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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 huttenmannische 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 Zurich, Schweiz. Ges. N. Denkschr.
Allg. Syn. Suikerfab.	Algemeen Syndicat van Suikerfabrikanten in Nederl.-Indie. With Arch-Suikerind, etc.
Allg. Zts. Bierbr. Malzfabr.	Allgemeine Zeitschrift fur 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. Toscano	Giornale Toscano 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 fur 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 (Koninckliik 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
Anät. 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. Microgr.	Annales de Micrographie specialement consacrees a la Bacteriologie, aux Protophytes et aux Protozoaires
Ann. Mines	Annales des Mines...redigees et publiees sous l'Autorisation du Ministre des Travaux Publics
Ann. Museo Ind Ital.	Annali del R. Museo Industriale Italiano
Ann. Natur. Hist.	Annals of Natural History
Ann. Oculist	Annales d'Oculistique et de Gynecologie
Ann. Pharm.	Annals of Pharmacy
Ann. Pharm. Louvain	Annales de Pharmacie, Louvain
Ann. Phil.	Annals of Philosophy
Ann. Phys.	Annalen der Physik
Ann. Phys. Chem.	Annalen der Physik und Chemie
Ann. Ponts et Chauss.	Annales des Ponts et Chaussees
Ann. R. Staz. Chim.	Annali della R. Stazione Chimico Agraria Sperimentale di Roma
Ann. Rep., U. S. Dept. Agric.	Annual Report of the United States Department of Agriculture
Ann. sci. agron.	Annales de la science agronomique francaise et étrangére
Ann. Sci. Bot. Nat.	Annales des Sciences Naturelles, Botanique
Ann. Sci. Lomb. Veneto	Annali delle Scienze del Regno Lombardo-Veneto
Ann. Sci. Nat.	Annales des Sciences Naturelles. Botanique. Zoologie et Paleontologie, comprenant l'Anatomie, la Physiologie, la Classification et l'Histoirie Naturelle des Animaux
Ann. Sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy
Ann. Scott. Natur. Hist.	The Annals of Scottish Natural History
Ann. Surg.	Annals of Surgery
Ann. Storia Natur.	Annali di Storia Naturale
Ann. Telegr.	Annales Telegraphiques
Annab.-Buchh. Ver. Naturk. Ber.	Bericht uber den Annaberg-Buchholzer Verein fur Naturkunde
Annab.-Buchh. Ver. Naturk. Jahr.	Jahresbericht des Annaberg-Buchholzer Vereins für Naturkunde
Annaes Sci. Natur.	Annaes de Sciencias Naturaes
Anneè Biol.	L'Anneè Biologique. Comptes Rendus annuers des Travuax de Biologie Generale
Annot. Zool. Jap.	Annotationes Zoologicae Japonenses, Auspiciis Societatis Zoologicae Tokyonensis seriatim editae
Annuaire Ancienne Normandie	Annuaire des cinq. Departements de l'Ancienne Normandie, par l'Association Normandie
Annuaire Inst. Provinces	Annuaire de l'Institut des Provinces, des Societes Savantes, et des Congres Scientifiques
Annuaire met. France	Annuaire Meteorologique de la France
Annuaire Mines Russie	Annuaire du Journal des Mines de Russie
Anthropol. (Paris)	Materiaux pour l'Histoire de l'Homme. Revue d'Anthropologie. Revue d'Ethnographie reunis.
Anthropol. Congr	See Congr. Int. Anthrop. C. R.
Anthropol. Inst. J.	The Journal of the Anthropological Institute of Great Britain and Ireland

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

Archiv. Hyg	Archiv. fur 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. fur Naturgeschichte
Archiv. Naturk. (Dorpat)	Archiv. fur 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. fur Ohrenheilkunde
Archiv. Ophthalm.	Albrecht von Graefe's Archiv fur Ophthalmologie
Archiv. Ophthalm Otol.	Archives of Opthalmology and Otology
Archiv. Otol.	Archives of Otology
Archiv. Parasit.	Archives de Parasitologie
Archiv. path. Anat.	Archiv fur pathologische Anatomie und Physiologie und fur klinische Medizin (Virchow's)
Archiv. Pharm.	Archiv. der Pharmacie, Archiv des Apothekervereins im nordlichen Deutschland.
Archiv. Pharm og Chemi	Archiv. de Pharmaci og Chemi, Copenhagen
Archiv. Physiol.	Archives de Physiologie Normale et Pathologique
Archiv. Psychiatr.	Archiv. fur Psychiatrie und Nervenkrankheiten
Archiv. Sci.	Archives of Science and Transactions of the Orleans County Society of Natural Sciences
Archiv. sci. med.	Archivio per les scienze mediche
Archiv. Sci. Phys. Nat.	Bibliotheque Universelle. Archives des Sciences Physiques et Naturelles
Archiv. Sci. Pract. Med.	Archives of Scientific and Practical Medicine
Archiv. Slaves Biol.	Archives Slaves de Biologie
Archiv. Verdauungskrankh	Archiv. fur Verdauungs-krankheiten
Archiv. Wiss. Heilk.	Archiv. des Vereins fur gemeinschaftliche Arbeiten zur Forderung der wissenschaftlichen Heilkunde
Archiv. Wiss. Prakt. Thierheilk.	Archiv. fur wissenschaftliche und praktische Thierheilkunde
Archiv. Zool. Anat. Fis.	Archivio per la Zoologia, l'Anatomia, e la Fisiologia
Archiv. Zool. Exper.	Archives de Zoologie Experimentale et Generale
Arcueil, Mem. Phys.	Memoires de Physique et de Chimie de la Societe d'Arcueil
Argent. Inst. Geogr. Bol.	Boletin del Instituto Geografico Argentino
Argent. P.	Argentine Patent
Argent. Soc. Ci. An.	Anales de la Sociedad Cientifica Argentina

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

Australia Med. Rec:	Medical Records of Australia
Australian P.	Australian P.
Australian Sugar J.	Australian Sugar Journal
Autun, Mem. Soc. Eduenne	Memoires de la Societe Eduenne
Auvergne, Ann. Sci.	Annales Scientifiques, Litteraires, et Industrielles de l'Auvergne
Auxerre, Bull. Soc. Sci.	Bulletin de la Societe des Sciences Historiques et Naturelles de l'Yonne
Badischen Aerzt. Verein. Mitth.	Mittheilungen des Badischen ärztlichen Vereins
Bah. P.	Bahamas Patent
Ballenstedt, Archiv.	Archiv fur 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 uber 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 fur Physik, Mathematik, und verwandte Wissenschaften
Bayer. Gewerbeztg.	Bayerische Gewerbezeitung
Bayer. Kunst. Gewerbebl.	Kunst und Gewerbeblatt (Poletechn. Verein Königreich Bayern)
Bayer, Landw. Ver. Erg.	Ergebnisse landwirthschaftlicher und agrikulturchemischer Versuche an der Station des General-Comite des Bayerischen Landwirthschaftlichen Vereines in München

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

Bergens Mus. Aarb.	Bergens Museums Aarbog for...Afhandlinger og Aarsberetning udgivne af Bergens Museum
Berggeist	Der Berggeist
Berghaus, Ann.	Annalen der Erd-, Volker- und Staatenkunde
Berghaus, Zts Erdk.	Zeitschrift fur 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 Koniglich Preussischen Akademie der Wissenschaften zu Berlin
Berlin Ann. Telegr.	Annalen der Telegraphie
Berlin Astron. Jahr.	Berliner Astronomisches Jahrbuch
Berlin Bot. Gartens Jahr	Jahrbuch des Koniglichen Botanischen Gartens und des Botanischen Museums zu Berlin
Berlin Bot. Gartens Notizbl.	Notizblatt des Konigl. 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 fur Erdkunde zu Berlin
Berlin Ges. Erdk. Zts.	See Berlin Zts. Erdk.
Berlin Ges. Geburtshlf. Gynäk.	See Zts. Geburtshlf. Gynak.
Berlin Ges. Naturf. Freunde Mag.	Magazin der Gesellschaft Naturforschender Freunde zu Berlin, fur 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 fur Land- und Forstwirthschaft am Kaiserlichen Gesundheitsamte
Berlin Ind. Ztg.	Industrie Zeitung, Berlin
Berlin Jahr. Pharm.	Berlinisches Jahrbuch fur die Pharmacie und fur 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 uber die Verhandlungen der Gesellschaft fur Erdkunde zu Berlin
Berlin Naturf. Freunde Sitzber.	Sitzungs-Berichte der Gesellschaft Naturforschender Freunde zu Berlin
Berlin Neue Zts. Geburtsk.	Neue Zeitschrift fur 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 fur 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 fur Geschichte der Mathematik. Journal d'Histoire des Mathematiques. Bibliotheca Mathematica. Zeitschrift fur 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
Blatter Blech-Arb.	Deutsche Blatter fur Blecharbeiter
Blatter Kunstgew.	Blatter fur Kunstgewerbe
Blatter Zuckerrub	Blatter fur Zuckerrubenbau
Bleekrode, Nieuw Tijdschrift	Nieuw Tijdschrift gewijd aan alle takken van Volksvlijt, Nijverheid, Landbouw, Mijnwezen, Handel, Spoorwegen, Telegraphie en Scheepvaart
Blois, Mem. Soc. Sci.	Memoires de la Société des Sciences et des Lettres de Blois
Blois, Soc. Loir et Cher Mem.	Memoires de la Société des Sciences et Lettres de Loir et Cher

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

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

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

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

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

Bull. Soc. vaudoise	Bulletin de la Société vaudoise des Ingenieurs et des Architects
Bull. Torrey Bot. Club	Bulletin of the Torrey Botanical Club, New York
Bull. Vulc. Ital.	Bullettino del Vulcanismo Italiano (e di Geodinamica generale)
C. A.	Chemical Abstracts
Cabanis, J. Ornithol.	Journal 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 Karnten
Carl, Rep Physik	Repertorium für Experimental Physik, etc (Rep der Physik)
Carlsberg Lab	See under Kiobenh
Carlsruhe	See Karlsruhe
Carlsruhe, Verh Naturwiss Ver.	Verhandlungen des Naturwissenschaftlichen Vereins
Carloinisches Medico-Chirurgisches Institut.	See under Stockh Physiol Lab Mitth
Carus, Zool Anzeiger	Zoologischer Anzieger
Casopis	Casopis pro Pestovani Mathematiky a Fysiky (Journal for the Advancement of Mathematics and Physica)
Casopis Cesketho Lekarn	Casopis Cesketho Lekarnitura
Casper Vierteljahrssch	Vierteljahrsschrift fur gerichtliche und offentliche Medicin
Casper Wochensch	Wochenschrift fur die gesammte Heilkunde
Cassel Jahr	Jahresbericht, dann Bericht, uber die Thatigkeit des Vereins fur Naturkunde in Cassel
Cassier s Mag.	Cassiers's Magazine
Castings	Castings
Catania Atti Accad Gioen	Atti dell'Accademia Gioenia di Scienze Naturali di Catania
Catania Boll Accad. Gioen	Bollettino delle Sedute della Accademia Gioenia
Cattaneo Bibl. di Farm	Biblioteca di Farmacia, Chimica, etc.
Cattaneo Giorn Farm.	Giornale di Farmacia
Cell. Ind.	Die Celluloid Industrie
Cellule	La cellule
Cement	Cement
Cement Age	Cement Age
Cement Eng. News	Cement and Engineering News
Cement Record	Cement Record
Centr Agrik Chem.	Central-Blatt fur Agrikulturchemie und rationellen Wirthschafts-Betrieb Referirendes Organ fur naturwissenschaftliche Forschungen in ihrer Anwendung auf die Landwirthschaft
Centr Allg Path.	Centralblatt fur allgemeine Pathologie

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

Cherbourg Soc. Sci. Natl. Mem.	Memoires de la Société Nationale des Sciences Naturelles et Mathematiques de Cherbourg
Chester Soc. Sci. Proc.	Proceedings of the Chester Society of Natural Science (and Literature)
Chicago Acad. Sci. Bull.	Bulletin of the Chicago Academy of Sciences
Chicago Acad. Sci. Bull. Nat. Hist. Surv.	The Chicago Academy of Sciences. Bulletin...of the Natural History Survey
Chicago Acad. Sci. Trans.	Transactions of the Chicago Academy of Sciences
Chicago Entom. Soc. Mem.	Occasional Memoirs of the Chicago Entomological Society
Chicago Field Columb. Mus. Publ.	Publications of the Field Columbian Museum
Chile, Anales Univ.	Anales de la Universidad de Chile
Chile P.	Chilean Patent
Chili Soc. Sci. Act.	Actes de la Société Scientifique du Chili (Actas de la Sociedad Cientifica de Chile)
Chim. et Ind.	Chimie et Industrie
Chimiste	Chimiste, Le
Christiania, Forh.	Forhandlinger i Videnskabs-Selskabet i Christiania
Christiania, Norsk Mag.	Norsk Magazin for Laegevidenskaben
Christiania Skr. (Math.-Nat. Kl.)	Skrifter udgivne af Videnskabsselskabet i Christiania. Mathematisk-naturvidenskabelig Klasse
Christiania, Univers. Lab.	Das chemische Laboratorium der Universität Christiania
Chron. ind.	Chronique de l'industrie
Chur, Jahresber. Naturf. Gesell.	Jahresbericht der Naturforschenden Gesellschaft von Graubundten 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.	Beitrage 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 fur Schweizer Aerzte
Corresp. Blatt Zahn.	Correspondenzblatt 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 fur Naturwissenschaft und Heilkunst
Cron. med. mex.	Cronica medica mexicana, Mexico
Croydon Micro Club Proc.	Proceedings and Transactions of the Croydon Microscopical and Natural History Club
Croydon Micro. Club Rep	.. Report and Abstract of Proceedings of the Croydon Microscopical (and Natural History) Club
Cuba P.	Cuban Patent
Cuba, Rep. Fis Nat.	Repertorio fisico-naturale de la isla de Cuba
Cuir	Cuir, Le
Cumberland Assoc. Trans.	Transactions of the Cumberland and Westmorland Association for the Advancement of Literature and Science
Cuyper, Rev. Univ.	Revue Universelle des Mines, de la Metallurgie, &c.
D'Alton u. Burm. Ztg. Zool.	Zeitung fur Zoologie, Zootomie, und Palaeozoologie
Dan. Biol. Stat. Rep.	Report of the Danish Biological Station to the Home Department (Board of Agriculture)
Dan. P.	Danish Patent
Danzig, Neu. Schrift.	Neueste Schriften der Naturforschenden Gesellschaft in Danzig
Danzig, Schrift.	Schriften der Naturforschenden Gesellschaft in Danzig
Darmst. Beitr. Geol.	Beitrage zur Geologie des Grossherzogthums Hessen und der angrenzenden Gegenden
Darmst. Ver. Erdk Notiz.	Notizblatt des Vereins fur Erdkunde zu Darmstadt und des Mittelrheinischen Geologischen Vereins
Davenport Acad Proc.	Proceedings of the Davenport Academy of Natural Sciences
Dax Soc. Borda Bull.	(Bulletin de la) Société de Borda, Dax (Landes)
Delft Ecole Poly. Ann.	Annales de l'Ecole Polytechnique de Delft
Delhi, Med. J.	Quarterly Medical and Surgical Journal for the North-West Provinces
Denison Univ. Sci. Lab Bull.	Bulletin of (the Scientific Laboratories of) Denison University
Dent. Cosmos	Dental Cosmos, Philadelphia
Dent. Digest	The Dental Digest, Chicago
Dent. Rev.	The Dental Review
Deut Amer. Apoth Ztg.	Deutsch-Amerikanische Apotheker Zeitung, New York
Deut. Amer. Gewerbeztg.	Illustrierte Deutsch-Amerikanische Gewerbe und Industrie-Zeitung (Newark, N. J)
Deut. Arch. Klin. Med.	Deutsches Archiv. fur Klinische Medizin
Deut. Bot. Ges Ber.	Berichte der Deutschen Botanischen Gesellschaft
Deut. Bot. Monats.	Deutsche Botanische Monatsschrift
Deut. Buchdr. Ztg.	Deutsche Buchdruker-Zeitung
Deut. Eisenbahn Ztg.	Zeitung des Vereins Deutscher Eisenbahn-Verwaltungen
Deut. Elektro. Ges.	See Zts. Elektroch.

