 75-80°, whereby the rayon does not show any decrease in strength and has obtained a slightly matt surface so that its luster is equal to that of natural silk. By using a second scouring bath, degumming soap may be recovered from the first bath.

In a comprehensive investigation on the sizing of acetate silk[3], strength, elongation at rupture, elasticity, residual elongation, rigidity, slipping properties, amount of size fixed on the fiber and penetration of the size were determined on Rhodiaseta brands acetate filaments sized with diastase-treated starch, soluble starch, ammonium alginate, gelatin, boiled linseed oil + carnauba wax, Japan wax and starch + alginate, and compared with the corresponding values for the unsized fiber. The change in strength on sizing varied from —9.3% (linseed oil at end of 7 days) to 16.5% (diastase-treated starch); the strength of fiber sized with linseed oil increased with time, and at the end of 21 days was 5.5% higher than that of the unsized fiber.

1. I. G. Farbenindustrie, A.-G., E. P. 341021; abst. Rayon and Synthetic Yarn J. 1932, **15**, 10.
2. W. Fermazin, Melliand Textilber, 1932, **13**, 82; abst. C. A. 1932, **26**, 4956; Chem. Zentr. 1932, I, 2254.
3. G. Farkas, Russa, 1932, **7**, 45, 171, 313; abst. C. A. 1932, **26**, 6145.

Sizing in most cases increased elasticity, the increase being most pronounced with boiled linseed oil and with gelatin. The rigidity (determined by Tchoubar's method) was practically unaffected by Japan wax or by boiled linseed oil + carnauba wax, was slightly increased by ammonium alginate and by soluble starch, and was increased to 1.20 by boiled linseed oil, 1.24 by gelatin and 1.58 by diastase-treated starch (as compared with the unsized fiber taken as 1). Best penetration (determined by photomicrographs) was obtained with soluble starch, ammonium alginate, and especially boiled linseed oil. It is concluded that best results from the standpoint of weaving are obtained by sizing with boiled linseed oil and ammonium alginate. Desizing is facilitated by adding to the soap solutions of special products such as Pellastol EN or triethanolamine. A. Lauffs[1] has described the influence on the properties of acetate silk by means of ordinary waxing agents, and G. Rudolph[2], the sizing of rayon.

E. Schuelke[3] has pointed out that in the cleaning of acetate fabrics, whereas most cleaning agents swell the filaments, in practice a swelling due to the absorption of a solvent up to the weight of the goods is not harmful. Cellulose acetate fabrics when boiled 15 min. in trichlorethylene, with or without soap, were found uninjured, but some dyes were not fast to this treatment. Trichlorethylene is recommended as preferable to carbon tetrachloride. F. Verpillot[4] has reported on the linseed oil sizing of artificial filaments, and their desizing[5].

In one method of filament manufacture[6], the filaments are dried by a current of dry air moving downwards, the lower part of the spinning cell being surrounded by a heating envelope, while the upper part is surrounded by a heat-

1. Seide, 1932, **37**, 83; abst. Chem. Zentr. 1932, I, 2654.
2. Kunstseide, 1932, **14**, 14; abst. C. A. 1932, **26**, 2869.
3. Rayon, 1932, **13**, #6, 12; abst. C. A. 1932, **26**, 6145.
4. Russa, 1932, **7**, 23; abst. C. A. 1932, **26**, 2869.
5. Heberlein & Co., A.-G., E. P. 367965; abst. J. S. C. I. 1932, **51**, 417-B.
6. Aceta G. m. b. H., F. P. 725721; abst. C. A. 1932, **26**, 4952.

ing chamber in communication with the gas exit which is at the lower part of the cell. In hydrolyzing the acetylcellulose[1], and amount of water is used more than 45% of the weight of the dry cellulose over that of the water required for binding excess of acetic anhydride.

In the process of British Celanese, Ltd., C. Addy and H. Sims[2], filtered solutions of organic cellulose derivatives are extruded through relatively large orifices into an evaporative atmosphere to effect a preliminary concentration to a point where the derivative is still in the dissolved condition, and the concentrated solution is then extruded to form the finished product. The evaporative medium may be circulated in a closed path through the cell and a cooling chamber by convection alone, and made to impinge on the filaments issuing from the nozzle from one side only of the cell[3]. In another method of procedure[4] in the downward dry spinning, the evaporative atmosphere is drawn off from a point at or towards the upper end of the spinning cell, a stationary deflector being placed at one end of the cell at a short distance below the spinning nozzle so that the atmosphere traveling up that side of the cell is made to pass obliquely or horizontally across the face of the nozzle. For the manufacture of untwisted acetate silk[5], 3 or 4 individual fibers in definite distances are treated with dissolving or swelling agents (as acetone-water 80:20) dissolved in acetone. Or the fibers may be sprinkled with solvent in conjunction with dry spinning between the spinner and the absorption apparatus.

To produce highly flexible films[6], a solution containing an organic cellulose derivative with 2-20 wt./% each of a

1. Algemeene Kunstzijde Unie N. V., Holl. P. 24805; abst. C. A. 1932, **26**, 2053. Holl. P. 26266; abst. C. A. 1932, **26**, 3919.
2. E. P. 377233; abst. J. S. C. I. 1932, **51**, 930-B.
3. "Chatillon" Soc. Anon. Ital. per la Seta Artificiale, E. P. 372503; abst. J. S. C. I. 1932, **51**, 795-B.
4. Courtaulds, Ltd., and C. Diamond, E. P. 368022; abst. J. S. C. I. 1932, **51**, 417-B.
5. N. V. Nederlandsche Kunstzijdefabriek, Holl. P. 23541; abst. Chem. Zentr. 1932, I, 2258.
6. British Celanese, Ltd., E. P. 369896; abst. J. S. C. I. 1932, **51**, 417-B.

di- or poly-hydric alcohol (ethyleneglycol or glycerol), and an oleaginous substance (fatty acid, glyceride or mineral oil) is extruded into a coagulating medium or evaporative atmosphere. Or the spinning solution (as cellulose acetate in acetone)[1] may be extruded through a film of limited thickness composed of a coagulating liquid which is less volatile than the solvent (as aqueous diacetone alcohol or ethyl lactate or tartrate), so that the filaments carry with them an amount of liquid insufficient to cause them to cling together, the filaments being finally set by the usual dry spinning methods. The solvents or swelling agents used in the coagulating bath, after-treatment bath, or spinning solution, consist of lower aliphatic acid esters of di- or poly-hydric alcohols other than mono- or di-acetin, such as glycol or methylglycol monoacetates[2].

In spinning cellulose acetate filaments by the wet spinning process[3], improved results are said to be obtained where the spinning bath contains a relatively high-boiling solvent (20% of ethyl lactate) and a lower aliphatic acid (30% acetic acid), preferably with the addition of such substances as sodium acetate which reduce the solubility of the acid and/or the high-boiling solvent in the non-solvent medium, water being suitable. In the fixation of extruded acetylcellulose filaments[4], liquids are applied to the filaments by their longitudinal movement in contact with a surface fed by a film or liquid and transversely to this surface. By this means a spinning solution may be extruded through an amount of coagulating liquid insufficient to cause the union of the threads, and higher spinning speeds thereby obtained[5].

1. British Celanese, Ltd., and W. Taylor, E. P. 371360; abst. J. S. C. I. 1932, **51**, 675-B.
2. British Celanese, Ltd., W. Dickie and P. Sowter, E. P. 378858; abst. J. S. C. I. 1932, **51**, 977-B. See E. P. 340324, 340436.
3. *Ibid.* E. P. 380819, Addn. to E. P. 340324; abst. J. S. C. I. 1932, **51**, 1074-B.
4. H. Dreyfus, F. P. 726030; abst. C. A. 1932, **26**, 4953.
5. A. Bosse, A. Seidel and H. Sedlacek, D. R. P. 551792; abst. C. A. 1932, **26**, 4951.

Solutions of acetylcellulose may be spun by the wet method with strong drawing[1], by using as solvent a mixture of non-solvents, one at least of which is soluble in the precipitating bath. An example is given of draw-spinning a solution of acetylcellulose in a mixture of cellulose acetate in dichlorethylene and ethyl alcohol, with water at 40-50° as precipitating bath. Hollow or voluminous filaments are obtained by dry spinning cellulose derivatives by applying a precipitating agent to the filaments at the start of their drying and afterwards provoking a rapid evaporation of the solvent[2].