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

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

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

Elektrochem Zts	Elektrochemische Zeitschrift
Elektrotech Zts	Electrotechnische Zeitschrift
Elliott Soc J.	Journal of the Elliott Society of Natural History
Elliott Soc Proc	Proceedings of the Elliott Society of Natural History
Elsner, Mitth	See Chem. Tech. Mitth.
Emden Naturf Ges Jahr.	.. Jahresbericht der Naturforschenden Gesellschaft in Emden
Emden Naturf Ges Schr	Kleine Schriften der Naturforschenden Gesellschaft in Emden
Eng.	Engineering
Eng Contr	Engineering and Contracting
Eng Digest	Engineering Digest
Eng Mag	Engineering Magazine, The
Eng Mining J (Eng Min. J.)	Engineering and Mining Journal, The
Eng News	Engineering News
Eng Record	Engineering 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 Societat 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' Evkonyvei
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 fur 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 Sallskapets 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
Florke, Repert	Repertorium des neuesten und wissenwurdigsten aus der gesammten Naturkunde
Foldt. Kozlön	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
Forster, Allg. Bauztg	Allgemeine Bauzeitung
Fortschr. Chem.	Fortschritte der Chemie, Physik und Physikalischen chemie
Fortschr. Med.	Fortschritte der Medicin
Fortschr. Phys.	Die Fortschritte der Physik.
Fortschr. Rontgenstr.	Fortschritte auf dem Gebiete der Rontgenstrahlen
Fortschr. Theerfarben-Fabrikation	Fortschritte der Theerfarbenfabrikation und ver wendter Industriezweige
Foundry	Foundry, The
F. P.	French Patent
France, Congr. Med. Chir.	Congres Medico-Chirurgicale de France
France, Congr. Sci.	Sessions des Congres Scientifiques de France
France Gites Miner. Etudes	Etudes des Gites Mineraux de la France
France, Inst. Provinces Annuaire	Annuaire de l'Institut des Provinces et des Congres Scientifiques de France
France, Inst. Provinces Mem.	Memoires de l'Institut des Provinces de France. Sciences physiques et naturelles
France Soc. Agric. Bull.	Bulletin des Seances de la Société Nationale d'Agriculture de France
France Soc. Agric. Mem.	Memoires publies par la Société Nationale d'Agriculture de France
France Soc. Bot. Bull.	Bulletin de la Société Botanique de France
France Soc. Entom.	See Abeille., Paris, Soc. Ent. Ann., Paris, Soc. Ent. Bull., Rev. Ent.
Franc Soc. Miner. Bull.	Bulletin de la Société Mineralogique de France. Bulletin de la Société Francaise de Mineralogie. (Ancienne Société Mineralogique de France)
France Soc. Zool.	See Paris, Caus. Sci.
France Soc. Zool. Bull.	Bulletin de la Société Zoologique de France

France Soc. Zool. Mem.	Memoires de la Société Zoologique de France
Frankfurt	See Senckenberg
Frankfurt, Jahr. Phys. Ver.	Jahrbuch zur Verbreitung naturwissenschaftlicher Kenntnisse, veranstaltet vom Physikalischen Verein zu Frankfurt a/Main
Frankf. Ver. Pflege Phot.	See Wien, Photogr. Correspond.
Frankfurt, Zool. Garten	Der Zoologische Garten Frankfurt a/M.
Frankfurter Zts. Pathol.	Frankfurter Zeitschrift fur Pathologie
Franzos. Ann.	Franzosische Annalen fur die allgemeine Naturgeschichte, Physik, &c.
Freiberg, Jahr. Berg Hütt.	Jahrbuch fur den Berg- und Hüttenmann. Herausg. von der Konigl Berg-Akademie zu Freiberg
Freiburg, Beitr	Beiträge zur Rheinischen Naturgeschichte
Freiburg, Ber	Berichte über die Verhandlungen der Naturforschenden Gesellschaft zu Freiburg i. B.
Freie K.	Freie Kunste
Frelon	Le Frelon. Journal d'Entomologie descriptive
Fries, Bot. Notiser	Botaniska Notiser
Froriep, Notizen	Notizen aus dem Gebiete der Natur- und Heilkunde
Fuhling'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 uber den Naturwissenschaftlichen Verein in Schleiz
Gerber	Der Gerber
Germar, Mag Entom	Magazin der Entomologie
Germar, Zts Entom	Zeitschrift fur die Entomologie
Gergonne, Ann Math	Annales de Mathematique
Gesundh. Ing.	Gesundheits-Ingenieur
Gew. Ztg.	Wieck's Gewerbezeitung
Gewerbebl Schw.	Schweizerisches Gewerbeblatt
Gewerbebl. Wurt	Gewerbeblatt aus Wurttemberg
Gewerbeh	Gewerbehalle
Gewerks Ztg	Oesterreichische Gewerkszeitung
Giessen, Oberhess Ges. Ber.	Berichte der Oberhessischen Gesellchaft fur Natur- und Heilkunde
Gievel, Zts.	See Zts Gesammt. Naturwiss.
Gilbert, Ann Phys	See Ann. Phys.
Gill. Tech. Micro Repos	Technical and Microscopical Repository
Giorn. Arcad	Giornale Arcadico di Scienze
Giorn. farm. chim.	Giornale de farmacia, di chimica
Giorn Gen. civ.	Giornale del Genio civile
Giron. Ist. Lomb	See Bibl. Ital
Giorn Mineral. Crist Petr.	Giornale di Mineralogia, Cristallografia e Petrografia
Gironde Comm. Meteorol.	See Bordeaux Soc. Sci. Mem.
Gironde, J. Med.	Journal Medical de la Gironde
Gistl, Faunus	Faunus
Glasgow. Inst. Engin. Trans.	Transactions of the Institution of Engineers and Shipbuilders in Scotland
Glasgow Med. Chir. Soc. Trans.	Transactions of the Medico-Chirurgical Society of Glasgow
Glasgow Med. J.	Glasgow Medical Journal
Glasgow Natur. Hist. Soc. Proc. & Trans.	Proceedings and Transactions of the Natural History Society of Glasgow
Glasgow Path. Clin. Soc. Trans.	Transactions of the Glasgow Pathological and Clinical Society

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

Guia Minero	Guia del Minero: Periodico cientifico, industrial y mercantil
Guillemin, Archiv. Bot.	Archives de Botanique, ou Recueil Mensuel de Memoires originaux, etc.
Gummi-Ztg.	Gummi-Zeitung
Günsburg, Zts. Klin. Med.	Zeitschrift fur klinische Medizin, mit dem Verein für physiologische Heilkunde in Breslau
Gurlt, Mag. Ges. Thierheilk.	Magazin für die gesammte Thier-Heilkunde
Guy's Hosp. Rep.	Guy's Hospital Reports
Haarlem Kolon. Mus. Bull.	Bulletin van het Koloniaal Museum te Haarlem
Haarlem, Mus. Teyler Archiv.	Archives du Musee Teyler
Haarlem, Natuurk. Verh. Maatsch. Wet.	Natuurkundige Verhandelingen van de (Bataafsch) Hollandsche Maatschappij der Wetenschappente Haarlem
Haaxman, Tijdschr.	Tijdschrift voor Wettenschappelijke Pharmacie, etc.
Habana Acad. Anales.	Anales de la (Real) Academie de Ciencias Medicaes Fisicas y Naturales de la Habana
Haeser, Archiv. Med.	Archiv fur die gesammte Medicin
Hage	See Gravenhage
Hahnemann. Month.	Hahnemannian Monthly, Philadelphia
Haidinger, Abh.	Naturwissenschaftliche Abhandlungen
Haidinger, Ber.	Berichte uber die Mittheilungen von Freunden der Naturwissenschaften in Wien
Hainaut Soc. Mem.	Memoires et Publications de la Société des Sciences, des Arts et des Lettres du Hainaut
Hall, Bijdragen	Bijdragen tot de Natuurkundige Wetenschappen
Halle, Abr. Naturwiss. Ver.	Abhandlungen des Naturwissenschaftlichen Vereins fur Sachsen und Thüringen in Halle
Halle aux cuirs, La	Halle aux cuirs, La
Halle, Jahr. Naturwiss. Ver.	Jahresbericht des Naturwissenshaftlichen Vereins in Halle
Halle Kryptog. Lab.	See Beitr. Physiol Morphol.
Halle, Naturf. Ges. Abh.	Abhandlungen der Naturforschenden Gesellschaft zu Halle
Halle, Naturf. Ges. Ber.	Bericht der Naturforschenden Gesellschaft zu Halle
Halle, Naturf. Ges. Neu. Schr.	Neue Schriften der Naturforschenden Gesellschaft zu Halle
Halle, Zts. Ges. Naturwiss.	Zeitschrift fur 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 fur 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 fur 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 fur Kryptogamische Literatur. Hedwigia. Organ fur (specielle) Kryptogamenkunde (und Phytopathologie) nebst Repertorium fur (Kryptogamische) Literatur.
Heidelb. Jahr. Lit.	Jahrbucher der Literatur. Verhandlungen des Naturhistorisch-Medicinischen Vereins zu Heidelberg
Heidelb. Naturhist. Med. Festschr.	Festchrift zur Feier des funfhundertjahrigen Bestehens der Ruperto-Carola dargebracht von dem Naturhistorisch-Medicinischen Verein zu Heidelberg
Heidelb. Naturhist. Med. Verh.	Verhandlungen des Naturhistorisch-Medicinischen Vereins au Heidelberg
Heidelb , Verh.	Verhandlungen der in Heidelberg versammelten Augenarzte
Heis, Wochenschr.	Wochenschrift für Astronomie, Meteorologie, und Geographie
Heller, Archiv.	Archiv fur physiologische und pathologische Chemie und Mikroskopie
Helsingfors, Acta Soc. Sci. Fenn.	Acta Societatis Scientiarum Fennicae
Helsingfors, Bidrag Finlands Natur o. Folk.	Bidrag till kannedom om Finlands Natur och Folk, utgifna af Finska Vetenskaps-Societeten
Helsingfors, Bidrag Finlands Naturkänn.	Bidrag till Finlands Naturkännedom, Etnografi och Statistik, utgifna af Finska Vetenskaps-Societeten
Helsingfors, Faun. Flor. Fenn. Acta.	Acta Societatis pro Fauna et Flora Fennica
Helsingfors, Fauna Flora Fenn. Medd.	Meddelanden af Societas pro Fauna et Flora Fennica
Helsingfors, Faun. Flor. Fenn. Notiser	Notiser ur Sallskapets pro Fauna et Flora Feennica Forhandlingar
Helsingfors, Öfvers, Finaka Vet. Soc.	Öfversigt af Finska Vetenskaps-Societatens Förhandlingar
Helv. Chim. Acta	Helvetica Chimica Acta
Henle und Pfeufer, Zts.	See Zeitschrift für rationelle Medicin
Hermannstader Verh.	Verhandlungen und Mittheilungen des Siebenbürgischen Vereins für Naturwissenschaften in Hermannstadt

Hermbstatt, Archiv.	Archiv der Agriculturchemie für denkende Landwirthe
Hermstadt, Bull.	Bulletin des Neuesten und Wissenwürdigsten aus der Naturwissenschaft, etc.
Hermbstädt, Museum	Museum des Neuesten und Wissenwurdigsten aus dem Gebiete der Naturwissenschaft, der Künste, der Fabriken, der Manufakturen, der technischen Gewerbe, der Landwirthschaft, der Produktenwaaren und Handelskunde, und der burgerlichen Haushaltung, &c.
Hertha	Hertha
Herts. Natur. Hist. Soc. Trans.	Transactions of the Hertfordshire Natural History Society and Field Club
Hessen, Naturhist. Verg.	Verhandlungen des Naturhistorischen Vereins für das Gross herzogthum Hessen und Umgebung
Heusinger, Zts.	Zeitschrift 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 fur Ophthalmologie
Hippone	See Bone
Hisinger, Afh.	Afhandlingar i Fysik, Kemi, och Mineralogie
Hobart Town	See Tasmania
Hoeven en Vriese, Tijdschr.	Tijdschrift voor Natuurlijke Geschiedenis en Physiologie
Hoff, Mag.	Magazin fur die gesammte Mineralogie, Geognosie, etc.
Hoffman, Phytogr. Blatt.	Phytographische Blatter
Holl. P.	Holland Patent
Holland, Beitr.	Hollandsiche Beitrage zu den anatomischen und physiologischen Wissenschaften
Holland, 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 fur die Anfanger 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 Beitrage 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.	Illustrierte landwirtschaftliche Zeitung
Illust. Off J.	Illustrated Official Journal, The (Patents)
Illust. Wochenschr. Entom.	Illustrierte Wochenschrift fur Entomologie. Internationales Organ für alle Interessen der Insektenkunde. Offizielles Organ der Berliner Entomologischen Gesellschaft
Impr.	L'imprimerie
Ind. Chim.	Industria chimica
Ind. lait.	L'Industrie laitiere
Ind. Text.	L'industrie textile
Ind. Ztg.	Deutsche Industrie Zeitung
Index Med.	Index Medicus, Washington
India Agric. Soc. J.	Journal of the Agricultural and Horticultural Society of India
India, Agric. Soc. Proc.	Proceedings of the Agricultural and Horticultural Society of India
India Agric Soc. Trans.	Transactions of the Agricultural and Horticultural Society of India
India Bot. Surv. Records	Records of the Botanical Survey of India
India Dept. Agric.	India Department of Agriculture, Publications
India, Govt. Records (For. Dept.)	Selections from the Records of the Government of India. (Foreign Department)
India, Govt. Records (Home Dept.)	Selections from the Records of the Government of India
India P.	Indian Patent
India Rev.	India Review and Journal of Foreign Science and the Arts
India Rub. J.	India Rubber Journal
India Rub. World	India Rubber World
Indian Ann.	Indian Annals of Medical Science
Indian J. Med. Phys. Sci	Indian Journal of Medical Science
Indian Med. Gaz.	The Indian Medical Gazette, a monthly record of Medicine, &c.

Indian Meteorol. Mem.	Indian Meteorological Memoirs: being occasional Discussions and Compilations of meteorological data relating to India and the neighboring countries
Indian Mus. Notes	Indian Museum Notes
Industrieztg. Ungarn	Industriezeitung für Ungarn
Ingenieur	Der Ingenieur
Inghirami, Opuscoli	Nuova Collezione di Opuscoli e Notizie di Scienze
Innsbruck, Jahr.	Jahresbericht der k. k. Ober-Realschule zu Innsbruck
Innsbruck Naturwiss. Med. Ber.	Berichte des Naturwissenschaftlich-medizinischen Vereines in Innsbruck
Innsbruck, Neue Zts.	Neue Zeitschrift des Ferdinandeums für Tirol
Innsbruck, Zts. Ferdinandeums	Zeitschrift des Ferdinandeums fur Tirol und Voralberg
Inst.	L'Institut
Inst. Act. J.	Journal of the Institute of Actuaries (and Assurance Magazine)
Inst. Brewing Trans.	Transactions of the Institute of Brewing
Inst. Civ. Eng. Proc.	Minutes of the Proceedings of the Institution of Civil Engineers
Inst. Egypt. Bull.	Bulletin de l'Institut Egyptien
Inst. Egypt. Mem.	Memoires (ou Travaux originaux) presentes (et lus) a l'Institut Egyptien
Inst. Elect. Engin. J.	Journal of the Institution of Electrical Engineers
Inst. Mechan. Engin. Proc.	Institution of Mechanical Engineers. Proceedings
Inst. Min Eng. Trans.	Transactions of the Institution of Mining Engineers
Inst. Min. Met. Trans.	Transactions of the Institution of Mining and Metallurgy
Inst. Solvay Trav.	Institut Solvay. Travaux de Laboratoire
Intell. Observer	The Intellectual Observer
Intl. Beitr. Path. Therap.	Internationale Beiträge zur Pathologie und Therapie, die Ernahrungsstorungen, 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 Zurich, 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. Zergl ied.	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 fur praktische Chemie
J. Psychol. Med	Journal of Psychological Medicine and Mental Pathology
J. Roy Agric Soc.	Journal of the Royal Agricultural Society
J. Roy. Astron Soc. Canada	Journal of the Royal Astronomical Society of Canada
J. Roy. Inst. Pub. Health	Journal of the Royal Institute of Public Health
J. Roy. San Inst.	Journal of the Royal Sanitary Institute
J. Roy. Soc N. S. Wales	Journal of the Royal Society of New South Whales
J. Roy. U. S. Inst	Journal Royal United Service Institution
J. Russ. Phys. Chem. Soc.	Journal of the Russian Physical Chemical Society
J. S. C. I.	Journal of the Society of Chemical Industry
J. Savants	Journal des Savants
J. Sci.	The Journal of Science
J. sci. math. physi. nat.	Journal de sciencias mathematicas, physicas naturaes
J. Soc. Arts	Journal of the Royal Society of Arts
J. Soc. Dyers Col.	Journal of the Society of Dyers and Colorists
J. soc. pharm. Anvers	Journal de pharmacie, organe de la société de pharmacie d'Anvers
J. Soc. Telegr. Eng.	Journal of the Society of Telegraphic Engineers
J. State Med.	The Journal of State Medicine
J. suisse chim. pharm.	Journal suisse de chimie et pharmacie
J. Travel	The Journal of Travel and Natural History
J. Trop. Med.	The Journal of Tropical Medicine
J. U. S. Artill.	Journal of the United States Artillery
J. Univ. Med.	Journal universel et hebdomadaire de Medecine et de Chirurgie pratiques et des Institutions medicales
J. Univ. Sci. Med.	Journal Universel des Sciences Medicales
J. Wash. Acad. Sci.	Journal of the Washington Academy of Sciences
J. Western Soc. Eng.	Journal of the Western Society of Engineers

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

Kampen, Mag.	Magazin voor Wetenschappen, Kunsten, &c.
Kan. Acad. Sci. Trans.	Transactions of the....annual meeting of the Kansas Academy of Science
Kan. Univ. Quart.	The Kansas University Quarterly
Karlsruhe Bact. Inst. Arb.	Arbeiten aus dem bacteriologischen Institut der technischen Hochschule zu Karlsruhe
Karlsruhe Naturwiss. Ver. Verh.	Verhandlungen des Naturwissenschaftlischen Vereins in Karlsruhe
Kärnten, Berg-Verein, Zts.	Zeitschrift des Berg- u. Hüttenmännischen Vereins für Kärnten
Kärnten Landesmus. Jahr.	Jahrbuch des naturhistorischen Landes-Museums von Kärnten
Kärnten, Zts.	Zeitschrift des berg- und hüttenmännischen Vereines für Kärnten
Karsten	See Botan. Untersuch.
Karsten, Archiv.	Archiv fur Mineralogie, Geognosie, Bergbau, und Huttenkunde
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 Funfzigjährigen Bestehens
Kastner, Archiv. Chem.	Archiv. fur 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
Kiobenh. Bot. For.	See Bot. Tidsskr.
Kiobenh. 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
Kiobenh. Dansk. Vid. Selsk. Afh.	Det Kongelige Danske Videnskabernes Selskabs naturvidenskabelige og mathematiske Afhandlinger

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

Kreutzer's Jahr. Phot	Kreutzer's Jahresbericht der Photographie
Kristiania, Geogr. Selsk Arb.	Det Norske Geografiske Selskabs Arbog
Kristiania, Norw. Mar. Investig. Rep.	Report on Norwegian Fishery and Marine Investigations
Kroyer, Naturhist Tidssk.	Naturhistorisk Tidsskrift
Kuhn-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 dès Krainischen Landes Museums in Laibach
Laibach, Mus.-Ver. Krain Mitth.	Mittheilungen des Museal-Vereins fur 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 Wissenschaften
Leather	Leather
Leather Mfr.	Leather Manufacturer
Leather Tr Rev.	Leather Trades Review
Leather World	Leather World, The
Lederind.	Lederindustrie (Deutsche Gerber-Zeitung)
Ledermarkt	Ledermarkt, Der (See also Collegium)
Leeds, Trans. Phil Soc	Transactions of the Philosophical and Literary Society of Leeds
Leicester, Lit. Phil Soc Selection	Selection of Papers, of the Literary and Philosophical Society of Leicester
Leicester Soc. Rep.	Leicester Literary and Philosophical Society ..Report of the Council
Leicester Soc. Trans.	Transactions of the Leicester Literary and Philosophical Society

Leide	See Leyden
Leiiden, Ann. Acad.	Annales Academiae Lugduno-Batavae
Leiden, Tijdschr. Entom.	Tijdschrift voor Entomologie
Leipzig, Abh. Jablon. Ges.	Abhandlungen bei Begründung der k. Sächsischen Gesellschaft der Wissenschaften am Tage der zweihundertjahrigen Geburtsfeier Leibnizens
Leipzig, Abh. Math. Phys.	Abhandlungen der Mathematisch-Physischen Classe der Koniglich Sachsischen 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 uber die Verhandlungen (Math. Phys Classe) der Königlich Sachsischen Gesellschaft der Wissenschaften zu Leipzig
Leipz. Farb. Ztg.	Leipziger Farber- und Zeugdrucker-Zeitung
Leipzig Jablon. Preisschr.	Preisschriften gekront und herausgegeben von der furstlich Jablonowski' schen Gesellschaft zu Leipzig
Leipzig, Monatschr. Text. Ind.	Leipziger Monatsschrift fur 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 Huttenmannisches Jahrbuch der k. k. Montan. Lehranstalten zu Leoben und Pribram
Leonhard Bronn	See Neues Jahr. Mineral
Leonhard Bronn, Jahr.	Jahrbuch fur Mineralogie, Geognosie, Geologie, und Petrefaktenkunde
Leonhard Bronn, Neu. Jahr.	Neues Jahrbuch fur Mineralogie, Geognosie, Geologie und Petrefaktenkunde
Leonhard, Taschenbuch	Taschenbuch fur die gesammte Mineralogie
Leonhard, Zts.	Zeitschrift fur 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 fur 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 fur 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 uber das Museum Francisco-Carolinum in Linz
Lisboa, Acad. Sci. Mem.	Historia e Memorias da Academia Real das Sciencias de Lisboa
Lisboa, Actas	Actas das Sessoes da Academia Real das Sciencias de Lisboa
Lisboa, Ann.	Annaes das Sciencias e Lettras
Lisboa, J. Math. Sci.	Jornal de Sciencias Mathematicas, Physicas e Naturaes publicado sob os Auspicios da Academia Real das Sciencias de Lisboa
Litterar. Annal.	Litterarische Annalen der gesammten Heilkunde
Liverpool Biol. Soc. Proc.	Proceedings and Transactions of the Liverpool Biological Society
Liverpool, Lit. Phil. Soc. Proc.	Proceedings of the Literary and Philosophical Society of Liverpool
Liverpool Mar. Biol. Comm	See Liverpool Biol. Soc. Proc.; Liverpool Biol. Soc. Proc. & Trans ; Liverpool Lit. Phil. Soc. Proc.
Liverpool Med. Chir J.	Liverpool Medico-Chirurgical Journal
Liverpool School Trop Med. Mem.	Liverpool School of Tropical Medicine. Memoirs
Liverpool. Thompson Yates Lab. Rep.	The Thompson Yates Laboratories Report
Loc. Gov. Bd. Rep. (Med. Off.)	...Annual Report of the Local Government Board Supplement containing the Reports of the Medical Officer
London	See Int. Congr. Hyg. Trans , 1891; Int. Congr Zool. Proc. 1898
London, Ann Med. Surg.	Annals of Medicine and Surgery, Records of the occurring Improvements, &c.
London, Cryst. Soc Proc.	Proceedings of the Crystallological Society
London Elec. Soc. Proc.	Proceedings of the London Electrical Society
London, Fed. Inst. Brewing J.	Journal of the Federated Institutes of Brewing containing the Transactions of the various Institutes
London J. Med.	London Journal of Medicine
London, Med. Phys. J.	The Medical and Physical Journal
London, Med. Soc. Trans.	Transactions of the Medical Society of London

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

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

Magyar Tud. Akad. Ertek. (Termt.)	Ertekezesek a Termeszettudomanyok korebol. Kiadja a Magyar Tudomanyos Akademia. (Memoirs in the Natural Sciences. Published by the Hungarian Academy of Science)
Magyar Tud. Akad Evk.	A Magyar Tudomanyos Akademia Evkonyvei. (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 fur 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 fur Anatomie und Physiologie
Meckel, Deut. Archiv	Deutsches Archiv. fur die Physiologie
Med. Assoc. J.	Journal edited for the Provincial Medical and Surgical Association
Med. Bot. Soc. Trans.	Transactions of the Medico-Botanical Society of London
Med. Chem. Unters.	Medicinish-chemische Untersuchungen; aus dem Laboratorium fur angewandte Chemie zu Tubingen
Med. Chir Soc. Proc.	Proceedings of the Royal Medical and Chirurgical Society of London
Med.-Chir. Trans.	Medico-Chirurgical Transactions
Med. Chir. Ztg.	Medicinisch-chirurgische Zeitung
Med. Congr.	See Congr. Int. Med. C. R., Congr. Int. Sci. Med. C. T., Congr. Med. Int. Atti., Int. Med. Congr. Trans., Int. Med. Congr. Verh.
Med. Jahr.	Medizinische Jahrbucher, 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 fran K. Vetenskapsakademiens Nobel-institut
Meisner, Ann.	Annalen der allgemeinen Schweizerischen Gesellschaft fur die gesammten Naturwissenschaften
Meisner, Anzeiger	Naturwissenschaftlicher Anzeiger der Allgemeinen Schweizerischen Gesellschaft fur die gesammten Naturwissenschaften
Melbourne	See Victoria
Mem. accad. Lincei	Memorie della r. accademia dei Lincei, Classe di scienze fisiche, mathematiche e naturali
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino
Mem. Chem. Soc.	Memoirs and proceedings of the Chemical Society of London prior to 1848
Mem. Coll. Sci. Eng. Kyoto	Memoirs of the College of Science and Engineering, Kyoto Imperial University
Mem. Fis. Sperim.	Memorie di Fisica sperimental
Mem. Imp. Mineral. Soc. Petrograd	Memoirs of the Imperial Mineralogical Society of Petrograd
Mem. Lepidopt., St. Petersb.	Memoires sur les Lepidopteres

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

Milano, Atti Ginnas.	Atti dell' I. R. Ginnasio Liceale Convitto Longone in Milano
Milano, Atti Ist. Lomb.	Atti dell' I. R. Istituto Lombardo di Scienze, Lettere, ed Arti
Milano, Atti Soc. Ital.	Atti della Societa Italiana di Scienze Naturali
Milano, Cagnola Atti	Atti della Fondazione Scientifica Cagnola dalla sua istituzione in poi.
Milano, Giorn. Soc. Incor.	Giornale della Societa d'Incorragiamento delle Scienze, etc , stabilita in Milano
Milano, Ist. Lomb. Adunanze	Solenni Adunanze del R. Istituto Lombardo di Scienze e Lettere
Milano, Ist. Lomb. Rapporti	Rapporti sui Progressi delle Scienze del R. Istituto Lombardo di Scienze
Milano, Ist. Lomb. Rend.	Rendiconti dell' Istituto Lombardo di Scienze e Lettere —Classe di Scienze matematiche e naturali
Milano, Mem. Ist. Lomb.	Memorie dell' I. R. Istituto Lombardo di Scienze, etc.
Milano, Mem. Ist. Lomb. Veneto	Memorie dell' I. R. Istituto del regno Lombardo-Veneto
Milch Zentr.	Milchwirtschaftliches Zentralblatt
Milch Ztg.	Milch Zeitung
Min. Eng. World	Mining and Engineering World
Min. J.	The Mining Journal
Min. Rev.	Mining Review, a Monthly Record of Geology
Min. Sci.	Mining Science
Min. Sci. Press	Mining and Scientific Press
Min. Smelt. Mag.	The Mining and Smelting Magazine: a monthly review of Practical Mining, Quarrying, and Metallurgy
Min Soc. J.	See Min Mag
Mineral. Mag.	The Mineralogical Magazine and Journal of the Mineralogical Society of Great Britain and Ireland
Mineral. Mitth.	Mineralogische Mittheilungen
Mineral. Petr. Mitth.	(Tschermak's) Mineralogische und Petrographische Mittheilungen
Mines and Minerals	Mines and Minerals
Minn. Acad. Sci. Bull	Bulletins of the Minnesota Academy of Natural Sciences
Minn. Acad. Sci. Pap.	The Minnesota Academy of Natural Sciences at Minneapolis, Minn. Occasional Papers
Minn. Bot. Stud.	Geological and Natural History Survey of Minnesota. Minnesota Botanical Studies
Miquel, Bull.	Bulletin des Sciences Physiques et Naturelles en Neerlande
Misc. Ent.	Miscellanea Entomologica
Mitau, Quatember	Die Quatember
Mitth. Artil. Geniew.	Mittheilungen über Gegenstände des Artillerie- und Genie-wesens
Mitth. Bohmen. Archit. Ing. Ver.	Mittheilungen des Architekten und Ingenieur Vereins im Königreiche Bohmen
Mitth. Centralst. Wiss.-tech. Unters.	Mittheilungen aus der Centralstelle für wissenschaftlichtechnische Untersuchungen
Mitth. Gewerbever. Nassau	Mittheilungen fur den Gewerbeverin für Nassau
Mitth. Kais. Gesundhts.	Mittheilungen aus dem Kaiserlichen Gesundheitsamte, Berlin
Mitth. Königl. Materialprufungsamt	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 koniglichen 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 Huttenkunde
Moll, Efemeriden	Efemeriden der Berg- und Huttenkunde
Moll, Jahr. Berg.	Jahrbucher der Berg- und Huttenkunde
Moll, Neue Jahr.	Neue Jahrbucher 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 Abbhandlungen aus den Sitzungsberichten der kaiserlichen Akademie der Wissenschaften
Monats. Dermatol.	Monatshefte fur praktische Dermatologie
Monatsbl. Hannover Gewerbever.	Monatsblatt des Gewerbevereins fur Hanover
Monatschr. Text.-Ind.	Leipziger Monatsschrift fur Textil-Industrie
Monatschr. Zahn	Monatschrift fur Zahnarzte
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. fur Anatomie, Physiologie, und wissenschaftliche Medicin.
München, Akad. Abh.	Abhandlungen der Mathematisch-Physikalisch Classe der koniglich Bayerischen Akademie der Wissenschaften
München, Akad. Sitzber.	Sitzungsberichte der Mathematisch-Physikalischen Classe der k. B. Akademie der Wissenschaften Munchen
München Bot. Ver.	See Bot. Centrbl.
München, Bull. Akad.	Bulletin der k. Akademie der Wissenschaften
München, Denkschr.	Denkschriften der Konigl. Baierischen Akademie der Wissenschaften zu München
München, Entom. Ver. Mitth.	Mittheilungen des Munchener Entomologischen Vereins
München, Gelehrte Anz.	Gelehrte Anzeigen

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

N. Y. Acad. Med. Bull.	Bulletin of the New York Academy of Medicine
N. Y. Acad. Med. Trans.	Transactions of the New York Academy of Medicine
N. Y. Agric. Soc. Trans.	Transactions of the New York State Agricultural Society
N. Y. Bot. Club Bull.	Bulletin of the Torrey Botanical Club
N. Y. Entom. Soc. J.	Journal of the New York Entomological Society
N. Y. Insects Report	Report on the Noxious, Beneficial and other Insects of the State of New York
N. Y. J. Med.	New York Journal of Medicine and the Collateral Sciences
N. Y. Linn. Soc. Trans.	Transactions of the Linnaean Society of New York
N. Y. Lit. Phil. Soc. Trans.	Transactions of the Literary and Philosophical Society of New York
N. Y Lyceum Ann.	Annals of the Lyceum of Natural History of New York
N. Y. Lyceum, Proc.	Proceedings of the Lyceum of Natural History in the City of New York
N. Y. Med. J.	New York Medical Journal
N. Y. Med. Repos.	Medical Repository of New York
N. Y. Med. Soc. Trans.	Transactions of the Medical Society of the State of New York
N. Y. Mus. Bull.	University of the State of New York. Bulletin of the New York State Museum
N. Y. Mus. Mem.	Memoirs of the New York State Museum
N. Zeal. Inst. Trans.	Transactions and Proceedings of the New Zealand Institute
N. Zeal. Inst. Min. Engin. Trans.	Transactions of the New Zealand Institute of Mining Engineers
N. Zeal. J. Sci.	The New Zealand Journal of Science
N. Zeal. P.	New Zealand Patent
N. Zeal. Pap. & Rep.	New Zealand. Papers and Reports relating to Minerals and Mining
Nachr. konig. Ges.	Nachrichten von der königlichen Gesellschaft der Wissenschaften zu Gottingen. (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-Blatter
Neu-Vorpommern Mitth.	Mittheilungen aus dem naturwissenschaftlichen Vereins fur 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
Niederosterr. 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 fur 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 fur Wissenschaft, Kunst, und offentliches Leben
Oesterr. Zts. Berg. Hüttenw.	Oesterreichsche Zeitschrift fur Berg- und Huttenwesen
Oesterr.-ung Zts. Zuckerind.	Oesterreichisch-ungarische Zeitschrift fur Zuckerindustrie und Landwirtschaft
Off. Gaz.	Official Gazette, United States Patent Office
Offenbach. Ver. Naturk. Ber.	Bericht des Offenbacher Vereins fur Naturkunde uber seine Thatigkeit
Oil Colour J.	Oil and Colourman's Trade Journal
Oil, Paint Drug. Rep.	Oil, Paint and Drug Reporter
Oise	See Beauvais
Oise Mem. Soc. Acad.	Memoires de la Société Academique d'Archeologie, Sciences, et Arts du departement de l'Oise
Oken Isis	Isis, oder Encyclopadische Zeitung
Omaha Drug.	Omaha Druggist (The), Omaha
Omodei Ann. Univ.	Annali Universali di Medicina
Ontario Entom. Soc. Rep.	Report of the Entomological Society of Ontario
Oporto	See Porto
Ophthalm. Bibliothek	Ophthalmologische Bibliothek
Ophthalm. Hosp. Reports	Ophthalmic Hospital Reports and Journal of the Royal London Ophthalmic Hospital
Ophthalmic Rev.	The Ophthalmic Review: a Quarterly Journal of Ophthalmic Surgery and Science
Organ Rübenzuckerind.	Organ des Centralvereins fur Rubenzuckerindustrie
Orgelb	Die Orgelbauzeitung
Orleans Ann.	Annales de la Société Royale des Sciences, Belles-Lettres, et Arts d'Orleans
Orleans, Bull.	Bulletin des Sciences Physiques, Medicales, et d'Agriculture d'Orleans
Ornis	Ornis, oder das Neuste und Wichtigste der Vögelkunde, etc.
Ornith. Jahr.	Ornithologisches Jahrbuch
Ornith. Monatsber.	Ornithologische Monatsberichte
Ornithol.	The Ornithologist
Ornithol. Ool.	The Ornithologist and Oologist
Örsted Tidsskrift	Tidsskrift for Naturvidenskaberne
Orvos-Termesz. Ertes.	Orvos-Termeszettudomanyi Ertesitó a Kolozsvari Orvos-Termeszettudomanyi Tarsulat es az Erdelyi Museum-Egylet Termeszettudomanyi Szakosztalyanak az..szaküleseiról..(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 Osnabruck
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 fur...
Passau, Jahr. Naturhist. Ver.	Jahresbericht des Naturhistorischen Vereins
Pathol Soc. Trans.	Transactions of the Pathological Society of London
Pavia Ist. Bot. Atti	Atti dell' Istituto Botanico dell' Universita di Pavia. Seguito dell' Archivio Triennale del Laboratorio di Botanica Crittogamica
Pavia Lab. Crittog. Archiv.	Archivio del Laboratorio di Botanica Crittogamica presso la R. Universita di Pavia
Peabody Acad Mem.	Memoirs of the Peabody Academy of Science
Peabody Acad. Report	Sixth Annual Report of the Trustees of the Peabody Academy of Science.
Penn Univ. Publ.	Publications of the University of Pennsylvania
Penzance Soc. Trans.	Transactions of the Natural History and Antiquarian Society of Penzance
Perf. Essent Oil Rec.	Perfumery and Essential Oil Record
Perthsh. Soc. Sci. Trans. & Proc.	Transactions and Proceedings of the Perthshire Society of Natural Science
Peru P.	Peruvian Patent
Pet. Nouv. Entom.	Petites Nouvelles Entomologiques
Petermann, Mitth	Dr. A. Petermann's Mittheilungen aus Justus Perthes' Geographischer Anstalt
Peters, Zts.	Zeitschrift fur populare Mittheilungen aus dem Gebiete der Medicin, Chirurgie, und Pharmacie; in Verbindung mit einem Vereine von Aerzten und Pharmaceuten der Herzogthumer Schleswig und Holstein
Petroleum	Petroleum
Petroleum Gaz.	Petroleum Gazette
Petroleu m Rev.	Petroleum Review
Pfluger, Archiv. Physiol	Archiv. fur die gesammte Physiologie des Menschen und der Thiere
Pharm.	Pharmakologie
Pharm.-Ber. Deut.-Arzbuch.	Pharmakopoe-Bericht. Die vegetablischen Drogen des Deutschen Arzneibuches, 5te. Ausgabe, Caesar & Loretz, Halle
Pharm. Centr.	Pharmaceutisches Central-Blatt
Pharm. Centralh.	Pharmaceutische Centralhalle fur Deutschland
Pharm. Era	Pharmaceutical Era
Pharm. J.	The Pharmaceutical Journal (and Transactions)
Pharm. Post	Pharmazeutische Post
Pharm. Weekblad	Pharmazeutische Weekblad
Pharm. Ztg.	Pharmazeutische Zeitung