In the formation of thin-walled tubes of cellulose acetate[3], the product is removed from a form by turning inside out after deposition (suitably from a mixture of cellulose acetate in a mixture of ethyl acetate, methyl alcohol and toluene, or methyl acetate and diglycol phthalate (glycol phthalate), and a softening agent as methyl-*p*-toluenesulfamide[4]. In the production of bristles, straw and similar products of reduced luster from acetylcellulose or cellulose ethers (see pp. 2173, 2373), a suspension of a white pigment as titanium dioxide in ethyleneglycol is applied to a number of filaments, which are then made to coalesce by treatment with acetone[5]. Or[6], finely divided antimony oxide with olive oil or ethyleneglycol may be incorporated in the solution before spinning, or in the spun filaments by means of a swelling agent. Very finely divided bismuth oxychloride, hydroxide or oxide[7] has also been patented as a dulling agent in this connection, or by precipitating calcium, strontium, barium or lead sulfates in

1. A. Wacker Ges. für Elektrochemische Industrie, G. m. b. H., F. P. 717419; abst. C. A. 1932, **26**, 2863; Chem. Zentr. 1932, I, 2115.
2. H. Dreyfus, F. P. 728348; abst. C. A. 1932, **26**, 5756.
3. R. Serenyl, E. P. 353208; abst. C. A. 1932, **26**, 5419.
4. R. Weingand, U. S. P. 1864006; abst. C. A. 1932, **26**, 4470.
5. British Celanese, Ltd., E. P. 376833; abst. J. S. C. I. 1932, **51**, 930-B. C. Dreyfus, F. P. 726301; abst. C. A. 1932, **26**, 4952.
6. *Ibid.* E. P. 377486; abst. J. S. C. I. 1932, **51**, 930-B.
7. *Ibid.* E. P. 378319; abst. J. S. C. I. 1932, **51**, 930-B. See E. P. 378228.

nuclei at the surface of the filament[1], e.g., by emulsifying with the solution before spinning, or by the use of barium or strontium oleates in an organic solvent which is but little soluble in the solution[2]. In the softening of filaments, there has been described alkyl xanthates above C_6 as sodium, potassium or ammonium cetylxanthates[3], or xanthates formed from alcohols corresponding with cocoanut oil acids, these products also exerting a delustring action.

H. Franke[4] steeps the acetylcellulose filaments in 0.4% aqueous titanium sulfate at 80°, hydroextracted, and then heated in an autoclave at 1.5-3 atms. Alternately, the filaments are steeped for 2-24 hrs. at room temperature in 10-30% aqueous calcium, lithium or magnesium chlorides and then immersed 1-20 min. in a boiling bath containing naphthalenesulfonic acid 0.208%, pyrogallol 0.21%, anthranilic acid 0.137%, phosphoric acid 0.066% or HCl 0.365%, most satisfactory results being obtained with the latter. The luster of textiles containing cellulose acetate or cellulose ethers[5] is increased or made uniform by a treatment with superheated steam under pressure.

Laminated Glass. Glass sheets are united with an intervening sheet of acetylcellulose containing butyl tartrate as plasticizer[6], the clarity of the product being improved by treating the cellulose ether in finely divided form with a liquid or solvent which is a non-solvent for the bulk of the cellulose derivative (ether being suitable for treating acetone-soluble acetylcellulose)[7]. A urea-phenol-formalde-

1. Algem. Kunstzijde Unie N. V., E. P. 375735; abst. J. S. C. I. 1932, **51**, 881-B.
2. A. Kampf, D. R. P. 538026, Addn. to D. R. P. 500008; abst. C. A. 1932, **26**, 1784.
3. Deuts. Hydrierwerke, A.-G., E. P. 369977; abst. J. S. C. I. 1932, **51**, 769-B.
4. Kunstseide, 1932, **14**, 300; abst. J. S. C. I. 1932, **51**, 1076-B.
5. H. Dreyfus, F. P. 39564, Addn. to F. P. 686644; abst. C. A. 1932, **26**, 4964.
6. W. Moss, U. S. P. 1849504; abst. C. A. 1932, **26**, 2838. See U. S. P. 1831462. Can. P. 318145.
7. British Celanese, Ltd., E. P. 353849; abst. C. A. 1932, **26**, 5418. See U. S. P. 1849504.

hyde synthetic resin may be added to increase the tensile strength[1], or a resin made by polymerizing lactic acid alone[2] may be incorporated with the cellulose derivative. If it is desired to prepare the glass in a "flexible" condition[3], the wires of a metal screen are lightly coated with a phenol-aldehyde resin, and the material then coated and its meshes closed with cellulose acetate or a cellulose ether. Chance Bros. & Co., Ltd.[4], have described a method for incorporating the metallic reinforcement.

According to the process of J. Sherts[5], after uniting the different materials by heat and pressure, a higher fluid pressure is applied, as while the sheets are immersed in ethyl carbitol. A synthetic resin made from aniline and formaldehyde[6], or an alkyd resin under a pressure increasing from 50-200 lb. per sq. in., and a temperature decreasing from 110° to room temperature may be applied to the glass sheets with coating between[7]. A composite glass sheet may be cemented together with a non-brittle composition containing chlorinated naphthalene and a resinous adhesive, with or without the addition of a cellulose ester[8].

Translucent films suitable for use in the manufacture of non-splintering glass[9] are formed by mixing pyroxylin or other cellulose ester with sufficient solvent to form a dough-like mass, which is extruded under high pressure, the solvent being afterwards removed by evaporation, dissolving out or displacement with a non-solvent which is afterwards evaporated. In the preparation of fancy glass-

1. W. Moss and K. Crutchfield, U. S. P. 1870018; abst. C. A. 1932, **26**, 5396. Can. P. 318145, 323574.
2. W. Moss, U. S. P. 1871725; abst. C. A. 1932, **26**, 6090.
3. *Ibid.* U. S. P. 1860687; abst. C. A. 1932, **26**, 3888.
4. F. P. 725073; abst. C. A. 1932, **26**, 4929.
5. U. S. P. 1870693; abst. C. A. 1932, **26**, 5720. E. P. 369028; abst. J. S. C. I. 1932, **51**, 424-B. See U. S. P. 1781084.
6. R. Kienle and W. Scheiber, Can. P. 323870; abst. C. A. 1932, **26**, 4719.
7. H. Rohlfs, E. P. 367523; abst. J. S. C. I. 1932, **51**, 423-B.
8. H. Gardner, U. S. P. 1836914; abst. J. S. C. I. 1932, **51**, 936-B.
9. G. Esselen, E. P. 354339; abst. C. A. 1932, **26**, 5419.

ware[1], solidification of the plastic mass holding the glass together is effected by introducing through a tube into the space filled with the plastic mass, a reagent to effect the coagulation[2]. To increase adhesion[3], it is recommended to moisten the acetylcellulose sheet with triacetin before uniting with the glass under pressure. Glass sheets may be united either with a polyvinyl alcohol[4], or ethyl polyacrylate[5], and a condensation product of maleic acid or anhydride with an unsaturated alcohol or compound yielding one by splitting off water, as castor oil or butyleneglycol. Rubber may also be added to the cellulose acetate compound by means of the harmonious solvent cyclohexane[6], or a resin made by condensing formaldehyde with toluenesulfamide[7].