Pharm. Zts.	Pharmazeutische Zeitschrift
Pharm. Zts. Russland	Pharmaceutische Zeitschrift für Russland
Phil. Mag.	Philosophical Magazine
Phil. Stud.	Philosophische Studien
Phil. Trans.	Philosophical Transactions of the Royal Society of London
Phila. Acad. Natur. Sci. J.	Journal of the Academy of Natural Sciences of Philadelphia
Phila., Acad. Natur. Sci. Proc.	Proceedings of the Academy of Natural Sciences of Philadelphia
Phila. Amer. Entom. Soc.	See Amer. Entom. Soc.
Phila. Coll. Pharm. Journ.	Journal of the Philadelphia College of Pharmacy
Phila. Eng. Club	Proceedings of the Engineers' Club of Philadelphia
Phila. Entom. News	Entomological News (and Proceedings of the Entomological Section of the Academy of Natural Sciences of Philadelphia)
Phila. Entom. Soc. Proc.	Proceedings of the Entomological Society of Philadelphia
Phila. Med. Mus.	Philadelphia Medical Museum
Phila. Med. Phys. J.	The Philadelphia Medical and Physical Journal
Phila. Phot.	The Philadelphia Photographer
Philippine J. Sci.	Philippine Journal of Science
Phot. Archiv	Photographisches Archiv
Phot. Bull.	Anthony's Photographic Bulletin
Phot. Chronik.	Photographische Chronik und allgemeine Photographen-Zeitung
Phot. J.	Wilhelm Horn's Photographische Journal
Phot. Corr. (Korr.)	Photographische Korrespondenz
Phot. Mag.	Photographisches Magazine
Phot. Mitth.	Photographische Mittheilungen
Phot. Monats.	Photographische Monatshefte
Phot. News	Photographic News
Phot. Rundsch.	Photographische Rundschau und Photographisches Centralblatt
Phot. Soc. J.	Journal of the Photographic Society of London
Phot. Soc. Trans.	Trans. of the Photographic Society of London
Phot. Times	The Photographic Times
Phot. Wochenbl.	Photographisches Wochenblatt
Phot. World	The Photographic World
Phot. Centr.	Photographisches Centralblatt
Phot. Ztg.	Deutsche Photographen-Zeitung
Phys. Rev.	Physical Review
Physikal.-Chem. Zentr.	Physikalisch-chemisches Zentralblatt
Physikal. 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
Plon Biol. Sta. Forschungsber.	Forschungsberichte aus der Biologischen Station zu Plon
Plymouth Inst. Trans.	Annual Reports and Transactions of the Plymouth Institution and Devon and Cornwall Natural History Society
Pogg. Ann.	Poggendorff's Annalen der Physik und Chemie
Pogg. Ann. Beibl.	Poggendorff's Annalen der Physik und Chemie Beiblatter
Poligrafo	Il Poligrafo: Giornale di Science, Lettere, ed Arti
Polit.	Il Politecnico
Pollichia, Jahr.	Jahresbericht der Pollichia, eines naturwissenschaftlichen Vereins der Baierischen Pfalz (der Rheinpfalz)
Polsk. Tow. Przyrod. Kopernika	See Kosmos (Lwow)
Poly. Centr.	Polytechnisches Centralblatt
Poly. Centralh.	Polytechnische Centralhalle
Poly. Mitth.	Polytechnische Mittheilungen
Poly. Notiz.	Polytechnisches Notizblatt
Polygraph Centr.	Polygraphisches Centralblatt
Pommer, Zts.	Schweizerische Zeitschrift fur Natur- und Heilkunde
Pop. Mag. Anthropol.	The Popular Magazine of Anthropology
Pop. Sci. Mon.	Popular Science Monthly
Popular Sci. Rev.	The Popular Science Review: a Quarterly Miscellany of entertaining and instructive articles on Scientific subjects
Pontif. Univ. Gregor.	Pontificia Universita Gregoriana. Continuazione del Bullettino Meteorologico dell' Observatorio del Cellegio Romano
Port. P.	Portuguese Patent
Portland, Soc. Natur. Hist. Proc.	Proceedings of the Portland Society of Natural History
Porto, Ann Soc. Lit.	Annaes da Sociedade Lit Portuense
Porto Soc. Instruc. Rev.	Revista da Sociedade de Instruccao do Porto
Potsdam Astrophys. Obs. Publ.	Publicationen des Astrophysikalischen Observatoriums zu Potsdam
Pottery Gaz.	Pottery Gazette
Pottery and Glass	Pottery and Glass
Power	Power
Prace Mat.-Fiz.	Prace Matematyczno-Fizyczne. (Mathematical and Physical Papers)
Pract. Drug.	Practical Druggist and Pharmaceutical Review of Reviews, New York
Pract. Mag.	The Practical Magazine (London)
Pract. Mechan. J	The Practical Mechanics Journal
Practitioner	The Practitioner
Prag, Abh.	Pojednani Kral. Ceske Spolecnosti Nauk. Abhandlungen der Konigl. 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. Bohm. Mus.	Jahrbucher des Bohmischen Museums fur Natur- und Länderkunde
Prag, Jahr. Realschule	Jahresbericht der k. k. Bohmischen Ober-Realschule zu Prag
Prag, Lotos Abh.	Abhandlungen des Deutschen Naturwissenschaftlich-Medicinischen Vereines fur Bohmen "Lotos"
Prag, Monatschr. Mus.	Monatsschrift der Gesellschaft des vaterlandischen Museums in Bohmen
Prag, Sitzber.	Zpravy o Zasedani (Vestnik) Kralovske Ceske Spolecnosti Nauk. Trida. Mathematicko-Prirodove-decka. Sitzungsberichte der Konigl Bohmischen Gesellschaft der Wissenschaften. Mathematisch-Naturwissenschaftliche Classe
Prag Sternw. Magn. Mereorol. Beob.	Magnetische und Meteorologische Beobachtungen an der K. K. Sternwarte zu Prag
Prag, Verh.	Verhandlungen der Gesellschaft des vaterländisches Museums in Bohmen
Prag, Vierteljahrschr	Vierteljahrschrift fur die praktische Heilkunde
Pressburg, Corresp. Blatt.	Correspondenzblatt des Vereins fur Naturkunde zu Pressburg
Pressburg, Verh.	Verhandlungen des Vereins fur Naturkunde zu Pressburg
Presse Sci.	Presse Scientifique des Deux Mondes
Preuss. Bot. Ver. Sitzber.	See Konigsberg Schriften
Preuss. Geod. Inst. Publ.	Publication des Konigl Preuss. Geodätischen Instituts
Preuss. Geod. Inst. Veroff.	Veroffentlichung des Konigl Preussischen Geodatischen Instituts
Preuss. Landes-Oekon -Kolleg. Archiv.	See Landw. Jbuch
Pribram Bergakad	See Wien, Berg- u Huttenm. Jbuch.
Princeton Mus. Contr.	Contributions from the (E. M.) Museum of Geology and Archaeology of Princeton College
Pringsheim, Jahr. Wiss. Bot.	Jahrbucher fur Wissenschaftliche Botanik
Print. Reg.	Printers' Register
Prog. agric. viti.	Progres agricole et viticole
Proc. Amer. Acad.	Proceedings of the American Academy of Arts Sciences
Proc. Amer. Inst. Elec. Eng.	Proceedings of the American Institute of Electrical Engineers
Proc. Amer. Micro Soc.	Proceedings of the American Microscopical Society
Proc. Amer. Pharm. Assoc.	Proceedings of the American Pharmaceutical Association
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society

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

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

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

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

Riv. Ital. Sci. Natur. Napoli	Rivista Italiana di Scienze Naturali e loro Applicazioni pubblicata per cura degli Aspiranti Naturalisti
Riv. Ital. Sci. Natur. Siena	Rivista Italiana di Scienze Naturali e Bollettino del Naturalista Collettore, Allevatore, Coltivatore
Riv. Mat.	Rivista di Matematica
Riv. Mineral. Crist.	Rivista di Mineralogia e Cristallografia Italiana
Riv. Patol. Veg.	Rivista di Patologia Vegetale
Riv. Sci.-Ind.	Rivista Scientifico-Industriale delle principali Scoperte ed Invenzioni fatte nelle Scienze e nelle Industrie
Riv. Sper. di Freniatria	Rivista Sperimentale di Freniatria e di Medicina legale...
Riv. Vit. Ital.	Rivista di Viticoltura ed Enologia Italiana...
Robin, J. Anat.	Journal de l'Anatomie et de la Physiologie normales et pathologiques de l'homme et des animaux
Rochelle	See under Charente-Inf.
Rochester Acad. Sci. Proc.	Proceedings of the Rochester New York Academy of Science
Rochester Trans. Elec. Med. Assoc.	Transactions of the National Electic Medical Association at its Third Meeting, at Rochester, U. S.
Rock Products	Rock Products
Rohr, 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
Romer, Archiv Bot.	Archiv fur die Botanik
Roser Wunderlich, Archiv	Archiv fur physiologische Heilkunde. Continued as the Archiv d. Heilk.
Rotterdam Nieuwe Verh.	Nieuwe Verhandelingen van het Bataafsch Genootschap der Proefondervindelijke Wijsbegeerte Rotterdam
Rouen, Bull. Soc. Emul.	Bulletins (des travaux) de la Société Libre d'Émulation de Rouen
Rouen, Soc. Sci. Bull.	Bulletin de la Société des Amis des Sciences Naturelles de Rouen
Rouen, Trav. Acad.	Precis analytique des Travaux de l' Academie des Sciences, Belles-Lettres, et Arts de Rouen
Roumanie Inst. Meteorol. Ann.	Annales de l'Institut Meteorologique de Roumanie Annalele Institutului Meteorologio al Romaniei
Roy. Engin. Papers	Papers on subjects connected with the duties of the Corps of Royal Engineers
Roy. Inst. J.	Journal of the Royal Institution of Great Britain

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

Saone-et-Loire Soc. Sci. Bull.	Bulletins de la Société des Sciences Naturelles de Saone-et-Loire
Saone-et-Loire Soc. Sci. Mem.	Memoires de la Société des Sciences Naturelle de Saone-et-Loire
Sarthe, Bull. Soc. Agric.	Bulletin de la Société d'Agriculture, Sciences, etc., de la Sarthe
Savoie Acad. Mem.	Memoires de l'Academie des Sciences, Belles-Lettres et Arts de Savoie
Savoie Soc. Hist. Natur. Bull.	Bulletins de la Société d'Histoire Naturelle de Savoie
Savoie Soc. Hist. Natur. (Compt. rend.)	Société d'Histoire Naturelle de Savoie a Chambery
Schaffhausen	See Schweizer. Entom. Gesell.
Scheik. Onderz.	See Utrecht. Scheik. Onderzoek
Schemnitz Bergakad.	See Wien, Berg- u. Huttenm. Jahr.
Scherer, J. Chem.	Allgemeines Journal der Chemie
Schlesw.-Holst. Naturwiss. Ver. Schr.	Schriften des Naturwissenschaftlichen Vereins für Schleswig-Holstein
Schlomilch, Zts.	Zeitschrift fur Mathematik und Physik
Schneider, Ann. Staatsarzneik.	Annalen der gessammten Staatsarzneikunde
School Mines Quart.	School of Mines, Quarterly, The
School of Mines, Records	Records of the School of Mines
Schrader, J. Bot.	Journal fur 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))
Schwab. Ges. Denkschr.	Denkschriften der Schwabischen 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 fui 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 koniglich bayerischen Akademie der Wissenschaften zu Munchen
Sitzber. könig. Akad. Wiss. Berlin	Sitzungsber der koniglich preussischen Akademie der Wissenschaften zu Berlin
Sitzber. konig. preuss. Akad.	Sitzungsberichte der koniglich preussischen Akademie der Wissenschaften
Skand. Archiv Physiol.	Skandinavisches Archiv fur Physiologie
Skand. Naturf. Forh.	Forhandlingar vid det af Skandinaviska Naturforskare och Lakare hallna Mote i Gotheborg
Skand. Naturf. Mod. Forh.	Forhandlingerne ved de Skandinaviske Naturforskeres 11te Mode i Kjobenhavn fra den 3die til den 9de Juli, 1873
Skand. Natur Möt. Forh.	Förhandlingar vid de Skandinaviska Naturforskarnes Tolfte Mote i Stockholm fran den 7 till den 14 Juli, 1880
Skandia	Skandia. Tidskrift för Vetenskap och Konst; utgifven af Svenska Litteratur-Foreningen
Skofitz	See Oesterreich. Botan Zeitschr.
Skofitz, Bot. Wochenbl.	Oesterreichisches Botanisches Wochenblatt
Skofits, Bot. Zts.	Oesterreichische Botanische Zeitschrift
Smithsonian Contrib	Smithsonian Contributions to Knowledge
Smithsonian Inst. Astrophys. Obs. Ann	Annals of the Astrophysical Observatory of the Smithsonian Institution
Smithsonian Inst. Bur. Ethnol. Report	Annual Report of the Bureau of (American) Ethnology to the Secretary of the Smithsonian Institution
Smithsonian Misc. Coll.	Smithsonian Miscellaneous Collections
Smithsonian Report	Annual Report of the Board of Regents of the Smithsonian Institution, showing the Operations, Expenditures and Condition of the Institution
Snelling's Phot. J.	Snelling's Photographisches Journal
Soc. Bot. Ital Bull.	See Nuovo Giorn. Bot. Ital
Soc. Broteriana	See Coimbra, Soc. Broter. Biol.
Soc. Elvet. Sci. Naturf. Atti	See Schweiz. Naturf. Ges. Verh.
Soc. Entom. Ross. Horae	Horae Societatis Entomologicae Rossicae variis sermonibus in Rossia usitatis editae
Soc. Franc. Bot.	See Rev. Bot.
Soc. Franc. Entom.	See Rev. Ent.
Soc. Freniatr. Ital.	See Riv. Sper. di Freniatria
Soc. Geogr. Finland	See Fennia
Soc. Helvet. Actes.	Actes de la Société Helvetique des Sciences Naturelles
Soc. Helvet. Sci. Naturf Act.	See Schweiz. Natf. Ges. Verh.
Soc. Ital. Antrop.	See Arch. Antropologia
Soc. Ital. Fis.	See Nuovo Cimento
Soc. Ital. Micro. Boll.	See Acireale, Soc. Ital. Micr. Boll.
Soc Ital. Sci.	See (Roma), Soc. Ital. Mem.
Soc. Ital. Sci. Nat.	See Milano, Soc. Ital.
Soc. Ligust. Sci. Natur Geogr.	See Genova, Soc. Ligust. Atti
Soc. Malacol. France	See Ann. Malacol.

Soc. Malacol. Ital. Bull.	See Bull. Malacol. Ital.
Soc. Meteorol. Ital.	See Moncalieri Oss. Boll.
Soc. Mex. Hist. Natur.	See Naturaleza
Soc. Napoli	Societa reale di Napoli. Rendiconto dell' Academia delle Scienze fisiche e mathematiche
Soc. Nat. Sicil.	See Nat. Sicil.
Soc. Pharm. Anvers	See J. de Pharm.
Soc. Public Analysts	See Analyst
Soc. Speleol.	See Spelunca, Paris
Soc. Telegr.-Engin. Elect.	See Telegr. Eng. J.
Soc. Tosc. Sci. Nat.	See Pisa Soc. Tosc.
Soc. Ven.-Trent. Sci. Nat.	See Padova Soc. Sci.
Soc. Zool. Suisse Ann.	See Rev. Suisse: Zool.
Soc. Zool. Tokyo	See Annot. Zool. Jap.
Somerset. Archaeol. Soc. Proc.	Proceedings of the Somersetshire Archaeological and Natural History Society
Somerset. Sov. Proc.	Somersetshire Archaeological and Natural History Society's Proceedings
Somme (Dep. de la)	See under Amiens
Southern Pharm. J.	Southern Pharmaceutical Journal
Span. P.	Spanish Patent
Spatula	Saptula (The), Boston
Spelunca. Paris	Spelunca. Bulletin de la Société de Speleologie
Sperimentale	Lo Sperimentale. Giornale Italiano di Scienze Meidche
Spettatore Vesuvio	Lo Spettatore del Vesuvio e de' Campi Flegrei
Spettrosc. Ital. Mem.	Memorie della Societa degli Spettroscopisti Italiani
Spongia, Comm.-Med.	Commentarii di Medicina
Sprechsaal	Sprechsaal
Spregnel, Jahr.	Jahrbucher 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 fur 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 fur das deutsche Eisenhuttenwesen
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 fur Steiermark
Steiermark Mitth.	Mittheilungen des Naturwissenschaftlichen Vereines fur Steiermark
Steiermark. Mont. Lehranst. Jahr.	Die Steiermarkisch standische montanistische Lehranstalt zu Vordernberg
Stein, Ann.	Annalen der Geburtshulfe uberhaupt und der Entbindungsanstalt zu Marburg insbesondere
Stettin, Entom. Ztg.	Entomologische Zeitung; herausg. v. d. Entomologischen Vereine zu Stettin
Steyermärk. Zts.	Steyermarkische 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 Tradgard 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 Ledamoter
Stockholm, Ymer	Ymer. Tidskrift utgifven af Svenska Sallskapet för Antropologi och Geografi
Strasbourg Soc. Hist. Natur. Mem.	Memoires de la Société du Museum d'Histoire Naturelle de Strasbourg
Strasbourg Soc. Sci. Bull.	Bulletin de la Société des Sciences Naturelles de Strasbourg
Strasbourg Soc. Sci. J.	Journal de la Société des Sciences, Agriculture, et Arts, du departement du Bas-Rhin
Strasbourg Soc. Sci. Mem.	Memoires de la Société des Sciences, Agriculture, et Arts, de Strasbourg
Stray Feathers	Stray feathers. A journal of Ornithology for India and its dependencies
Stricker	See Medizin. Jahr.
Sts. Settl. P.	Straits Settlement Patent
Student	The Student and Intellectual Observer of Science, Literature, and Art
Sturgeon, Ann. Elect.	Annals of Electricity, Magnetism, and Chemistry, and Guardian of Experimental Science
Sturgeon, Ann. Phil.	Annals of Philosophical Discovery and Monthly Reporter of the Progress of Practical Science
Sucr.	La sucrerie indigene
Sucr. Belge	Sucrerie Belge, La
Sucr. ind. colon.	Sucrerie indigene et colonaile, La
Suddeut. Apoth. Ztg.	Suddeutsche Apotheker Zeitung
Suisse Soc. Zool. Ann.	See Rev. Suisse Zool.
Surveyor	Surveyor and Municipal and County Engineer, The
Sussex Natur. Hist. Soc. Proc.	See Brighton Nat. Hist. Soc. Proc.
Svea	Svea. Tijdskrift for Vetenskap och Konst
Svensk farm. Tidskr.	Svensk farmaceutisk Tidskrift, Stockholm
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift
Svenska Lak. Sallsk. Forh.	Forhandlingar ved Svenska Lakare-Sallskapets Sammankomster
Svenska Mosskulturfor.	Svenska Mosskulturforeningens
Svenska Sallsk. 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. Blatter	Technische Blätter. Vierteljahrschrift des Deutschen Polytechnischen Vereins in Bohmen
Tech. Chem. Jahr.	Technisch-Chemisches Jahrbuch (Biedermann)
Tech. Gemeindebl.	Technisches Gemeindeblatt
Technikum	Technikum des Ledermarkts
Technol.	Le Technologiste (F. Malepeyre)
Technol Quart.	Technology Quarterly
Teign Field Club Proc.	Reports of the Proceedings of the Teign Naturalists' Field Club
Tekn. Tidskr.	Teknisk Tidskrift
Telegr. Eng. J.	Journal of the Society of Telegraph-Engineers and Electricians
Telegr. J.	The Telegraphic Journal and Electrical Review
Telegr. Ver. Zts.	Zeitschrift des Deutsch-osterreichischen Telegraphen-Vereins
Temminck, Verh.	Verhandelingen over de natuurlijke Geschiedenis der Nederlandsche overzeesche bezittingen, door de leden der Natuurkundige Commissie in Oost-Indie en andere schrijvers
Termr. Füz.	Termeszetrajzi Fuzetek...Kiadja a Magyar Nemzeti Muzeum. (Natural History Magazine...published by the Hungarian National Museum)
Termt. Közlön.	Termeszettudomanyi Kozlony...Kiadja a K. M. Termeszettudomanyi Tarsulat. (Natural Science Papers...Published by the Royal Hungarian Natural Science Society)
Terrestrial Magn.	Terrestrial Magnetism (and Atmospheric Electricity). An International Quarterly Journal
Texas Acad. Sci. Trans.	Transactions of the Texas Academy of Science
Text. Amer.	Textile American
Text. Col.	The Textile Colorist
Text. Farb. Ztg.	Textil und Farberei-Zeitung
Text. Mfr.	The Textile Manufacturer
Text. Rec	The Textile Record
Text. World Rec.	Textile World Record
Text. Ztg.	Textil Zeitung
Textilfreund	Der Textilfreund
Teyler's Verh.	Geologische Verhandel af Antwoord af de in 1828 uitgeschrevene en in 1830 herhaalde Prysvraag: Wat men van Geologie, etc.
Therap. Gaz.	The Therapeutic Gazette
Therap. Monats.	Therapeutische Monatshefte
Therap. Neuheit	Therapeutischen Neuheiten, Leipzig
Therapist	Therapist (The) London

Thomson, Ann. Phil.	Annals of Philosophy, or Magazine of Chemistry, Mineralogy, Mechanics, and the Arts
Thomson, Archiv. Entom.	Archives Entomologiques
Thomson, Rec.	Records of General Science
Thonind. Ztg.	Thonindustrie-Zeitung
Throndhjem, Skrifter	Der Kongelige Norske Videnskabers-Selskabs Skrifter i det 19 de Aarhundrede
Tidskr. Kemi. Farm. Terapi	Tidskrfit for Kemi Farmaci Terapi
Tidskr. Mat.	Tidsskrift for Matematik
Tidskr. Mat. Fys.	Tidskrift for Matematik och Fysik, tillegnad den Svenska Elementar-Undervisningen
Tidskr. Phys. Chem.	Tidskrift for Physik og Chemi samt disse Videnskabers Anvendelse
Tiedemann, Zts.	Zeitschrift fur Physiologie
Tijdschr. Entom.	Tijdschrift voor Entomologie; uitgegeven door de Nederlandsche Entomologische Vereeniging
Tijschr. Genootsch. Vis. Unita	Tijdschrift voor Genees-, Heel-, Verlos-, en Scheikundige Wetenschappen, van Wege et Genootschap: "Vis Unita Fortior," te Hoorn.
Tijdschr. Ing.	Tijdschrift van het Koninklijk Instituut van Ingenieurs
Tijdschr. nijv.	Tijdschrift ter befordering van nijverhed
Tijdstroom.	De Tijdstroom; Maandschrift gewijd van Wetenschap, etc.
Tilesius, Jahr.	Jahrbuch der Naturgeschichte zur Anzeige und Prufung
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
Topfer Ztg.	Deutsche Topfer 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	Tubinger Blatter fur Naturwissenschaften und Arzneikunde
Tubingen Bot. Inst. Unters.	Untersuchungen aus dem Botanischen Institut zu Tubingen
Tunis P.	Tunis Patent
Turin, Mem. Acad.	Memoires de l'Academie Royale des Sciences de Turin
Tyneside Natur. Field Club Trans.	Transactions of the Tyneside Naturalist's Field Club
U. K. Mar. Biol. Assoc. J.	Journal of the Marine Biological Association of the United Kingdom
U. S. Bur. Anim. Ind. Bull.	U. S. Department of Agriculture. Bureau of Animal Industry
U. S. Bur. Anim. Ind. Report	Annual Report of the Bureau of Animal Industry
U. S. Chief Signal Off. Ann. Report	Annual Report of the Chief Signal Officer (of the Army) to the Secretary of War
U. S. Coast Geod. Surv. Bull.	United States Coast and Geodetic Survey. Bulletin
U. S. Comm. Agric. Report	Report of the Commissioner of Agriculture
U. S. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U. S.
U. S. Dept. Agric. Report	Reports of the Department of Agriculture, U S.
U. S. Dept. Agric. Yearb.	Yearbook of the United States Department of Agriculture
U. S. Disp.	United States Dispensatory
U. S. Div. Biol. Surv. Bull.	U. S. Department of Agriculture. Division of Biological Survey. Bulletin
U. S. Div. Chem. Bull.	U. S. Department of Agriculture. Division of Chemistry. Bulletin
U. S. Div. Entom. Bull.	U. S. Department of Agriculture. Division of Entomology
U. S. Div. Entom. Insect Life	U. S. Department of Agriculture. Division of Entomology. (Periodical Bulletin.) Insect Life
U. S. Div. Entom. Tech. Ser.	U. S. Department of Agriculture. Division of Entomology. Technical Series
U. S. Div. Ornith. Mamm. Bull.	U. S. Department of Agriculture. Division of Economic Ornithology and Mammalogy. Bulletin
U. S. Div. Soils Bull.	U. S. Department of Agriculture. Division of (Agricultural) Soils. Bulletin
U. S. Entom. Comm. Bull.	Department of the Interior...Bulletin of the United States Entomological Commission
U. S. Entom. Comm. Report	(U. S.) Department of the Interior (Agriculture)... Report of the United States Entomological Commission
U. S. Fish Comm. Bull.	Bulletin of the United States Fish Commission
U. S. Fish Comm. Report	United States Commission of Fish and Fisheries. Report of the Commissioner

U. S. Geol. Surv.	United States Geological Survey
U. S. Monthly Weath. Rev.	(United States) Monthly Weather Review
U. S. Mus. Bull.	Department of the Interior...Bulletin of the United States National Museum
U. S. Mus. Proc.	Department of the Interior...Proceedings of the United States National Museum
U. S. Mus. Report	See Smithsonian Rep.
U. S. Mus. Spec. Bull.	Smithsonian Institution. United States National Museum. Special Bulletin
U. S. Naval Inst. Proc.	United States Naval Institute Proceedings
U. S. Naval Med. Bull.	United States Naval Medical Bulletin
U. S. Naval Obs. Publ.	Publications of the United States Naval Observatory
U. S. N. Amer. Fauna	U. S. Department of Agriculture. Division of Ornithology and Mammalogy. North American Fauna
U. S. P.	United States Patent
U. S. Ph.	United States Pharmacopoeia
U. S. Secty. Agric. Report	Report of the secretary of agriculture
U. S. Signal Serv. Notes	United States of America: War Department. Signal Service Notes
U. S. Signal Serv. Pap.	United States of America, War Department. Professional Papers of the Signal Service
U. S. Surv. Terr. Reports	...Annual Report of the United States Geological (and Geographical) Survey of the Territories
U. S. Weath. Bur. Bull.	U. S. Department of Agriculture. Weather Bureau. Bulletin
U. S. Weath. Bur. Report	U. S. Department of Agriculture. Weather Bureau. Report of the Chief of the Weather Bureau
U. Serv. Inst. J.	Journal of the royal United Service Institution, Whitehall Yard
Udine, Relazioni	Relazioni intorno agli Atti dell' Accademia di Udine
Uhland's Tech. Rund.	Uhland's Technische Rundschau
Umschau	Umschau, Die
Ung. Naturwiss. Ver. Jahr.	Abhandlungen aus dem dritten Bande der Jahrbücher des Ungarischen naturwissenschaftlichen Vereins zu Pest, in Deutscher Uebersetzung Red. von J. Szabo
Univ. Ill. Bull.	University of Illinois Bulletin
Unters. Naturlehre	Untersuchungen zur Naturlehre des Menschen und der Thiere
Upsala, Arsskrift	Universitets Arsskrift utgifven af Kongl. Vetenskaps-Societeten i Upsala
Upsala Bot. For.	See Bot. Notiser
Upsala, Diss. Acad.	Dissertationes Academicae Upsaliae habitae
Upsala, Frey Tidskr.	Frey Tidskrift för Vetenskap och Konst
Upsala Läkareför. 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 fur 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.	Veroffentlichungen 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 fur gerichtliche Medizin und offentliches Sanitatwesen
Vierteljahrschr. gesundheitspf.	Vierteljahrschrift fur Gesundheitspflege
Vierteljahrschr. Zahnheilk.	Vierteljahrschrift fur Zahnheilkunde
Virchow's Archiv path.	Virchows Archiv fur 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 Rucksicht auf die dazu gehorigen Hulfswissenschaften
Vosges Soc. Emul. Ann.	Annales de la Société d'Émulation du Department des Vosges
W. Austral. P.	West Australian Patent
Wag. Free Inst. Sci. Trans.	Transactions of the Wagner Free Institute of Science of Philadelphia
Wag. Jahr.	(Wagner's) Jahresbericht uber Chemische Technologie
Walker, Elect. Mag.	The Electrical Magazine
Warwick. Field Club Proc.	Proceedings of the Warwickshire Naturalists' and Archaeologists' Field Club
Warwick Natur. Hist. Soc. Rep.	Annual Reports of the Warwickshire Natural History and Archaeological Society
Washburn Obs. Publ.	Publications of the Washburn Observatory of the University of Wisconsin
Washington	Int. Med. Congr. Trans., 1887
Washington	See also under U. S.
Washington Biol. Soc. Proc.	Proceedings of the Biological Society of Washington
Washington, Mem. Natl. Acad.	Memoirs of the National Academy of Sciences
Washington, Natl. Inst. Bull.	Bulletin of the Proceedings of the National Institution for the Promotion of Science
Washington Phil. Soc. Bull.	Bulletin of the Philosophical Society of Washington
Wasser Abwasser	Wasser und Abwasser
Water Supply Papers	Water Supply Papers
Watford Nat. Hist. Soc. Trans.	Transactions of the Watford Natural History Society and Hertfordshire Field Club
Weale, Quart. Papers	Quarterly Papers on Engineering
Weber, Archiv	Archiv fur die systematische Naturgeschichte
Weimer, Zts. Geburtsk.	Gemeinsame Deutsche Zeitschrift fur 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 Beforderung der vaterlandischen Cultur in Minden
Westphäl, Ver. Jahr.	Jahres-Bericht des Westfalichen Provinzial-Vereins fur Wissenschaft und Kunst
Wetter	Das Wetter. Meteorologische Montasschrift für Gebildete aller Stande
Wetterau. Ges. Ann.	Annalen der Wetterauischen Gesellschaft fur 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 fur Zoologie und Zootomie
Wied. Zool. Mag.	Zoologisches Magazin
Wiegmann, Archiv	Archiv fur 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. Universitat 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. Blatter	Wiener technologishe Blatter
Wien Ver. Naturwiss. Kennt. Schr.	Schriften des Vereins zur Verbreitung Naturwissenschaftlicher Kenntnisse in Wien
Wien, Ver. Ges. Aerzte.	Verhandlungen der k. k. Gesellschaft der Aerzte zu Wien
Wien Verh. Gewerb-Vereins.	Verhandlungen des Neiderosterreichischen 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 funfundzwanzigjahrigen 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 fur Brauerei
Wochenschr. Centr.-Ver. Rubezuker-ind.	Wochenschrift des Central-Vereins für Rubenzuker-industrie in der Oesterr-Ung-Monarchie
Wochenschr. osterr. Ing. Ver.	Wochenschrift des osterreichischen Ingenieur und Architekten Vereins
Wochenschr. Ver. deut. Ing.	Wochenschrift des Vereins deutscher Ingenieure
Wollen-Gewerbe	Das Deutsche Wollen-Gewerbe
Wollen Ztg.	Wollen Zeitung
Wombat	The Wombat. The Journal of the Geelong Field Naturalists' Club, and the Gordon College Amateur Photographic Association
Woods Holl Mar. Biol. Lab. Bull.	Biological Bulletin. Edited by the Director and Members of the Staff, of the Marine Biological Laboratory, Woods Holl, Mass.
Woods Holl Mar. Biol. Lab Lect.	Biological Lextures delivered at (from) the Marine Biological Laboratory (of) Woods Holl (Mass.)
Woolhope Field Club Trans.	Transactions of the Woolhope Naturalists' Field Club
Woolwich, Proc.	Minutes of Proceedings of the Royal Artillery Institution
World's Paper Trade Rev.	World's Paper Trade Review
Wunderlich, Archiv. Heilk.	See Roser und Wunderlich
Wurttemberg. Aerzt. Ver. Mitth.	Mittheilungen des Wurttembergischen Aerztlichen Vereins
Wurttemberg, Jahresh.	Jahreshefte des Vereins für vaterländische Naturkunde in Wurttemberg
Wurzburg, Arb. Bot. Inst.	Arbeiten des Botanischen Instituts in Wurzburg
Wurzburg, Arb. Phys. Lab	Arbeiten aus dem Physiologischen Laboratorium der Wurzburger Hochschule
Wurzburg. Med. Zts.	Wurzburger medicinische Zeitschrift
Wurzburg. Naturwiss. Zts.	Wurzburger Naturwissenschaftliche Zeitschrift; Herausgegeben von der Physikalisch-Medicinischen Gesellschaft
Wurzburg Phys. Med. Festschr.	Festschrift zur Feier ihres fünfzigjahreign Bestehens herausgegeben von der Physikalisch-Medizinischen Gesellschaft zu Wurzburg
Wurzburg, Phys. Med. Sitzber.	Sitzungsberichte der Physikalisch-Medicinischen Gesellschaft zu Wurzburg
Wurzburg, Phys. Med. Verh.	Verhandlungen der Physikalisch-Medicinischen Gesellschaft
Wurzburg, 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 fur Natur und Volkerkunde 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 fur 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. osterr. 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 fur 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 fur Chemie
Zts. chem. Apparat.	Zeitschrift für chemische · Apparatenkunde (Discontinued)
Zts. Chem. Ind.	Zeitschrift für die Chemische Industrie mit besonderer Berucksichtigung der chemisch-technischen Untersuchungsverfahren 1887; later Zts. ang. Chem.
Zts. chem. Ind. Kolloide	Zeitschrift für Chemie und Industrie der Kolloide
Zts. Chemotherap.	Zeitschrift fur Chemotherapie und verwandte Gebiete. (formerly Folia Serologia)
Zts. deut. geol. Ges. Abh.	Zeitschrift der deutschen geologischen Gesellschaft Abhandlungen
Zts. deut. Landw.	Zeitschrift fur deutsche Landwirthe
Zts. Dreschler	Zeitschrift für Dreschsler, Elfenbeingraveure und Holzbildhauer
Zts. Dungerw.	Zeitschrift fur Düngerwesen
Zts. Electrochem.	Zeitschrift fur Electrochemie
Zts. Entom. (Breslau)	Zeitschrift fur Entomologie im Auftrage des Vereins fur schlesische Insektenkunde zu Breslau
Zts. Ethnol.	Zeitschrift fur Ethnologie
Zts. exper. Path. Therap.	Zeitschrift fur experimentelle Pathologie und Therapie, Berlin
Zts. Farben-Ind.	Zeitschrift fur Farben-Industrie
Zts. Feuerwehr.	Illustrirte Zeitschrift fur die deutsche Feuerwehr
Zts. Fischerei	Zeitschrift fur Fischerei
Zts. Fleisch. Milchhyg.	Zeitschrift fur Fleisch- und Milchhygiene
Zts. Geburtsh.	Zeitschrift fur Geburtshulfe und Frauenkrankheiten
Zts. Geburtsh. Gynakol	Zeitshrift fur Geburtshulfe und Gynakologie
Zts. ges. Brauw.	Illustrirte Zeitschrift das gesammte Brauwesen
Zts. ges. Getreidew.	Zeitschrift fur das gesamte Getreidewesen
Zts. ges. Naturwiss.	Zeitshrift fur die Gesammten Naturwissenschaften
Zts. Ges. Ornith.	Zeitschrift fur die gesammte Ornithologie
Zts. ges. Textilind.	Zeitschrift fur die gesamte Textilindustrie
Zts. ges. Wasserwirts.	Zeitschrift fur die gesamte Wasserwirtschaft
Zts. Heilk.	Zeitschrift fur Heilkunde, als Fortsetzung der Prager Vierteljahrsschrift fur praktische Heilkunde
Zts. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten
Zts. Immunit. Abt. I 13. Abt. Ref.	Zeitschrift fur Immunitatsforschung und experimentelle. Therapie. Abteilung I. 13 Abteilung II. or Ref. 1 vol
Zts. Induk. Abst. Vererbungslehre	Zeitschrift fur Induktive Abstammungs- und Vererbungslehre
Zts. Instrumentenk.	Zeitschrift fur Instrumentenkunde
Zts. Klin. Med.	Zeitschrift fur Klinische Medizin
Zts. Krebsforsch.	Zeitschrift fur Krebsforschung
Zts. Kryst. Mineral.	Zeitschrift fur Krystallographie und Mineralogie
Zts. landw. Versuchsw.	Zeitschrift fur das landwirtschaftliche Versuchswesen in Oesterreich
Zts. Malakozool.	Zeitschrift fur Malakozoologie
Zts. Math. Phys	Zeitschrift fur Mathematik und Physik
Zts. math. Unterr.	Zeitschrift fur mathematischen und naturwissenschaftlichen Unterrricht
Zts. Mikro. Tek.	Zeitschrift fur Mikroscopischen Teknik.
Zts. Morphol. Anthrop.	Zeitschrift fur Morphologie und Anthropologie
Zts. Nahr. Genuss. (Z. genuss)	Zeitschrift fur Untersuchung der Nahrungs und Genussmittel, sowie der Gebrauchsgegenstände
Zts. Naturwiss.	Zeitschrift für Naturwissenshaften...im Auftrage (Organ) des Naturwissenschaftlichen Vereins für Sachsen und Thuringen