The "soundproof" and heat-insulating material of W. Morgan[8] comprises glass sheets with an intervening celluloid stencil, a volatile solvent as acetone being applied in uniting the material. A vacuum apparatus for effectuating the above has been devised[9]. B. Ayers[10] colors but a portion of the plastic sheet between the glass panes so as to reduce glare when used as an automobile windshield[11]. As adhesive for the cellulose derivative[12], a mixture of diethyleneglycol monoethyl ether 40, diethyleneglycol monobutyl ether 30 and butyl phthalate 30 is recommended, as is also a mixture of gelatin and diethyleneglycol[13]. Sur-

1. S. Gromov, Russ. P. 25690; abst. C. A. 1932, **26**, 5720.
2. E. Beech, E. P. 378536; abst. J. S. C. I. 1932, **51**, 888-B.
3. G. Heyl, U. S. P. 1867009; abst. C. A. 1932, **26**, 4391. J. Brier, G. Watkins and W. Brown, U. S. P. 1872663; abst. C. A. 1932, **26**, 6090.
4. I. G. Farbenindustrie, A.-G., E. P. 367633; abst. J. S. C. I. 1933, **51**, 423-B. See E. P. 349283.
5. *Ibid.* E. P. 367658; abst. J. S. C. I. 1932, **51**, 423-B. See E. P. 349283.
6. *Ibid.* E. P. 375972; abst. J. S. C. I. 1932, **51**, 888-B.
7. *Ibid.* F. P. 724002; abst. C. A. 1932, **26**, 4929.
8. U. S. P. 1848190; abst. C. A. 1932, **26**, 2838.
9. J. Drake, U. S. P. 1870284; abst. C. A. 1932, **26**, 5720.
10. U. S. P. 1872553; abst. C. A. 1932, **26**, 6090.
11. J. Drake, U. S. P. 1872692, 1872693; abst. C. A. 1932, **26**, 6090.
12. G. Watkins, Can. P. 320840; abst. C. A. 1932, **26**, 2838.
13. *Ibid.* U. S. P. 1873691; abst. C. A. 1932, **26**, 6090. Can. P. 320841; abst. C. A. 1932, **26**, 2838.

faces of glass sheets to be contacted are preliminarily coated with an adhesive skin containing a vaporizable component as gelatin containing water[1], and are then assembled with an intervening sheet such as celluloid, the assembly being heated without pressure to vaporize the volatile portion, and then united under pressure[2]. The interposed sheet of plastic material may be submitted for several hours to the action of a vacuum to remove occluded gases or vapors[3].

In a recent process the glass is first moistened with a mixture of glycerol and acetic acid[4], a sheet of gelatin then sandwiched, and the whole united by pressure[5]. A mixture of amyl acetate and acetone forms the adhesive for cellulose derivative in another process[6]. General articles on the use of acetylcellulose have been contributed by A. Bresser[7], F. Ohl[8], T. Pesch[9], R. Gilmore[10] and P. Nicolardot[11]. It is claimed that the glass substituted Flexo-Glass and Glass-Cloth transmit only about 15% of the incident light[12], but nearly as far in the ultra-violet as fused quartz.

Organic Cellulose Ester Lacquers. Glyceryl azelate (product of condensation of glycerol with azelaic acid)[13], resinous polybasic esters of monoethylin[14], synthetic resins from the action of cresol with allyl alcohol[15], are examples

1. D. Adams, U. S. P. 1873248; abst. C. A. 1932, **26**, 6090.
2. Röhm & Haas, A.-G., E. P. 379006; abst. J. S. C. I. 1932, **51**, 937-B.
3. Soc. des Usines Chimiques Rhone-Poulenc, F. P. 727055; abst. C. A. 1932, **26**, 5189.
4. C. Hermann and T. Ditton, Can. P. 327041.
5. N. Voluinkin, Russ. P. 26029; abst. C. A. 1932, **26**, 5720.
6. O. Marckworth, U. S. P. 1867085; abst. C. A. 1932, **26**, 4691.
7. Chem. App. 1932, **19**, 62; abst. C. A. 1932, **26**, 4929.
8. Glastech. Ber. 1932, **10**, 75; abst. C. A. 1932, **26**, 5718. Kunst. 1932, **22**, 179; abst. C. A. 1932, **26**, 5395.
9. Glastech. Ber. 1932, **10**, 76; abst. C. A. 1932, **26**, 5718.
10. Plastics, 1932, #8, 307.
11. Science et Vie, 1931; Ceram. et verrerie, 1932, #835, 17; abst. C. A. 1932, **26**, 2835.
12. V. Lubovich and M. Maltbie, J. Colo. Wyo. Acad. Sci. 1930, **1**, No. 2, 40; abst. C. A. 1932, **26**, 3439.
13. Deutsche Gasglühlicht-Auer-Ges, E. P. 348593; abst. C. A. 1932, **26**, 5221.
14. W. Lawson, Can. P. 324955.
15. W. Moss and G. Seymour, Can. P. 324633.

of recently advocated resinous condensation products which have been put forward as desirable additions to cellulose acetate and cellulose ether lacquers to increase the hardness and brilliancy. They have the added value of low viscosity and hence great covering power per unit weight of solvent employed.

The W. Moss coating for wood, concrete and metal comprises a primer of cocoanut oil composition over which is placed an acetylcellulose lacquer[1], to which may be added a synthetic resin formed by the reaction between 2.4-dihydroxybenzophenone and formaldehyde, and a volatile solvent[2]. Compositions of matter containing cellulose derivatives have been described by British Celanese, Ltd.[3], in which cellulose acetate with a resin obtained by condensing a chlorketone as chloracetone, with a phenol in the presence of HCl forms the lacquer base. Dihydroxybenzophenones are used as plasticizers where the synthetic resin is of the diphenylolpropane-formaldehyde type. Another formula recommended as a lacquer for either indoor or outdoor work is cellulose acetate, methylxylenesulfonamide, butyl and amyl tartrates[4]. The lacquer coating may be rendered more impermeable by applying a top coat of cellulose nitrate[5].

In the preparation of flexible wood products[6], thin wooden sheets or rods are softened by treatment with hot alkali solution, and then impregnated with substances capable of stabilizing the wood in its softened state, after which the wood is treated with a cellulose acetate lacquer as a film-forming colloid. Lacquers containing one or more mixed cellulose esters as cellulose acetobutyrate or acetonitrate[7] are worked up with 100-250 wt./% of softening

1. U. S. P. 1857161; abst. C. A. 1932, **26**, 3944.
2. W. Moss, Can. P. 325615; abst. C. A. 1932, **26**, 5777.
3. E. P. 366586, 366587; abst. J. S. C. I. 1932, **51**, 437-B.
4. H. Dreyfus, F. P. 720866; abst. C. A. 1932, **26**, 4174.
5. C. Dreyfus, Can. P. 322573.
6. R. Herzog and A. Burgeni, D. R. P. 548164; abst. C. A. 1932, **26**, 3644. Soc. Anon. Pour L'Ind. Chim. A Bale, D. R. P. 554781; abst. C. A. 1932, **26**, 6159.
7. I. G. Farbenindustrie, A.-G., E. P. 367932; abst. J. S. C. I. 1932, **51**, 518-B.

agents as *p*-toluenesulfonamide or tolyl phosphate, and volatile solvents, such lacquers being especially suitable for coating cables and insulating fabrics. Mixed cellulose esters are specified in a patented process for the manufacture of abrasives[1], as being more resistant to water and hence excellent binders capable of being hardened by poly-alcohols in which the OH-groups are esterified partly by a higher fatty acid and partly by polybasic carboxylic acids.

In the formation of shot-cartridge cases[2], the cases are first coated with a cellulose ester composition and then impregnated with a waterproofing agent as paraffin, this being applied to the ends of the cases and absorbed into the interior by capillary attraction. Prior coating with the cellulose ester composition ensures better adherence than if the cases are first impregnated. A surface coating which will absorb practically all the radiations of the spectrum having the wave length of ultra-violet light has been described[3], comprising a carrier such as acetylcellulose and a compound of the diphenylbenzene or diphenylguanidine group, the coating being used for the protection of cellulose nitrate lacquers. In a variant of the above[4], cellulose nitrate lacquer coatings are protected against loss of luster through weathering and particularly through exposure to ultraviolet light by a coating of cellulose acetate containing 0.5-5% phenanthrene, anthracene, phthalimide, nitroanisole or quinaldine, which causes the acetylcellulose to absorb substantially all light around 3800 A. A plasticizer as triphenyl phosphate is preferably present.

The use of 0.25-10% of diphenylbenzene or diphenylguanidine in finishing cellulose acetate coats over a nitrocellulose coating[5] forms the basis of another coating process, 20-50% on the weight of the lacquer of triphenyl phos-

1. I.G.Farbenind., A.-G., F.P. 724726; abst. C.A. 1932, **26**, 4930.
2. Imperial Chem. Industries, Ltd., E. P. 370506; abst. J. S. C. I. 1932, **51**, 625-B.
3. Kodak-Pathe, F. P. 717554; abst. C. A. 1932, **26**, 2879.
4. Eastman Kodak Co., E. P. 371901; abst. J. S. C. I. 1932, **51**, 778-B.
5. F. Murray, E. P. 370699; abst. J. S. C. I. 1932, **51**, 614-B.

phate being added. Especially useful in filling the pores of Gaboon mahogany is said to be a cellulose ester lacquer containing kaolin as a filler[1], the latter having been treated with aluminum stearate. A composite material has been put forward[2], made by uniting hydrated cellulose foils with acetylcellulose foils by a gelatin solution in glacial acetic acid, the latter also being a solvent for the cellulose ester. The albuminoid is subsequently indurated by treatment with formaldehyde or aluminum sulfate. As a transparent wrapping material[3] such as gelatin or regenerated cellulose used for wrapping textiles which have been treated with such oily materials as sulfonated oils, the film may be coated with a thin layer of cellulose acetate to avoid the formation of emulsions on the wrapper by absorption of oil. The porous or permeable coating for use in galvanic cells as developed by G. Lüdecke[4] is a mixture of cellulose fibers and acetylcellulose, together with ethyl alcohol and ethyl acetate.

Dyeing of Cellulose Acetate. The coloring of cellulose acetate or cellulose ethers may be effected by applying unsulfonated azo dyestuffs obtained by coupling diazotized 2.4-dinitro-6-alkoxy-anilines with suitable coupling components[5], the fastness of the acetate silk being improved by treatment with 1-2% of a colorless amine above C_6, as dinitrodiphenylamine or *sec*-octylamine, the amine being retained in the finished dyeing[6]. In producing pattern effects on cellulose derivative textile materials[7], the fabrics

1. Strahl & Walter, Chem. Fab., D. R. P. 548264; abst. C. A. 1932, **26**, 3686.
2. Wolff & Co. and R. Weingand, E. P. 309019; abst. C. A. 1930, **24**, 499. See E. P. 304722.
3. Wolff & Co. and E. Czapek, E. P. 344833; abst. C. A. 1932, **26**, 4483.
4. E. P. 375388; abst. J. S. C. I. 1932, **51**, 804-B.
5. D. Mosby, H. Olpin and G. Ellis, Can. P. 325866.
6. British Celanese, Ltd., G. Ellis and W. Kirk, E. P. 378473; abst. J. S. C. I. 1932, **51**, 1076-B.
7. British Celanese, Ltd., and G. Ellis, E. P. 369572; abst. J. S. C. I. 1932, **51**, 676-B. Can. P. 325056.

are colored with a ground color, the formation of a halo around the printed parts being prevented by treating the fabric after the discharge but before the relatively lengthy ageing or steaming, with a reagent opposite in character (oxidizing or reducing) to the discharging agent. An alkali perborate is effective with reduction-discharge methods, especially when stannous chloride discharge paste is used[1]. Or[2], the cellulose acetate fabric may be printed with a resist paste containing an oxidizing agent as chlorate, chromate or permanganate, but preferably a sulfonated aromatic nitro-compound, and then overpointing with a paste containing a vat dye in its reduced form or together with reducing agents. Fixation of the vat dye is prevented in the resist-printed parts. Suitable stable dyes may be added to the resist paste and a colored resist pattern thereby obtained[3]. Where formaldehyde sulfoxylate is used[4], the effect is more complete on steaming when the discharge paste contains an ester as triacetin, ethylene chlorhydrin, ethyl tartrate or glycerol mono-, or di-chlorhydrin.

Azo dyes containing an anthracene nucleus which is not substituted at the *meso*-carbon atoms[5], such as the azo dyes obtained by coupling with an anthrol or anthramine diazo compound of the benzene, naphthalene or anthracene series, have been described for coloring organic cellulose derivatives. Dye effects on textiles may be produced by discharge agents[6], the residue of which is rendered without effect before at least a part of the steaming or other treatment. Thus, a reducing discharge agent is used which is rendered without effect by the application of an oxidizing agent. A suitable tinting solution for identification of

1. D. Mosby, H. Olpin and G. Ellis, Can. P. 325860.
2. British Celanese, Ltd., G. Ellis and J. Allan, E. P. 376331; abst. J. S. C. I. 1932, **51**, 932-B.
3. G. Ellis, H. Olpin and E. Kirk, Can. P. 325868.
4. British Celanese, Ltd., J. Allan and G. Ellis, E. P. 373653; abst. J. S. C. I. 1932, **51**, 839-B.
5. British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 356752; abst. C. A. 1932, **26**, 5769.
6. H. Dreyfus, F. P. 725047; abst. C. A. 1932, **26**, 4964.

yarns (see p. 2230) is said to be a diethyleneglycol solution of Acid Blue[1].

In the preparation of cellulose acetate pigmented bases[2], a non-aqueous mixture of a relatively large amount of pigment, a relatively small amount of fibrous cellulose derivative with ethyl acetate and ethyl alcohol, is kneaded for prolonged periods, the viscosity of the mixture being such that the pigment is dispersed and flocculation prevented. The ingredients may be mixed in one or more stages. In preparing effect threads[3], vegetable fibers are treated with boiling, aqueous solutions of alkalis and then with solutions of inert organic solvents of aromatic carbocyclic or sulfonic acid chlorides or phosphorous halogen compounds. A stamping ink for use in the artificial filament industry has been evolved[4], comprising a coloring matter with ethyl phthalate as a softening agent for the cellulose derivative in the fabric to be stamped. The color may be dissolved in benzyl alcohol.

Luster patterns are obtained on acetate silk by printing cellulose acetate silk fabric with thickened pastes containing agents which assist delustring (aliphatic chlorinated hydrocarbons, alcohols, phenols or naphthols)[5], drying, and passing the fabric through a boiling liquor containing neutral or slightly alkaline inorganic salts which retard delustring. In the preparation of alkyl ethers of amino-*b*-hydroxyanthraquinones which dye acetate silk[6], *O*-alkylation proceeds smoothly in presence of water, a water-soluble ketone, acetone, methylethyl ketone or diethyl ketone, cyclohexanone, and a basic compound of barium or

1. W. Whitehead, U. S. P. 1852137; abst. C. A. 1932, **26**, 3120. See Can. P. 317116.
2. W. Butler & Co., Ltd., and Robinson Bros., Ltd., E. P. 376989; abst. J. S. C. I. 1932, **51**, 948-B.
3. Chem. Fab. vorm. Sandoz, D. R. P. 545323; abst. C. A. 1932, **26**, 3120.
4. J. Ehrlich, F. P. 726220; abst. C. A. 1932, **26**, 4969.
5. Heberlein & Co., A.-G., E. P. 376097; abst. J. S. C. I. 1932, **51**, 883-B.
6. I. G. Farbenindustrie, A.-G., E. P. 370402; abst. J. S. C. I. 1932, **51**, 756-B.

other metal. Thus, 1-amino-2-methoxy-, m. pt. 220-222° gives orange on acetate silk; 1-amino-2.4-dimethoxy-, m. pt. 224-226°, yellow-red; 4-amino-1.2-dimethoxy-, m. pt. 283-284°, violet red; 1.4-diamino-2-methoxy-, violet red; 1.4-di-(methylamino)-5.6-dimethoxy-, blue-green; and 2-amino-3-methoxy-anthraquinone, m. pt. 261-263°, orange.

Monoazo dyes are obtained suitable for dyeing acetate silk[1] by coupling aromatic diazo compounds with amino-naphthols containing one or more unsubstituted sulfamino residues, some of the dyes being suitable for after-chroming. Coupling components such as Naphthol AS, 1-phenyl-3-methylpyrazolone, may be incorporated with cellulose ester solutions before spinning of film formation[2], the filament being subsequently impregnated with an arylamine, which is diazotized on the fiber or film, coupling being completed by neutralizing the mineral acid with sodium acetate. Acetate silk containing Naphthol AS is thus coupled with aminoazotoluene for producing a blue-red, *m*-amino-chlorbenzene for orange, or 4-chlor-*o*-anisidine, scarlet. Azo dyes may be produced on acetate silk by using as azo component the monoamino-5.6-benzocarbazole[3] described by F. Kehrmann, A. Oulevay and F. Regis[4]. In another method[5], the acetate fibers are treated with a neutral or acid bath of diazotizable aromatic bases or aminoazo compounds, with or without carboxyl groups, diazotizing on the fiber and developing with 2-hydroxycarbazole-3-carboxylic acid. If acetate silk is treated with aminoazobenzene and this diazotized on the fiber, and then treated with 2-hydroxycarbazole in NaOH, the result is a light- and wash-fast yellowish brown shade.