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

CHAPTER III

RAW MATERIALS

Comprehensive knowledge and proper appreciation of the nature, limitations, inner mechanics and technical possibilities and applicability in an art involving chemical technology presupposes a fundamental knowledge of the basic materials—the foundation upon which the superstructure is to be erected—and especially be this true with the etherified celluloses, concerning which a thorough understanding of the substituent groups and aggregates entering into and comprising these ethers is necessary for an adequate conception and proper perspective of their relative value and industrial possibilities; and an intimate acquaintance with the modern concepts, physical inter-relations, spacial configurations and the general reactions of the various celluloses industrially employed for etherification purposes, is a necessary pre-requisite to a lucid discussion of the cellulose ethers themselves.

The subject matter of this Chapter is intended to be confined to those points of relevancy and pertinency bearing directly upon the cellulose ethers as unfolded in the Chapters succeeding.

Cellulose. Not so long ago, the general impression among chemists seemed to be that the chemistry of cellulose formation in nature was comparatively simple, carbon dioxide, being absorbed by growing plants, and under the beneficient influence of chlorophyl, became converted into cellulose, sugars and similar products. We now know, that, instead of this being the *answer*, it is but the *starting point.*

Research work on cellulose during the past decade has been vitally influenced by the application of two physical methods, namely optical rotation measurements and X-ray analysis, and although the value of these two methods has

perhaps been over-rated and led to erroneous calculations and interpretations, valuable contributions have been made to constitutional research[1]. A third, that of the freezing point method of molecular weight determination, has recently been found unreliable in many cases.

Optical Activity. C. Hudson[2] in agreement with W. Haworth[3], attributes the pyranose or 6-atom cellulose ring to *a*- and *b*-glucose, *a*- and *b*-glucosides, *b*-mannose, xylose and xylosides, the furanose or 5-atom ring being assigned to *a*-mannose and *a*-mannoside, galactose and galactosides, and to the secondary glucose residue in maltose[4], conclusions which are fundamental in importance in carbohydrate chemistry. The methyl derivative of *a*-methylmannoside (tetramethyl-*a*-methylmannoside) has been proven by Haworth to be a pyranoside or 6-atom ring derivative, whereas if *a*-methylmannoside is a furanoside or 5-atom ring series, then ring shifting must take place during methylation.

The assumption has been that furanosides hydrolyze some thousand times quicker than pyranosides, cellobiose being a typical pyranoside, but if maltose which hydrolyzes with a speed similar to cellobiose, is assumed from its optical behavior to be a furanoside, then the relationship between ring system and hydrolytic speed becomes no longer tenable. Starch behaves in the same manner as cellulose, but as its constants are higher, it is more readily hydrolyzed. It is known that both starch and cellulose after methylation form the same 2.3.6-trimethylglucose.

Identification of Cellulose. Cotton cellulose in its carefully purified condition in which treatments applied thereto have not been drastic, represents the purest form of natural cellulose known, and those properties which most nearly simulate cotton cellulose of maximum purification serve for

1. K. Freudenberg, J. S. C. I. 1931, **50**, 287-T.
2. J. A. C. S. 1930, **52**, 1680; abst. C. A. 1930, **24**, 2726; J. S. C. I. 1930, **49**, 747-A.
3. J. A. C. S. 1930, **52**, 4168; abst. C. A. 1930, **24**, 5726.
4. C. Hudson, J. A. C. S. 1930, **52**, 1707; abst. C. A. 1930, **24**, 2727; J. S. C. I. 1930, **49**, 747-A.

the identification of pure cellulose. Some of these distinguishing marks are as follows:

1. The substance should quantitatively hydrolyze to *d*-glucose, with a rate of hydrolysis similar to that of cotton[1].

2. On acetolysis appreciable amounts of cellobiose octoacetate should be formed, in yields comparable with those obtained from cotton cellulose under identical conditions.

3. The substance should give rise to a triacetate of similar properties to that obtained from cellulose, both in the normal and partially hydrated stages.

4. The triacetate upon treatment with methanol-hydrochloric acid, should quantitatively yield an equilibrium mixture of *a*- and *b*-methylglucosides.

5. The original purified cellulose should be transformable into a trimethyl ether, which on careful hydrolysis is convertible into 2.3.6-trimethylglucose.

6. Nitrates should be formable of similar nitrogen content and solubilities with those obtainable under strictly comparable conditions—a difficult thing to do—from cotton, and which upon denitration should yield a product having a refractive index close to 1.53.

7. A cuprammonium solution should show the same optical rotation as that manifested by a cuprammonium solution of purified cotton.

8. X-ray diagrams or patterns should point to the identity of the substance with cotton cellulose, both having received identical pretreatment.

While cellulose has been loosely defined as the homogeneous carbohydrate $(C_6H_{10}O_5)_n$ as typified by the purified cottonseed hair, yet it has also indiscriminately been applied to a variety of partially purified celluloses derived from various plant substances, and differentiated from the former by ultimate composition and the presence of certain

1. L. Wise, Cellulose, 1930, **1**, #1, 5; abst. C. A. 1930, **24**, 1971.

reactive groupings[1], but most important in this connection, by fundamental variations in finished product obtained when subjected to etherification. Cellulose has been hazardously defined as the sum total of organic substance in the plant cell-wall remaining after volatile solvent extraction, chlorination or bromination, followed by sulfite or ammoniacal treatment. While scientifically this definition may be stretched rather beyond its elastic limit, from a technical viewpoint it is satisfactory, and at the same time comprehensive.

By carefully regulated and benign chemical and physical treatment, it is possible to obtain from many of the compound celluloses, material which approximates in chemical characteristics to cotton cellulose, and it is now tacitly agreed that the term "normal cellulose" should be restricted to such cellulosic bodies as substantially conform in analytical values and chemical properties to those exhibited by a properly purified cotton cellulose. But in addition to the physical standards and analytical figures obtained as to the similarity of one cellulose with another, the final verdict as to identity and suitability—at least from a technical viewpoint—is its behavior under manufacturing conditions, as in the etherification process. Nuances of variation are here observed which are analytically indistinguishable; and therefore technically in the cellulose art, analyses are merely informative and indicative, the real test as to applicability being deportment under actual factory conditions. This is strikingly exemplified in the viscose rayon industry, where the speed of ageing of alkalicellulose, deportment under xanthation, solubility of xanthated cellulose in dilute NaOH solution, and viscosity against ageing time of the ripening phase are paramount factors not sufficiently discernible by analysis alone. *What it contains is important, but what it does, is more so.* And the latter is the real criterion.

1. J. Macdonald, J. S. C. I. 1927, **46**, 251-T; abst. C. A. 1927, **21**, 2982; J. S. C. I. 1927, **46**, 649-B; Chem. Met. Eng. 1927, **34**, 504; Pulp & Paper Mag. 1927, Dec. 1, 1560. See also R. Montonna, Paper Trade J., 1928, **86**, 61.

Molecular Magnitude. The determination of molecular magnitude is of considerable importance in the knowledge of cellulose, as furnishing an insight as to its intensity of reactivity under known conditions; and with highly polymeric compounds of known constitution it appears that important properties such as stability, solubility, swelling power and also the nature of the solution, depend quite considerably upon the length of the molecule, and hence on the degree or profundity of depolymerization[1].

Various assumptions have been hazarded concerning the chain length of the cellulose molecule. K. Freudenberg assumes that it is extraordinarily large, in fact, that it contains hundreds of glucose residues, without, however, being able to state anything definite about the molecular magnitude[2]. E. Heuser[3] determined the molecular weight of methylcellulose in aqueous solution with the idea that through the absence of OH groups, no association occurs. He found connections between molecular weight, the method of formation of the various polymeric methyl celluloses, their softening temperature and temperature of hydration, arriving at a molecular weight for cotton cellulose of 6000-8000, corresponding to a degree of polymerization of 40-50. This value has not been confirmed, and appears too small.

K. Meyer and H. Mark[4] on the basis of the determination of the crystallite magnitude of R. Herzog[5], hold the view that 30-50 glucoses are bound in a main valence chain, and advance the assumption that the main valence chains extend through the crystallite, so that the latter forms bundles of chains, a hypothesis, that as yet, lacks adequate

1. H. Staudinger, K. Frey, R. Signer, W. Starck and G. Widmer, Ber. 1930, **63B**, 2308; abst. C. A. 1931, **25**, 1280; J. S. C. I. 1930, **49**, 1415-A.
2. K. Freudenberg and E. Braun, Ann. 1928, **460**, 288; abst. C. A. 1928, **22**, 3635; J. S. C. I. 1928, **47**, 399-A; Chem. Zentr. 1928, I, 1848.
3. Zts. Elektrochem. 1925, **31**, 498; abst. C. A. 1926, **20**, 110; J. C. S. 1925, **128**, 1387.
4. Ber. 1928, **61B**, 593; Zts. Phys. Chem., Abt. B., 1929, **2**, 128; abst. C. A. 1929, **23**, 1263.
5. J. Phys. Chem. 1926, **30**, 457; abst. C. A. 1926, **20**, 2068.

confirmation. P. Karrer[1] first refuted the former concepts of the constitution of cellulose on the basis of the observation that starch can be completely converted into maltose by enzymes, and cellulose into derivatives of cellobiose to the extent of 60%[2], and postulated the idea that the molecule of cellulose is not only a highly polymeric substance, but according to his conception, was a biose-anhydride, which is similar to the views of M. Bergmann[3] and of K. Hess[4]. They assumed that micelles were formed by aggregation of small basic molecules, thus having a structure similar to the micelles in a soap solution. Differences between various cellulose derivatives with reference to swelling power and viscosity of the solution were attributed to variations in micelle magnitude, and not to those of molecular magnitude.

The X-ray investigations of P. Scherrer[5] and of R. Herzog and W. Jancke[6] have shown that these materials are crystalline. O. Sponsler and W. Dore[7] in 1926, on the basis of the Bragg atom model, have shown that the chain-forming cellulose molecule could be arranged in the form of a lattice, and that many properties of cellulose as stability and swelling power then became explainable. H. Mark and K. Meyer carried the investigations a step further and submitted an exact picture of crystalline cellulose which fits the newer chemical concepts more conclusively.

In the hydrolysis of trialkylcellulose with acetic anhydride, a mixture of polytrialkylcelloglucan diacetates should

1. Polymer Kohlehydrate, Leipzig, 1925. P. Karrer and C. Nageli, Helv. Chim. Acta, 1921, **4**, 185; abst. C. A. 1921, **15**, 2629; J. S. C. I. 1921, **40**, 361-A; Chem. Zentr. 1921, I, 934.
2. H. Staudinger and M. Luethy, Helv. Chim. Acta, 1925, **8**, 41; abst. C. A. 1925, **19**, 1245. See also Ber. 1930, **63B**, 1503, 1528.
3. Ber. 1926, **59**, 2973; abst. C. A. 1927, **21**, 1271; J. S. C. I. 1927, **46**, 166-A.
4. Chemie der Cellulose, 1925.
5. R. Zsigmondy's Lehrbuch der Kolloidchemie, O. Spamer, Leipzig, 1920.
6. Ber. 1920, **53**, 2162; abst. C. A. 1921, **15**, 1311.
7. O. Sponsler and W. Dore, Fourth Colloid Symposium Monograph, 1926, 174-202; abst. C. A. 1927, **21**, 3268.

be obtained[1], and this has been successful. Trimethylcelluloses it is known[2] are difficult of preparation in comparison with incompletely methylated cellulose, and the truth has never been ascertained as to whether the last hydroxyl was really methylated. A polymer-homologous series of trimethylcelluloses but not of maximum methylation has been studied by E. Heuser and N. Hiemer[3] and compared with the homologous series of the polyoxymethylenes.