Acetate silk may be padded with an amino-derivative of a diaryl, arylazoaryl, or arylaminoarylazoaryl free from sulfonic, carboxyl or hydroxy groups, the diamine then tet-

1. I.G.Farbenind., A.-G., E.P. 347288; abst. C.A. 1932, **26**, 2872.
2. *Ibid.* E. P. 375393; abst. J. S. C. I. 1932, **51**, 932-B.
3. *Ibid.* F. P. 727461; abst. C. A. 1932, **26**, 5213.
4. Ber. 1913, **46**, 3712; abst. C. A. 1914, **8**, 695.
5. F. Gund, D. R. P. 549641; abst. C. A. 1932, **26**, 4962.

razotized on the fiber and developed with an arylamide of *p*-cresotic acid. Thus[1], dianisidine + *o*-toluidine, yellow-brown, or with anilide, red-brown; 4.4′-diamino-2-methoxy-2′.5′-dimethylazobenzene + 5-methoxy-*o*-toluidide, orange-brown; 2.2′-dichlorbenzidine + 2.5-dimethoxyanilide, yellow; 4.4′-diaminobenzene-1-azonaphthalene + anilide, red-brown; and 4-amino-4′-*p*-aminoanilino-5-methoxy-2-methylazobenzene + *o*-toluidine, brown.

Wool-containing fabrics also having acetate filaments therein[2] are treated with a single liquid organic solvent as methyl acetate which is capable of removing any cellulose acetate present and also of dissolving fatty and oily impurities, the solvent itself being removable from the fabric at temperatures below 60° by washing with water. In using vat colors[3], Soledon dyes are printed on cotton fabric, using a paste thickened with cellulose esters, such as those obtained by treating cellulose with pyridinesulfonic acid in acetic acid or pyridine, and precipitating the product with ethyl alcohol. Solid printed shades on material containing cellulose esters and regenerated cellulose[4] are obtained by applying a direct azo printing paste and alkali in presence of a soluble aromatic nitro-compound as sodium *m*-nitrobenzenesulfonate.

In the production of planographic printing bases[5], the desired printing design is produced on a sheet of saponifiable cellulose derivative (cellulose acetate) and covered with a protective layer; the uncovered material is hydrolyzed with 10% NaOH solution, and after washing, the sheet is inked with a fatty ink which is retained by the unchanged ester, but not by the saponified areas. To in-

1. I. G. Farbenindustrie, A.-G., E. P. 375321; abst. J. S. C. I. 1932, **51**, 932-B.
2. R. Brauckmeyer, U. S. P. 1851893; abst. C. A. 1932, **26**, 3120.
3. Imperial Chem. Industries, Ltd., B. Wylam and J. Wilson, E. P. 366543; abst. J. S. C. I. 1932, **51**, 418-B.
4. Imperial Chem. Industries, Ltd., H. Briggs and R. Hardacre, E. P. 374950; abst. J. S. C. I. 1932, **51**, 932-B.
5. Kalle & Co., A.-G., E. P. 368083; abst. J. S. C. I. 1932, **51**, 416-B.

crease the dyeing properties of acetylcellulose filaments[1], they are incorporated with small amounts of proteids in solution. The affinity for dyestuffs may also be increased by adding to the cellulose acetate a small proportion of cellulose cyanoacetate, cellulose aminobenzoate or other organic acid containing nitrogen is esterified with the cellulose[2]. Effect materials such as "immunized" cotton (see p. 2313)[3] are rendered substantially proof to heat and storage by treatment with an acid-binding substance as urea or thiourea which has no saponifying effect on the cellulose ester in the fibers.

In the production of direct, polyazo colors, excess of diazobenzene remaining after coupling benzidine + H-acid with diazotized aniline[4] is removed by coupling 4'-hydroxydiphenylazo-H-acid (made by boiling benzidine + H-acid); the product is then coupled as usual with *m*-phenylenediamine or toluylenediamine, the green-black dye being obtained in improved yield free from dyes of the chrysoidine type. In black dyeing of cellulose acetate fibers[5], the material is first treated with *α*-naphthylamine and, after this is absorbed, is further treated with nitrous acid. Dyes producing yellow, red and brown shades on acetate silk or wool[6] are obtained by the use, as one component, of aminohydroxyanthrahydroquinone sulfuric esters obtainable by acid or alkaline oxidation of 2-aminoanthraquinone-9.10-disulfuric ester or its substitution products having the 1-position free.

Dyes suitable for coloring acetate silk yellow to orange to red are obtained by coupling diazotized esters of nucleally unsulfonated *o*-aminophenols (such as *o*-aminophenol

1. J. Loiseleur and L. Velluz, F. P. 711645.
2. Lonza Elektrizitätswerke u. Chem. Fabr., A.-G., G. Levi and G. Benaglia, E. P. 369017; abst. J. S. C. I. 1932, **51**, 461-B.
3. E. Stocker, U. S. P. 1867035; abst. C. A. 1932, **26**, 4724.
4. W. Ralph, U. S. P. 1832322; abst. J. S. C. I. 1932, **51**, 975-B.
5. A. Hall, U. S. P. 1851507; abst. C. A. 1932, **26**, 3120.
6. D. Fairweather, J. Thomas and Scottish Dyes, Ltd., E. P. 347120; abst. C. A. 1932, **26**, 2871.

p-toluenesulfonate)[1], with nucleally unsulfonated compounds of the benzene series which contain a residue such as sodium anilinemethanesulfonate, treating the products with caustic alkali, and then replacing the H atom by an aliphatic residue containing not more than 3 C-atoms[2]. Dyes for acetylcellulose are also formed by coupling diazo compounds of the benzene or naphthalene series such as those derived from aniline or monacetyl-*p*-phenylenediamine with an alkyl- or alkoxy-hydroxynaphthalene derivative, such as methyl or ethyl 1.4-naphtholcarboxylate[3]. *Sym*-1.4-Dihydroxyethylaminoanthraquinones are prepared by treating their leuco derivatives (by condensing leuco-1.4-dihydroxyanthraquinones with monoethanolamine) with oxygen in the presence of concentrated monoethanolamine[4], the products being used for dyeing acetate silk.

Acetate silk is dyed blue shades when a leuco derivative of an *o*-hydroxyaminoanthraquinonesulfonic acid in which a sulfo group is in *o*-position to an *a*-hydroxy group[5], is heated with ammonia or a primary aliphatic or araliphatic amine in the presence of water, to effect replacement of the OH groups by amino, alkylamino or aralkylamino groups, the products being used in suspensions[6].

H. Chadwick[7], C. Fischer[8], H. Franke[9], H. Lachs

1. F. Felix, U. S. P. 1848772; abst. C. A. 1932, **26**, 2871. Soc. Anon. Pour L'Ind. Chim. A Bale, E. P. 356716; abst. C. A. 1932, **26**, 4487.
2. P. Grossmann, U. S. P. 1868202; abst. C. A. 1932, **26**, 5215.
3. F. Felix and F. Straub, U. S. P. 1854894; abst. C. A. 1932, **26**, 3383.
4. Soc. Anon. Pour L'Ind. Chim. A Bale, F. P. 718089; abst. C. A. 1932, **26**, 2871. E. P. 370716; abst. J. S. C. I. 1932, **51**, 765-B.
5. *Ibid.* E. P. 355657; abst. C. A. 1932, **26**, 5769. See F. P. 697541.
6. Silver Springs Bleaching & Dyeing Co., Ltd., E. P. 337746; abst. Rayon, 1932, **13**, #6, 10. In lubricating cellulose acetate yarns (W. Whitehead, Can. P. 323145) the yarn is passed across the edge of a disc that is rotating in a plane not parallel to the path of the yarn, the lower edge of the device being submerged in a bath of the lubricating liquid to be applied.
7. Dyer, 1932, **67**, 423; abst. C. A. 1932, **26**, 3929.
8. Z. ges. Textil. Ind. 1932, **35**, 75, 87; abst. C. A. 1932, **26**, 6143; Chem. Zentr. 1932, I, 2240.
9. Z. ges. Textil. Ind. 1932, **35**, 155; abst. C. A. 1932, **26**, 6144.

and S. Parnas[1], K. Lauer[2], C. Mullin[3], F. Ohl[4], L. Rinoldi[5], J. Sterling[6], G. Rudolph[7] and N. Planovskii and V. Laryushkina[8] have contributed recent articles on the dyeing and finishing of cellulose acetate filaments and fabrics.

Applications of the Organic Cellulose Esters. Textile fabrics, felt, straw plait, and asbestos fabrics may be stiffened without loss of luster and elasticity, so that they are not liable to "spot" with water[9], by impregnation with a solution of polystyrene, with or without the addition of a cellulose ester, followed by drying and pressing into shape. Clouding which is fast to water is produced on paper by passing a solution of a cellulose derivative in an organic solvent into a precipitation bath kept in agitation[10], and incorporating the gelatinous filaments formed, preferably without previous drying, in the pulp which is transformed into paper in the usual way. Imitation leather is composed of woven fabric of two-ply or double-web thickness[11], the plies being interwoven or stitched together with a slight space left between them, with a coating of cellulose derivative and powdered mica applied to one face of the composite fabric in such a manner as to pass through the interstices of one ply and into the space between the two plies. The coating is applied under pressure.

In joining cellulose surfaces to articles[12], one or more components of which are cellulose plastics, a solid prepara-

1. Z. physikal. Chem. 1932, **160**, 425; abst. J. S. C. I. 1932, **51**, 908-A.
2. Kolloid Zts. 1932, **61**, 91; abst. J. S. C. I. 1932, **51**, 1075-B.
3. Rev. Gen. Matieres Col. 1932, **36**, 37; abst. Chem. Zentr. 1932, I, 2255.
4. Metallbörse, 1932, **22**, 817, 881; abst. C. A. 1932, **26**, 4955.
5. Boll. laniera, 1931, **45**, 747; abst. C. A. 1932, **26**, 4177.
6. Textile Mfr. 1932, **58**, #688, 159.
7. Kunstseide, 1932, **14**, 17; abst. C. A. 1932, **26**, 2867.
8. Anilinokrasochnaya Prom. 1932, **2**, #2, 37; abst. C. A. 1932, **26**, 4721.
9. I. G. Farbenindustrie, A.-G., E. P. 367126; abst. J. S. C. I. 1932, **51**, 418-B.
10. *Ibid.* F. P. 725069; abst. C. A. 1932, **26**, 4953. F. P. 726619; abst. C. A. 1932, **26**, 4953.
11. J. Holmes Bias Fabrics, Ltd., and J. Holmes, E. P. 342673.
12. Celluloid Corp., E. P. 367515; abst. J. S. C. I. 1932, **51**, 475-B.

tion of acetylcellulose with plasticizers is used with heat and pressure. If desired, the joining compound may also contain the cellulose derivative, in which case at least 60% of plasticizer should accompany the cellulose derivatives. In order to melt cellulose acetate[1], rosin is added directly to it and heated to 170-200° when both cellulose ester and rosin are melted. By incorporating triacetin or oily xylene-monomethylsulfonamide, the operation takes place at a lower temperature. Two layers are formed which may be readily separated, and the rosin re-used. In the formation of moldable articles[2], plastifying agents are incorporated with cellulose derivatives in a liquid vehicle (as ethyl ether) and the vehicle eliminated by evaporation before shaping of the cellulose derivative[3]. To produce hollow articles[4], a closed hollow article made of a cellulose acetate thermoplastic composition is inserted in a closed mold, the temperature being then raised to a point of softening of the plastic, when the gas confined within the hollow article expands and forces the material against the walls of the mold. Articles containing organic cellulose derivatives may be coated with a solution of cellulose nitrate containing fire retardants as triphenyl phosphate or tritolyl phosphate[5], and also plasticizers as camphor, ethyl phthalate or butyl phthalate. The treated articles are more impermeable and intended for wrapping food, confectionery and tobacco.

The G. Schneider thermoplastic composition contains organic cellulose esters, an aryl sulfonanilide and an aryl sulfonamide[6]. Where an exceptional degree of inflammability is required, triphenyl phosphate, tricresyl phosphate or halogen compounds may be added. W. Moss[7] prepares a cellulose acetate lacquer by the addition of polymerization

1. C. Dreyfus, W. Cameron and G. Schneider, U. S. P. 1870175.
2. H. Dreyfus, F. P. 713848; abst. C. A. 1932, **26**, 1783.
3. *Ibid.* Can. P. 293068.
4. C. Dreyfus, Can. P. 322776.
5. *Ibid.* Can. P. 322573; abst. C. A. 1932, **26**, 3918.
6. G. Schneider, Can. P. 323142; abst. C. A. 1932, **26**, 4145.
7. W. Moss, U. S. P. 1849107; abst. C. A. 1932, **26**, 2879.

products of lactic acid, the coating application being especially suitable for wood and metals. E. Felger[1] has detailed a process for combining resin-like condensation products with cellulose esters, the condensation being carried out in in the presence of high-boiling solvents which are afterwards worked up into the finished lacquer or plastic mass, depending upon the amount of volatile solvent present.

The scrap resulting from the operation, if necessary with the addition of a small amount of cellulose ester and solvent may be used again. For example, 3 kgm. cellulose ester are dissolved in 0.4 kgm. ethyl acetate and 0.2 kgm. ethylacetanilide, and the mixture introduced into 2 kgm. of phenol which is heated to 130°, and 0.7 kgm. paraformaldehyde added in portions. The mixture is then kneaded 1-15 hrs. at 130°. The resin thus obtained shows resistive properties in the cold, but is soluble in acetone, partly in boiling ethyl acetate and benzyl alcohol, insoluble in alcohol, benzine, chloroform, carbon tetrachloride, amyl alcohol and amyl acetate. It assumes rubber-like properties at 90-100°, becomes plastic at 150-160°, and can be molded at this temperature in cooled forms by the spraying process, from which molds it is easily removable in the finished condition. The solution of the cellulose ester can also take place in dichlorhydrin or ethyl phthalate.

In preparing stereotype matrices and embossing dies[2], an original is pressed into a block formed of a thin layer of thermoplastic material as cellulose acetate, carried on a hard, non-elastic material such as cardboard, press-spahn or sheet zinc, and covered with a thin sheet of material which does not soften, such as metal foil. Elastic products are obtained by subjecting carbohydrate esters containing a fatty acid residue[3], a cyclic substituted fatty acid residue. Examples are cellulose naphtheno-oleate (oleonaphthenate) and cellulose naphthenate-oleate-laurate (naphtheno-oleo-

1. E. Felger, D. R. P. 541911; abst. Chem. Zentr. 1932, I, 1957.
2. W. Forstmann, P. Menzel and O. Boll, E. P. 359018; abst. C. A. 1932, **26**, 4145.
3. M. Hagedorn, D. R. P. 550652; abst. C. A. 1932, **26**, 4982.

laurate, oleo-naphtheno-laurate). The cellulose acetate composition of W. Webb and H. Clarke[1] employs tri-*o*- and tri-*p*-chlorphenyl phosphates as combined plasticizer and inflammability-reducer, using 5-20 parts to 100 of the cellulose acetate. The optimum quantities are cellulose acetate 100, dissolved in 400 parts acetone containing 20 parts tri-*o*-chlorphenyl phosphate. In another procedure for preparing plastic masses[2], sufficient volatile solvents are added to the cellulose acetate and softeners for complete dissolution and the mixture is then evaporated at raised temperatures in a kneading machine until a plastic mass of the desired consistency results.

In preparing a material suitable for flooring[3], oxidized or polymerized drying oils, powdered cork, wood flour with resins and coloring matter in finely pulverized condition, are subjected to repeated treatment with hot air, as a combined drying and oxidation, then intimately mixing them with acetylcellulose, a plasticizer and castor oil, and the mixture rolled out by means of hot rolls, and finally molded by heat and pressure. The stencil sheet of A. Davis[4] has a base of acetylated gum tragacanth(?). As a thickener for a paint and varnish remover[5], cellulose esters are added to retard evaporation, and chlorinated hydrocarbons to diminish possibility of combustion. The J. Ehrlich stamping ink for wood pads[6] contains one or more liquid, nonhygroscopic substances other than oils or fats, ethyl phthalate being specifically recommended, as it does not soften rubber nor warp wood.