Physical Properties of Cellulose. The infra-red absorption spectra of cellulose in the region of fluorite dispersion has been reported upon by R. Herzog and G. Laski[4] in the absorption of thin films of cellulose and nitrocellulose being measured with a fluorite-prism spectrometer and sensitive microradiometer in the wave-length region of 2-8 microns. In neither case does mercerization cause any alteration in the spectrum. It appears that if any of the atoms or radicals in a molecule are replaced by others, the amplitudes of the system of bands corresponding with the remaining radicals show a change.

When cellulose or starch is distilled *in vacuo,* glucosan is formed which yields a tribenzoate[5], m. pt. 199.5-200°, and a triacetate, m. pt. 110°[6]. The heat of combustion of cellulose has been given as 1480, tests on 6 samples of ramie

1. H. Staudinger, K. Frey, R. Signer, W. Starck and G. Widmer, Ber. 1930, **63**-B, 2308; abst. C. A. 1931, **25**, 1280; J. S. C. I. 1930, **49**, 1415-A.

2. W. Denham, J. C. S. 1921, **119**, 77; abst. C. A. 1921, **15**, 1693; J. S. C. I. 1921, **40**, 211-A; Ann. Rep. Soc. Chem. Ind. 1921, **6**, 133; Bull. Soc. Chim. 1921, (4), **30**, 425; Chem. Zentr. 1921, I, 892; Cellulose Chem. 1921, **2**, No. 6, 74; Caout. et Gutta. 1922, **19**, 11379.

3. Cellulosechem, 1925, **6**, 101, 125, 153; abst. C. A. 1926, **20**, 818; J. S. C. I. 1926, **45**, 502-A; Chem. Zentr. 1926, I, 1391.

4. Zts. physik. Chem. 1926, **121**, 136; abst. C. A. 1926, **20**, 2455; J. S. C. I. 1926, **45**, 677-A.

5. A. Pictet and J. Sarasin, Helv. Chim. Acta. 1918, **1**, 78; abst. C. A. 1918, **12**, 2187. See J. Sarasin, Arch. Sci. Phys. Nat. 1918, **46**, 5; abst. C. A. 1918, **12**, 2187.

6. E. Vongerichten and F. Müller, Ber. 1906, **39**, 241; abst. J. C. S. 1906, **90**, i, 198; Chem. Zentr. 1906, I, 748; Jahr. Chem. 1905-1908, II, 1948; Bull. Soc. Chim. 1906, **36**, 1145; Rep. de Chim. 1906, **6**, 229.

fiber showing a mean of 5173.7 gms/cal, per gm.[1] Neither cellulose nor hydrocellulose reacts with liberation of methane with magnesium methyl iodide (Grignard's Reagent) in ether at ordinary temperatures, or in dimethylaniline at 120°[2].

Measurements have been made of the rate of adsorption of water from saturated water vapor at 20° and at 30° by standard cotton cellulose, α-cellulose and nitrocellulose[3]. From 6-10 days are required for attainment of equilibrium. The adsorption decreases with increase in temperature. Standard cellulose adsorbed about 16.7% water at the saturation pressure at 20°. The fact that cellulose hydration curves are unbroken, indicating a continuously variable vapor pressure consistent only with the presence of physically held water, and that lack of evidence of a definite vapor pressure such as would be expected in the case of a true hydrate, leads C. Fox[4] to the opinion that a cellulose hydrate is non-existent, an opinion not shared by J. Strachan[5].

Hydrate celluloses exhibit lower resistance to sacchari-

1. M. Prettre, Mem. Poudres, 1931, **24**, 223; abst. C. A. 1932, **26**, 2641; J. S. C. I. 1932, **51**, 229-A.

2. F. Wood, J. S. C. I. 1931, **50**, 257-T.

3. S. Oguri and M. Nara, J. S. C. I. Japan, 1930, **33**, 267-B; abst. C. A. 1930, **24**, 5479. A comparison of the isohygrometric curves for viscose, mercerized cotton and standard cotton made by S. Oguri and S. Terui (J. S. C. I. Japan, 1931, **34**, 229; abst. C. A. 1932, **26**, 590; J. S. C. I. 1931, **50**, 1005-B), placed the moisture contents (50% relative humidity at 9.8%, 5.8% and 5.5% respectively). A determination of the rates of moisture adsorption by the standard cellulose at 20°, yielded typical sorption curves, 88% of the total change occurring in 20 min. They found (J. S. C. I. Japan, 1931, **34**, 182-B; abst. J. S. C. I. 1931, **50**, 836-B) that the absorption of water vapor by cellulose in an enclosed vessel is independent of temperature (12-30°) if the relative humidity is kept constant. When the various isotherms are plotted against relative humidity, the curves converge into one.

4. Paper Maker and Brit. Paper Trade J. 1926, **71**, 366-A; World's Paper Trade Rev. 1926, **85**, 1060; Paper Makers Monthly J. 1926, **64**, 140; abst. C. A. 1926, **20**, 2069.

5. Paper Maker and Brit. Paper Trade J. 1926, **71**, 366-A, 366-D; World's Paper Trade Rev. 1926, **85**, 1062, 1116; Paper Makers Monthly J. 1926, **64**, 141; abst. C. A. 1926, **20**, 2069.

fication and greater capacity for reaction in other ways[1]. The most readily saccharified are those precipitated from solutions in which the celluloses are dissolved as esters, then come those precipitated from indifferent solutions, and finally mercerized celluloses which yield, on the average, half as much dextrose as the natural celluloses. The action of NaOH solution becomes appreciable at concentrations above 10%, increasing rapidly to 16-18%, and slowly afterwards. Hydrate solutions prepared with salt (potassium iodide, zinc chloride) solutions behave as regards saccharification like natural celluloses, and the salt solutions do not enhance the action of the soda in mercerization. The hydrocelluloses exhibit about the same resistance to saccharification as the natural celluloses, with appreciable differences for varying types.

The percentage of ash, of ether- and alcohol-soluble resin, α-cellulose content, pentosan content, copper number and permanganate number (indicative of lignin content) of different cellulose materials have been determined in order to afford a means of distinguishing between them[2]. Straw cellulose has very high ash and pentosan content and correspondingly lower α-cellulose content. Sulfate- differs from sulfite-cellulose in that it has less resin, lower copper number, and somewhat higher pentosan content. Bleached sulfite-cellulose has a smaller lignin, pentosan, and α-cellulose content than unbleached. Purified cellulose has a smaller lignin, ash and resin content, and a much higher α-cellulose content than ordinary bleached material.

H. Hibbert and J. Barsha[3] have reported that the membrane formed by the action of *Acetobacter xylinum* on dextrose is a true cellulose, since various derivatives ob-

1. P. Leone, Annali Chim. Appl. 1929, **19**, 432; abst. J. S. C. I. 1930, **49**, 10-B.

2. S. Fotjew and W. Jakimanskij (S. Fotiev and V. Yakimanskii), Zellstoff. u Papier, 1929, **9**, 834; abst. C. A. 1930, **24**, 5151; J. S. C. I. 1930, **49**, 96-B.

3. J. A. C. S. 1931, **53**, 3907; abst. C. A. 1931, **25**, 5981; J. S. C. I. 1931, **50**, 1401-A.

tained from it are identical with those prepared similarly from cotton celluloese.

Constitution of Cellulose. Cellobiose which was discovered by A. Franchimont and the constitution of which was elucidated by W. Haworth becomes the starting point for the determination of the constitution of this polysaccharide. The increment of knowledge leading up to these discoveries and their application to the constitution of cellulose is indicated in skeleton form herein, as evidenced by the contributions of the past decade only.

In 1921 the constitutional formula for cellulose was generally recognized as embracing the *p*-dioxan ring of A. Green[1] and the formula of A. v. Eulen[2] comprising a chain of hexose molecules of any desired length. As has been pointed out by P. Karrer and F. Widmer[3], any consideration of the structure of the cellulose molecule must embrace a knowledge of the maximum proportion of cellobiose obtainable from the cellulose (see topic "Cellobiose"). Probably the best method for isolating cellobiose from cellulose consists in hydrolysis by means of a mixture of acetic anhydride and a small amount of concentrated sulfuric acid, this being formed at the ordinary temperature[4]; at higher temperatures the reaction proceeding more rapidly, but at the expense of yield. They treated various celluloses and cellulose compounds with acetic anhydride and sulfuric acid under similar conditions, the resulting cellobiose octo-acetate being crystallized from alcohol, and its amount determined. Comparison of yields lead to the conclusion that

1. Zts. Farb. Text. Ind. 1904, **3**, 309; abst. J. C. S. 1905, **88**, i, 22.

2. Chem. Ztg. 1921, **45**, 977, 998; abst. J. C. S. 1921, **120**, i, 769; C. A. 1922, **16**, 644; J. S. C. I. 1921, **40**, 764-A; Chim. et Ind. 1922, **8**, 141.

3. Helv. Chim. Acta. 1921, **4**, 174; abst. C. A. 1921, **15**, 2629; J. S. C. I. 1921, **40**, 342-A; J. C. S. 1921, **120**, i, 310; Chem. Zentr. 1921, I, 936.

4. H. Ost, 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.

cellulose must contain about 50% or more, ready formed cellobiose complex.

Methylation of cellobiose by means of alkali and methyl sulfate yields unsatisfactory results, since in faintly alkaline solution the methylation is incomplete, while in strongly alkaline solution partial hydrolysis and decomposition takes place. If, however, the aldehyde group of cellobiose is fixed by glucoside-formation, methylation proceeds smoothly. Methylation of methylcelloside by means of excess of methyl sulfate in 20% NaOH solution gives an almost quantitative yield of hexamethylmethylcelloside.

K. Hess[1] studied the action of acetyl bromide on ethylcellulose, and was able to isolate a well crystallized bromacetylethylglucose, propionyl chloride forming brompropionylethylglucose. H. Hibbert[2] based his formula for cellulose on the hydrolysis data of methylcellulose and on acetolysis of cellulose[3]. It remained for J. Irvine and E. Hirst[4] to show that cellulose could be converted into 2.3.6-trimethylglucose in 89% yield, and that no isomeric trimethylglucose was formed, indicating the identity of all the glucose residues. In view of the impossibility of accounting for more than 50-60% of cellobiose in the acetolysis of cellulose, Irvine, as a precaution, postulated cellulose as a tri-1.5-anhydroglucose. The cellulose formulæ up to that time (1923) then became untenable through their inability to quanti-

1. Ber. 1921, **54B**, 2867; abst. C. A. 1922, **16**, 1400; J. C. S. 1922, **122**, i, 12; Bull. Soc. Chim. 1922, **32**, 244.

2. J. I. E. C. 1921, **13**, 256, 334; abst. C. A. 1921, **15**, 1990; Paper Trade J. 1922, **74**, 54; Chem. Tech. Uebers, 1921, **45**, 192.

3. R. Fabre, J. pharm. Chim. 1923, **28**, 398, 446; abst. C. A. 1924, **18**, 1195. See E. Heuser and E. Boedecker, Zts. ang. Chem. 1921, **34**, 461 Auf.; abst. C. A. 1922, **16**, 340. Paper Trade J. 1922, **75**, #9, 47; abst. C. A. 1922, **16**, 4058. P. Karrer and A. Smirnoff, Helv. Chim. Acta, 1922, **5**, 181; abst. C. A. 1922, **16**, 1747. P. Karrer and W. Fioroni, Helv. Chim. Acta, 1923, **6**, 396; abst. C. A. 1923, **17**, 2416. J. Irvine, W. Denham and E. Hirst, Chem. Trade J. 1922, **71**, 291; abst. C. A. 1923, **17**, 1713. J. Irvine and E. Hirst, J. C. S. 1923, **123**, 518; abst. C. A. 1923, **17**, 1956.

4. J. C. S. 1923, **123**, 518; abst. C. A. 1923, **17**, 1956; J. S. C. I. 1923, **42**, 710-A.

tatively yield 2.3.6-trimethylglucose[1]. Cellulose has been looked upon as a dimeride of anhydrocellobiose (cellosan), polymerization taking place through subsidiary valences leaving the oxygen bridges intact, the strong cohesion in the polymerized cellulose molecule being due to valency forces of unusual strength.

It still remains to be determined in what way the orthoglucosan (anhydroglucose) groups are held together in the cellulose molecule, and the size of the latter[2]. K. Hess[3] holds that cellulose consists of the units $C_6H_{10}O_5$, held together by "association," and not by condensation or polymerization, hydrocellulose being assumed as the opening up of an anhydride position with the formation of an aldehyde group, and yet without the depolymerization of the cellulose molecule.

No satisfactory chemical method is as yet available for determining the size of the cellulose molecule. Roentgen ray spectrographs indicate cellulose in plant fibers is composed of crystals symmetrically disposed with respect to the axis of the fiber, forming a parallelopiped, the group $C_6H_{10}O_5$ being regularly repeated, indicating that cellulose is constructed of anhydroglucose entities.

The celloisobiose of H. Ost and R. Prosiegel[4], according to G. Bertrand and S. Benoist[5] is a mixture of cellobiose and procellose, the latter being apparently a trisaccharide, and has been assigned a chain formula obtainable by hydrolysis at one of the glucosidal linkages in the Irvine formula.

1. A. Schorger, I. E. C. 1924, **16**, 1274; abst. C. A. 1925, **19**, 727.

2. *Ibid.* I. E. C. 1924, **16**, 141; abst. C. A. 1924, **18**, 901.

3. K. Hess, W. Weltzien and E. Messmer, Ann. 1923, **435**, 1; abst. C. A. 1924, **18**, 1384; J. S. C. I. 1924, **43**, 88-B; Chem. Zentr. 1924, I, 751.

4. Zts. ang. Chem. 1920, **33**, 100; abst. Cellulosechem. 1922, **3**, 25; abst. C. A. 1920, **14**, 3656.

5. Compt. rend. 1923, **176**, 1583; **177**, 85; abst. C. A. 1923, **17**, 3018, 3168.

According to H. Gray[1] the empirical formula of cellulose may be satisfactorily expressed by $[(C_6H_{10}O_5)_x]_y$, where x represents the simple molecule, and y the aggregate of molecules (probably by means unknown at present). R. Herzog and W. Jancke[2], as the result of X-ray analysis have shown that x must be one, two or four. Chemical evidence as adduced by viscose[3] and cellulose xanthanilid[4] (which see) indicates that one hydroxyl per C_{24} is different from the other 11 OH. H. Gray has proposed a formula for cellulose consisting of 4 glucose residues, three of which contain the amylene ring and the fourth the butylene, the preponderance of amylene rings being chosen because W. Charlton, W. Haworth and S. Peat[5] have shown that the structure of normal glucose contains the amylene ring, although C. Hudson[6] claims the butylene oxide ring is more applicable for cellulose.

G. Oddo[7] has comprehensively summed up our knowledge as to the facts of pertinency in establishing a formula for cellulose:

1. Composition $C_6H_{10}O_5$, and molecular weight a multiple of this.

2. Very resistant to the hydrolytic action of acids, enzymes, alkalis and other reagents.

3. Can be completely hydrolyzed to *d*-glucose by concentrated HCl, and to cellobiose octo-acetate by acetic an-

1. I. E. C. 1926, **18**, 811; abst. C. A. 1926, **20**, 3085; Pulp and Paper Mag. 1926, **24**, 1516.

2. Ber. 1920, **53**, 2162; Zts. ang. Chem. 1921, **34**, 385; abst. C. A. 1921, **15**, 983, 1453; Chem. Zentr. 1921, I, 564; J. C. S. 1921, **120**, ii, 531. Naturwiss. 1921, **9**, 320. R. Herzog, Umsohau, 1921, **25**, No. 5. R. Herzog, W. Jancke and M. Polanyi, Zts. Physik. 1920, **3**, 196, 343; 1921, **5**, 61.

3. Mitscherling, paper presented before Division Cellulose Chemistry, Madison, Wis., May 28, 1926. "Cellulose Chemistry," Heuser, 1924, 69.

4. L. Lilienfeld, E. P. 231800, 231801, 231802, 231803, 231804, 231805, 231806, 231807, 231808, 231809, 231810, 231811.

5. J. C. S. 1926, **129**, 89; abst. C. A. 1926, **20**, 1060. E. Hirst, J. C. S. 1926, **129**, 350; abst. C. A. 1926, **20**, 1595.

6. J. A. C. S. 1926, **48**, 1434; abst. C. A. 1926, **20**, 1981.

7. Gazz. chim. ital. 1928, **58**, 301; abst. C. A. 1929, **23**, 699.

See page 476, n. 6.

hydride and concentrated sulfuric acid, and thence to cellobiose by alcoholic KOH.

4. Forms levo-glucosan by vacuum distillation, and brommethylfurfural by the action of HBr in chloroform.

5. Contains 3 free OH groups per C_6 molecule, which are in the 2-, 3- and 6-position in the glucose molecule, one of the OH groups being more easily attacked than the others.

6. It forms hydrocellulose, cellulose hydrate and oxycellulose, which give hydrazones with no alteration of the fibrous structure.