According to Kalle & Co.[7], planographic printing surfaces are prepared on a base of acetylcellulose, the parts

1. U. S. P. 1884433.
2. Lonza Elektrizitätswerke u. Chem. Fabr., A.-G., E. P. 380950; abst. J. S. C. I. 1932, **51**, 1042-B. F. P. 722866; abst. C. A. 1932, **26**, 4142. Can. P. 322892.
3. Greenwich Inlaid Linoleum Co., Ltd., and A. Dewar, E. P. 364837; abst. Chem. Zentr. 1932, I, 2405.
4. U. S. P. 1861209; abst. C. A. 1932, **26**, 3887.
5. Chemische Fabriken Joachim Wierink & Co., A.-G., F. P. 719266; abst. C. A. 1932, **26**, 3391.
6. J. Ehrlich, E. P. 376612; abst. J. S. C. I. 1932, **51**, 948-B.
7. E. P. 368083.

which are not to print being treated with a saponifying agent to convert the cellulose derivative to cellulose hydrate capable of retaining water, whereas the cellulose derivative itself acts to retain a fatty ink. Plasticizing agents may be added to the cellulose derivative to render it more elastic and enable a better print to be produced. For reproduction purposes without a half-tone screen[1], drawings in one or more colors are made on acetylcellulose film. Matts may be made by heating cellulose acetate to near the m. pt. and impressing it on a positive electro[2].

As suitable synthetic resinous products for incorporation with cellulose acetate, there have been patented urea-aldehyde condensates[3], and flexible resins prepared by heating glycerol and phthalic anhydride in the presence of a high-boiling indifferent organic compound as indene, biphenyl, anthracene, nitrobenzene or chlortoluene. Celluloid-like masses are obtainable by interpolymerization by the usual agents[4], of aqueous neutral to alkaline emulsions of mixtures of vinyl ethers with other unsaturated polymerizable compounds, such as vinylethyl ether, vinylbutyl ether and acrylonitrile, or glycolvinylethyl ether and methyl acrylate or acrylonitrile. W. Moss and G. Seymour[5] have described the properties of a synthetic resin formed by the reaction of a phenol with allyl alcohol, which is used for preparing lacquers or thermoplastic compositions.

Esters of carbohydrates of variable composition have been described[6], and formed when one or more organic acid halides are caused to react on polymerized carbohydrates in the presence of a tertiary aralkyl base and a heterocyclic tertiary base, the latter being present in amount

1. Meissner & Buch, D. R. P. 544243.
2. H. Semisch, D. R. P. 460523.
3. A. Keller, U. S. P. 1868067; abst. C. A. 1932, **26**, 5183. See E. P. 340372. Allgemeine Elektricitäts-Ges., D. R. P. 555001; abst. C. A. 1932, **26**, 5221.
4. I. G. Farbenindustrie, A.-G., E. P. 373643; abst. J. S. C. I. 1932, **51**, 851-B.
5. Can. P. 324633; abst. C. A. 1932, **26**, 4970.
6. I. G. Farbenindustrie, A.-G., D. R. P. 550761; abst. C. A. 1932, **26**, 4825.

at least equivalent to the acid halide. Thus, powdered agar-agar is dried and heated 1 hr. at 125-140° with naphthenic acid chloride in the presence of diethylaniline and pyridine. A hard, resin-like mass of the naphthenic acid ester of agar-agar results. Similarly, may be prepared the esters of cellulose, sulfite pulp, dextrin and wheat starch.

In the creping of textile yarns and fabrics[1], threads composed of organic cellulose derivatives are impregnated with aqueous citric acid, sodium citrate or lead acetate before applying at least part of the high degree of twist, and, after final twisting and incorporating into fabric, are treated with barium acetate or hydroxide, on or in the crepe threads. The fabric is subsequently scoured with hot water or soap solution, dyed and finished. The impregnating liquid may consist of an aqueous solution containing anions having a high coagulating or precipitating action on gels or solutions of the cellulose derivative, as sodium or potassium citrates, lactates or tartrates. H. Dreyfus[2] forms fabrics of highly twisted crepe yarns sized with material comprising a polymerized vinyl compound, and the fabric then subjected to a scouring bath. C. and V. Clémencon and H. Schmit[3] produce crepe effects on cloth using acetylcellulose silk which has been treated in a bath containing water, ethyl alcohol and gelatin. A shrinkage and swelling is said to take place which allows of much higher torsions being applied. R. Cottrell[4] has discussed the recent methods used for the treatment of crepes during the creping and scouring process.

A process for preparing airplane dope has been issued, consisting of cellulose acetate 4.5, cellulose nitrate 3, and tritolyl phosphate 3, with a mixed volatile solvent[5], including methyl alcohol, which is capable of dissolving each of

1. British Celanese, Ltd., H. Dreyfus, W. Dickie and R. Moncrieff, E. P. 378910; abst. J. S. C. I. 1932, **51**, 979-B.
2. E. P. 352451; abst. C. A. 1932, **26**, 5434.
3. F. P. 729473; abst. C. A. 1932, **26**, 6158.
4. Textile World, 1932, **82**, 534; abst. C. A. 1932, **26**, 6145.
5. G. Given, H. Letts and N. Thomson, Can. P. 324954; abst. C. A. 1932, **26**, 5439.

the above ingredients. E. Schmidt[1] in a study of surface protection of airplane fabrics, finds that the tensile strength of fabric doped with cellulose acetate is much reduced in damp atmosphere. In order to clarify cellulose acetate compound transparent sheets[2], they may be bleached in the solid form to prevent discoloration, especially when used with various associated auxiliary ingredients. In a study of the heat of adsorption of water vapor by cellulose acetates[3], the moisture adsorption isotherms of a cellulose acetate sheet were determined at 30°, 40° and 50° with a silica spring balance. The moisture adsorption decreases with increase in temperature at all humidities. The heats of adsorption calculated from the isotherms for the ranges 30-40° and 40-50° decreased with increasing moisture content of the cellulose acetate. The heat of adsorption of water vapor by a cellulose acetate sheet was determined calorimetrically at 25° and compared with the heats of adsorption calculated from the isotherms at 20° and 30°. The latter were considerably higher than the former. The heat of adsorption of water vapor by cellulose triacetate (44.8% acetyl) was less than that by a cellulose acetate of 38% acetyl[4].

A recent method for making motion picture screens has been published[5], comprising placing strips of coated fabric side by side with adjacent edges butted, softening the coating adjacent to the edge portions of these strips, and applying a softened strip of flexible transparent plastic material thereto. Cellulose ester films are dulled on the side remote from the emulsion by applying a solution of the same or another cellulose ester containing an insoluble

1. E. Schmidt, Farben-Chem. 1932, **3**, 165, 209; abst. J. S. C. I. 1932, **51**, 676-B.
2. British Celanese, Ltd., E. P. 347257; abst. C. A. 1932, **26**, 2863.
3. P. Newsome and S. Sheppard, J. Phys. Chem. 1932, **36**, 930; abst. C. A. 1932, **26**, 2635; J. S. C. I. 1932, **51**, 690-A.
4. Spicers, Ltd., and E. Barnes, E. P. 349652; abst. C. A. 1932, **26**, 5420.
5. R. McLean, U. S. P. 1856739.

dulling agent, as starch, china clay or precipitated calcium carbonate[1]. A thin gelatin layer may be attached to the dulled side[2]. Solutions of cellulose esters have been described as useful for making light-sensitive layers[3], and as usable for photomechanical resists. The Spicers, Ltd.[4], method for the preparation of color photographs by means of line or dot screens over a reflecting support is characterized by the fact that the screens are made on a thin layer of acetylcellulose, which is then fastened to a transparent carrier by means of a suitable adhesive.

In preparing cellulose acetate films with a light halo protecting layer[5], the back side of the layer carrier is first coated with a thin layer of a cellulose acetate of low precipitating value (75-25%), upon which the light halo protecting layer is brought. A film thus colored, after development, bleaches or fades out especially clearly. A. Sulzer[6] has described the manufacture of a motion picture film having the properties of satisfactory flexibility and transparency, with unusual flatness and low water impermeability, composed of cellulose acetate having a precipitation value of at least 90% in a solution consisting of water-acetone 40:60 at 20°, and a plasticizer for the acetylcellulose.

Lantern slides on film have advantages over glass slides in the space and weight saved[7], and should be made on film having safety base, such as cellulose acetate. During projection, they can be held flat between two glass plates hinged at one edge with cloth for convenience. T. Baker[8] has described the method of manufacture of the Spicer-Dufay color film, the completed matrix on acetate base con-

1. E. Lomberg, D. R. P. 496050; abst. C. A. 1932, **26**, 3196.
2. D. R. P. 546127.
3. Lackfabrik. E. Dörken, K. Dörken, E. Hochuli, H. Hermighaus, D. R. P. 542598.
4. D. R. P. 540375.
5. Kodak Pathe, Soc. Anon. France., F. P. 717066; abst. Chem. Zentr. 1932, I, 2127.
6. Can. P. 325532.
7. Atelier, 1931, **38**, 121.
8. Phot. J. 1932, **72**, 109.

sisting of three rulings of red, green and blue dye, one ruling being at right angles to the other two, so forming a checkered pattern. After coating with gelatin and nitrocellulose varnish, the matrix is coated with a special emulsion having a low gelatin-silver ratio to enable gamma infinity to be obtained with short times of development. The emulsion is stated to have great latitude in exposure. Development is carried out by the reversal method to give a direct positive. For average studio lighting, the film can be used without a color filter, a special filter having been designed for use with daylight.

E. Henry[1] claims it is much more economical of space to photograph valuable manuscripts on acetate motion picture film (a page to a frame) than to photostat them or copy them directly[2]. The T. Reese transfer print comprises a backing sheet carrying a coating forming film[3], which is insoluble in water, and may be formed of a cellulose ester composition, and this film carries a design formed by pigments permanently impregnated in the body of the film. In the F. Dehn decalcomania transfer paper[4], the body paper is coated first with a water-insoluble coating (starch or gum) and then with a water-insoluble coating (cellulose acetate) containing cobalt or manganese linoleate as a drier.

In the production of artificial staple fiber[5], filaments of cellulose acetate or cellulose ether are wound on a thin rod while rendered plastic by moistening with a solvent as vinyl acetate, or by heating the rod so as to acquire a curved set, the fibers being cut from the rod continuously with winding. Blankets for impression cylinders used in printing are formed of one or several layers of fabric impregnated with rubber over which is superposed a thick

1. Library J. 1932, **57**, 215.
2. E. Lehmann, Kinotechnik, 1931, **13**, 379; abst. C. A. 1932, **26**, 2931.
3. T. Reese, U. S. P. 1627407; abst. C. A. 1927, **21**, 2174.
4. Decorative Development, Inc., E. P. 374519; abst. J. S. C. I. 1932, **51**, 838-B.
5. British Celanese, Ltd., and W. Taylor, E. P. 372323; abst. J. S. C. I. 1932, **51**, 795-B.

coating of cellulose acetate to which softeners may be added[1]. In attaching rubber to metals, glass and ebonite[2], an intervening layer is used comprising a product obtained by acting on guttapercha or balata with sulfuric or sulfonic acids, and afterwards associating the product formed with a cellulose derivative. A surgical dressing has been described[3], having the surface that is intended to contact with the body, made of a fabric consisting essentially of cellulose acetate filaments enclosing a layer of absorbent material.

The Johnson & Johnson adhesive plaster[4] is prepared by treating one face of a plaster backing by singeing and then treating with a cellulose acetate lacquer, the medicated adhesive material being then applied to the other face of the plaster. In operating under the F. Puppe process[5], cartographic engravings are cut with the needle in a suitable coating on a transparent support of cellulose acetate. In finishing and sealing the edge of a braided textile covering[6], where the cross-section is non-circular, a layer of cellulose acetate film is wrapped around the edge of the covering and contiguous conductor portion and then softened by solvent to cause the acetylcellulose to coalesce into a unitary mass.

In the production of gramophone record masses[7], red acaroid resin and acetylcellulose are mixed while hot, the mass is cooled and finely ground, and plastifiers and fillers incorporated with the mass. The mixture is then ground and hot rolled at 260-320°. C. Avery and H. Kress[8] have described a rapid and economical way of coating textile insulated wire with a thin, flexible film of cellulose acetate,

1. Dunlop Rubber Co., Ltd., S. Brazier and F. Warren, E. P. 353947; abst. C. A. 1932, **26**, 4145.
2. Dunlop Rubber Co., Ltd., D. Twiss, A. Round and E. Murphy, E. P. 343531; abst. C. A. 1932, **26**, 2892.
3. C. Dreyfus, U. S. P. 1872076.
4. Johnson & Johnson, E. P. 348694; abst. C. A. 1932, **26**, 5183.
5. D. R. P. 477168. 6. R. Powell, U. S. P. 1871278.
7. Gramophone Co., Ltd., S. Whyte and W. Lord, E. P. 377809; abst. J. S. C. I. 1932, **51**, 948-B.
8. Bell System Tech. J. 1932, **11**, 231.

in which over 85% of the acetone is recovered by adsorption upon activated carbon, and E. Wood and D. Brobst[1] have illustrated the cellulose acetate treatment for textile insulation. The applications of acetylcellulose in the field of plastics have been reviewed by R. Ball and B. Andersen[2].

In producing textiles and yarns from organic cellulose derivatives and having a reduced scorching temperature[3], there is incorporated a substantially neutral substance which scorches at a temperature lower than the m. pt. of the cellulose derivative. The T. Baker sound-record cinematograph film comprises a method of making a sensitive film of the multi-color screen type[4], for use in the production of sound record cinematograph films in natural colors, and comprises applying to a cellulose acetate film along a narrow strip which is to serve as a sound record track, a layer of bitumen dissolved in benzene, coating the surface of the film with a layer of collodion on which the multi-color screen is formed, and then treating the film with benzene to remove the bitumen together with that portion of the collodion layer which overlies the bitumen. The film is then coated with photographic emulsion.

For the local augmentation of luster in textile materials containing cellulose derivatives which have been delustered by the action of hot, aqueous media[5], the material may be subjected to the action of superheated steam. Thin sheets or webs of cellulose derivatives may be expeditiously and economically dried[6], by causing the web to follow a downwardly directed sinuous path and passing air over the moving web in one direction along both sides. New cellulose derivatives have been described[7], obtained by heating swollen cellulose with a cyanide, and then with a halogen.

1. Bell System Tech. J. 1932, **11**, 213.
2. Chem. and Ind. 1932, **51**, 371; abst. C. A. 1932, **26**, 3373; J. S. C. I. 1932, **51**, 517-B.
3. C. Dreyfus, Can. P. 328724.
4. T. Baker, U. S. P. 1890557.
5. G. Ellis and H. Olpin, U. S. P. 1890643.
6. C. v. Hoessle and O. Schade, U. S. P. 1890832.
7. R. Haller and A. Heckendorn, U. S. P. 1892489.

In the method of C. v. Hoessle[1] for casting sheets from solutions of cellulose derivatives, a smooth, thin sheet is formed by interaction with a precipitating agent, first spreading the solution on a smooth surface, adding the gelatinant, then stretching the sheet while drying, the original opacity of the sheet upon precipitation changing to a transparency as the moisture is evaporated and the solvents dissipated. In the dyeing of cellulose acetate[2], the cellulose ester is impregnated with a vat dyestuff enolic ethereal salt by heating in an aqueous solution and then devoloping the dyestuff. The G. Zelger plastic compound comprises a cellulose ether or ester and diethylphenyl phosphate[3].

Cellulose derivative plastics are colored by dipping the object into a solution of an oil-soluble dye in butyl acetate[4]. In treating cellulose acetate photographic film base to make it resistant to abrasion, heated colloidal solution of a wax in alcohol is applied while the base is heated and has been freshly cast in order to increase penetration, and then seasoning the film in the usual manner[5]. To produce a high-twist crepe yarn[6], a high twist is imparted in one stage of the twisting, the remainder of the twist being imparted to the simple partly-twisted yarn in at least one more stage of twisting.

1. U. S. P. 1892657.
2. J. Wilson and J. Thomas, U. S. P. 1886441.
3. U. S. P. 1886775.
4. E. Bowley, U. S. P. 1891520.
5. C. Holzwarth, U. S. P. 1888952.
6. H. Dreyfus, Can. P. 328725.