H. Staudinger and O. Schweitzer[1] have demonstrated by hydrolysis of a series of polytriacetylcelloglucan diacetates, the molecular weight of which has been determined according to M. Bergmann and H. Machemer[2], and by measurement of viscosity[3], that a polymeric homologous series of polycelloglucan dihydrates result. The molecular weight of the dihydrates is uniformly greater than that of the corresponding acetates because of removal of the simplest portions of the hydrolyzate by the mother liquors. It is assumed that the chain length of the polycelloglucan diacetates remains intact during conversion into the hydrates, and that cellulose derivatives may be subjected to chemical change without altering the degree of polymerization[4]. K. Freudenberg adduces from the results of

1. Ber. 1930, **63B**, 3132; abst. C. A. 1931, **25**, 4398.
2. Ber. 1930, **63B**, 2877; abst. C. A. 1930, **24**, 2877.
3. H. Staudinger, K. Frey, R. Signer, W. Starck and C. Widmer, Ber. 1930, **63B**, 2308; abst. C. A. 1931, **25**, 280; J. S. C. I. 1930, **49**, 1415-A. See p. 910, n. 5.
4. The polycelloglucan dihydrates thus obtained are hemicolloids insoluble in water or formamide but soluble in Schweitzer's reagent; they are identical with the so-called cellodextrins or hydrocellulose. The behavior of solutions of hemicolloidal polycelloglucan dihydrates in Schweitzer's solution is less complicated than expected, provided that the concentration of the reagent is maintained uniform and it is used in excess so that more than 1 atom of Cu is present for each glucose residue. Solutions of a 70-polycelloglucan dihydrate do not change with time and obey the Hagen-Poiseuille law. Within the limits imposed by the volatility of the NH_3, the value is independent of the temperature, so that the hydrates are dissolved as molecules,

chemical, X-ray, and microscopical investigation[1], that cellulose is built up from glucoses or cellobiose residues, and lignin from coniferyl alcohol or phenolic residues in order to produce the structure of the wood fiber. There is no combination between cellulose and lignin, the whole structure rather resembling reinforced concrete in that the cellulose micelles are held in position by lignin and hemicellulose.

W. Haworth[2] claims cellulose to be a straight chain containing not more than 100 cellobiose or 200 glucose units, mol. wt. 25000-30000. The cleavage products from a completely (?) methylated cellulose showed that one of the glucose units contained one more methyl than the rest, it being possible to determine this compound quantitatively, and hence determine the size of the cellulose derivative. Applied to amyloses, the method showed the presence of 10 maltose or 20 *a*-glucose units, giving a mol. wt. of about 4000[3].

not micelles. The viscosity of the hemicolloidal heteropolar polycelloglucan dihydrate complexes in Schweitzer's solution resembles that of hemicolloidal polystyrenes in C_6H_6 or tetrahydronaphthalene. With the simpler dihydrates of degree of polymerization 30-100 the value K_m shows relatively little variation. With more complex products the value is less constant, possibly because of the imperfect applicability of the Bergmann-Machemer method. The viscosity of solutions of purified cotton in Schweitzer's reagent diminishes with time without becoming constant after 4 weeks. The change depends on the oxidative degradation of the macromolecules of the cellulose by copper oxide. Comparable values can be obtained only by use of solutions which have been preserved for equal intervals at the same temperature. About 0.2% solutions of cellulose in Schweitzer's reagent are gel solutions, which show deviations from the Hagen-Poiseuille law. The swelling of cellulose in Schweitzer's reagent is not evidence of micellary structure, but is equally reconcilable with the presence of long molecules. The stability of macromolecules in the solid state and in solution is discussed. The highest observed value for the molecule weight of cellulose can be regarded only as a minimum value for native cellulose, since it is not possible that degradation occurs during swelling and solution. Possibly native cellulose is an aggregated compound, the macromolecules of which are capable of existence only in the solid state embedded in the crystal lattice.

1. Papier Fabr. 1932, **30**, 189; abst. J. S. C. I. 1932, **51**, 605-A.
2. Nature, 1932, **129**, 365; abst. C. A. 1932, **26**, 2711; J. S. C. I. 1932, **51**, 370-A.
3. Ber. 1932, **65A**, 43; abst. C. A. 1932, **26**, 2968. See Nature, 1930, **126**, 238; abst. C. A. 1931, **25**, 84.

In a summation of our existing knowledge of the constitution of cellulose[1], there remains two sources of evidence for the occurrence of long chains and for the mode of linkage in these chains, one of which comprises the occurrence of tri- and tetra-saccharides, as well as a disaccharide and a monose among the hydrolytic degradation products of cellulose. These can be more readily isolated as methyl derivatives than as the free substances themselves. The methyl derivatives may be distilled, and from their sharp boiling points as well as their ability to crystallize, indubious purity may be obtained.

However, until we are able to prove absolutely the linkage of the oxygen bridge in glucose, and the value of x in $(C_6H_{10}O_5)_x$, any structural formula is purely speculative insofar as elucidating the structural formula of this body.

Much attention has been given in the last few years to the X-ray analysis of cellulose and its derivatives, which possesses a fibrous structure resulting from an orientation of "crystallites" or "micelles" parallel to one particular axis. These substances are interesting as a transition from simple molecules and structures towards the complex organizations adapted to the functions of life. The method of investigation[2] is essentially to examine the X-ray diagrams obtained under two sets of conditions. When the rays fall on the material in the direction of the fiber axis, a Debye-Scherrer pattern is obtained, because the micelles or microcrystals may have all possible orientations except for the direction of their long axes; when, however, the rays are incident perpendicular to the axis of the fibres, a different type of pattern is obtained, since the long axes are parallel (fiber diagram).

1. K. Freudenberg, Ber. 1929, **62B**, 383; abst. J. S. C. I. 1929, **48**, 430-A. J. S. C. I. 1931, **50**, 287-T; abst. C. A. 1931, **25**, 5554. H. Gray, J. Chem. Ed. 1930, **7**, 1803. K. Hess, Rec. Trav. Chim. 1929, **48**, 489; abst. C. A. 1929, **23**, 4340. D. MacGillavry, Rec. Trav. Chim. 1929, **48**, 18; abst. C. A. 1930, **24**, 3356. S. Malowan, Nitrocellulose, 1930, **1**, 58; abst. C. A. 1930, **24**, 3640.

2. For list of references, consult W. Bragg, Nature, 1930, **125**, 634.

By applying this method of analysis, the changes occurring in cellulose under the action of chemical reagents on various physical treatments can be investigated. Most of the work is too specialised to summarise, but may be exemplified by that of K. Andress[1], who concludes that the change occurring during the "mercerisation" of natural cellulose is the rearrangement of the main chains to more stable relative positions. H. Mark and K. Meyer[2] distinguish two kinds of reaction of cellulose, "micellar surface reactions" and "permutoid" reactions. In the first kind, the reagent penetrates between the micelles without attacking their internal structure; the orientation may, however, be disturbed and the "fiber" diagram changes to a Debye-Scherrer diagram. In the second kind of reaction, the reagent penetrates the whole structure, attacking specific chemical groupings at each point of the lattice.

Although they relate to a different type of structure, it is interesting to mention some measurements made by A. Müller[3]. He has found that while the short axes of long-chain normal paraffins change on the average by 6.8% and 1.9% respectively between the temperature of liquid air and the melting point, the change in the long axis is too small to measure. This indicates that the end groups of the molecules move apart, but that the length of the chain probably does not alter with increasing temperature.

Objection is raised to the opinion of Hess that the rotatory power of a solution of cellulose in Schweitzer's reagent is due to a complex formed between copper and every glucose unit of the cellulose complex, and the use made of this view in determining the molecular weight of cellulose is adversely criticised[4]. Equally insecure is the latter hypothesis that the structural unit of cellulose is a biosan,

1. Zts. Physikal. Chem. 1929, (B), **4**, 190.
2. *Ibid.* 1929, (B), **2**, 115.
3. Proc. Roy. Soc. 1930, (A), **127**, 417.
4. D. Macgillavry, Rev. Trav. chim. 1929, **48**, 18, 294; abst. J. S. C. I. 1929, **48**, 262-A, 763-A; K. Hess, Rec. trav. chim. 1929, **48**, 489; abst. J. S. C. I. 1929, **48**, 763-A.

since independent attempts to isolate the biosan acetate have shown[1] that this is probably a still highly complex breakdown product of cellulose and is not homogeneous. The isolation of hydrolysis products is in apparent agreement with the formula $(C_6H_{10}O_5)_3$ and $(C_6H_{10}O_5)_4$ is reported, but it is emphasized that the course of the hydrolysis of cellulose is not in harmony with the conception of a cellulose constitution based on small associated units[2].

Further considerations relating to the molecular size of cellulose as deduced from viscosity measurements have been put forward by H. Staudinger and O. Schweitzer[3]. The viscosity of solutions of purified cotton in Schweitzer's reagent diminishes with time without becoming constant after four weeks, the change depending on the oxidation degradation of the macromolecules of the cellulose by copper oxide. Calculation of the molecular weight of cellulose from the viscosity of its solutions in Schweitzer's reagent shows that a more or less profound degradation of the molecule occurs according to the method of purification. The highest observed value (190,000) is for purified cotton; slight degradation accompanies mercerization. Sulfite-cellulose and copper-silk are more appreciably affected (mol. wt. 80,000-65,000 and 35,000 respectively).

Micelle Chemistry of Cellulose. X-ray analysis of cellulose coupled with the results of chemical investigation, have made it possible in the last few years to develop clear-cut views concerning the structure of both the cellulose molecule and micelle. R. Herzog has shown that cellulose fibers in parallel arrangement give a Roentgen diagram similar to that of crystal particles arranged along one axis, and certain conclusions relative to the constitution

1. K. Freudenberg, Ber. 1929, **62**, (B), 383; abst. J. S. C. I. 1929, **48**, 430-A; J. R. Katz and P. J. P. Samwel, Annalen, 1929, **474**, 296; abst. J. S. C. I. 1929, **48**, 1277-A.

2. R. Willstätter and L. Zechmeister, Ber. 1929, **62**, (B), 722; abst. J. S. C. I. 1929, **48**, 544-A.

3. Ber. 1930, **63B**, 3132; abst. J. C. S. 1931, **134**, 202.

of cellulose may be drawn from the analogy[1]. From the value of the elementary parallelopiped it would appear that the group $(C_6H_{10}O_5)_4$ is regularly repeated. Further, it is most probable that the symmetry of the rhombic crystal system is represented in the cellulose molecule, although that of the monoclinic system, one degree lower than the rhombic, is not excluded. The fundamental units must each contain a cellobiose residue, and the entire cellulose molecule must be built up of cellobiose groups.

Three types of structure come into consideration: (a) Open chains of dextrose residues linked together in groups of four in series by means of oxygen bonds; (b) Closed rings of four dextrose components linked by oxygen bonds, but if the symmetry is that of the rhombic system this possibility is ruled out; (c) Cellulose may consist of internal anhydrides of cellobiose, and according to the rhombic system the constituent elements would be composed of dextrose residues in pairs linked by oxygen bonds through the second and sixth carbon atom. Cellulose exhibits crystal structure in contradistinction to acetyl- and ethyl-cellulose which are amorphous. It is possible, however, to re-establish arrangement effects by stretching and similar mechanical treatment whereby the tenacity is increased and the swelling capacity correspondingly diminished[2]. Not only has X-ray investigation revealed the fact that cellulose is composed of minute crystals lying beyond the range of microscopic visibility[3], but that it exhibits the same X-ray interference phenomena as found with crystalline substances. Employment of a monochromatic beam of X-ray shows that cellulose has only a single crystal structure[4].

1. Cellulosechem. 1921, **2**, 101; abst. C. A. 1922, **16**, 1663; J. S. C. I. 1922, **41**, 8-A.
2. R. Herzog and W. Jancke, Zts. ang. Chem. 1921, **34**, 385; abst. J. C. S. 1921, **120**, ii, 531. Zts. physik. 1920, **3**, 196, 343; abst. C. A. 1921, **15**, 983, 1453; Chem. Zentr. 1921, I, 564.
3. R. Herzog, Pulp and Paper Mag. 1926, **24**, 694, 1259; Paper Trade J. 1926, **83**, No. 51.
4. R. Herzog and W. Jancke, Zts. Physik. 1928, **49**, 27; abst. J. S. C. I. 1928, **47**, 819-A. See H. Gonell, Zts. Physik, 1924, **25**, 118; abst. C. A. 1924, **18**, 3112; J. C. S. 1924, **126**, ii, 588.

In native cellulose the micellar section perpendicular to the fiber axis is a rhombus of side 55±5 A, the micellar length being greater than 600 A.[1], observation of the width of lines at the temperature of liquid air showing the same results as at ordinary temperature. On extension by more than 280%, the crystals are replaced by the fiber diagram of stretched rubber, indicating crystallite size depends on the choice of conditions.

Our present knowledge of the X-ray structure of cellulose has been epitomized by G. Clark[2], E. Hauser[3], and C. Fox[4], as based upon the investigations of H. Mark and K. Meyer[5], W. Eccles and W. Bragg[6], O. Sponsler[7], and W. Seifriz[8].

1. J. Hengstenberg and H. Mark, Zts. Krist. 1928, **69**, 271; abst. C. A. 1929, **23**, 2292; J. S. C. I. 1930, **49**, 21-A; Chem. Zentr. 1929, I, 3088.

2. I. E. C. 1930, **22**, 474; abst. C. A. 1930, **24**, 3356; Cellulose, 1930, **1**, 174; J. S. C. I. 1930, **49**, 653-B.

3. I. E. C. 1929, **21**, 124; abst. C. A. 1929, **23**, 1263; J. S. C. I. 1929, **48**, 318-B.

4. J. S. C. I. 1930, **49**, 83-T; abst. C. A. 1930, **23**, 3356; J. Chem. Ed. 1930, **7**, 1951; Cellulose, 1930, **1**, 63.

5. Cellulosechem. 1930, **11**, 91; abst. C. A. 1931, **25**, 1987. See Zts. Physik. Chem. 1929, Abt. B, **2**, 115; abst. C. A. 1929, **23**, 5077. H. Mark and G. v. Susich, Zts. physik. Chem. 1929, Abt. B, **4**, 431.

6. Proc. Roy. Inst. Gt. Brit. Adv. copy Jan. 24, 1930, 16 pp; abst. C. A. 1930, **24**, 2356. W. Bragg, Nature, 1930, **125**, 634; abst. C. A. 1930, **24**, 3356. Cellulose, 1930, **1**, 80, 110; abst. C. A. 1931, **25**, 1987.

7. Nature, 1927, **120**, 767; abst. J. S. C. I. 1928, **47**, 48-A. Nature, 1930, **125**, 633; abst. C. A. 1930, **24**, 2356; J. S. C. I. 1930, **49**, 672-A.

8. J. Physical Chem. 1931, **35**, 118; abst. C. A. 1931, **25**, 1540; J. S. C. I. 1931, **50**, 532-A. K. Hess and C. Trogus (Zts. Physikal. Chem. Bodenstein Festband, 1931, 385) have compiled a summary of X-ray examination and analytical methods of two forms of cellulose, normal cellulose and mercerized cellulose, and of 16 of their derivatives. It is shown how the two celluloses and ten of their derivatives appear to be based on a periodicity along the fiber axis of 2x5.15 A. U., while of the remaining six derivatives, in order to interpret their X-ray photographs, it is necessary to assume for four of them 2x5.15 A. U., for another 4x5.15 A. U., and for still another (trinitrocellulose) 5x5.15 A. U., which is the length of a glucose residue, stands in a closer relation to cellulose than does the dimension 10.3 A. U., the length of a cellobiose residue, i. e., that the cellobiose residue does not pre-exist in the cellulose molecule, as has been suggested by W.

It has been established that all natural cellulose fibers as cotton, wood, hemp and regenerated cellulose produce diffraction patterns characteristic of crystal fibers. A

Haworth (see H. Mark and K. Meyer, Zts. Physikal. Chem. 1929, (2), 115. R. Andress, Ibid, p. 380. O. Sponsler, Nature, 1930, **125**, 633. R. Herzog and W. Jancke, Zts. Physikal. Chem. 1928, (A), 139, 235).

While it may be true that these anomalous fiber periodicities are disquieting with respect to the true nature of the cellulose chain, in view of the fact that many existing fiber photographs defy unambiguous evaluation, there appears to be insufficient reason to accept the conclusions of K. Hess and C. Trogus as final. The cellulose chain may be fundamentally based on a repetition of the cellobiose residue, but it does not necessarily follow that the periodicity of the chain should remain a constant multiple of 5.15 A. U. for each and every possible type of cellulose of which there is reasonable certitude with respect to the true size of the unit of pattern.

According to K. Meyer and H. Mark (Ber. 1928, 61B, 593) the cell of natural cellulose as shown by its fiber diagram, has the following dimensions: a, 8.7 A., b, 10.3 A., c, 7.8 A., and *b*, 90°, the most probable space group C_2 containing four molecules of "glucose residue." It is suggested that these molecules are not separated as in a molecular crystal, but are joined by a glucoside link through OH groups in "b" direction (which is the fiber axis), so as to form long-chain molecules held together at the sides by ordinary molecular forces. This would make cellulose an example of continuous linkages in one dimension, just as graphite and diamond linkages extend in two and three dimensions respectively. Mercerization, nitration and other chemical processes have been shown to unaffect the general structure, but only to alter the cell size and change the relative intensities of reflection in a reversible way. This is because the substituent groups attack only the sides of the chain without breaking the chains themselves. The high molecular weight of cellulose would, accordingly refer not to the molecule, but to the fibrous crystallites, which retain their structure even in solution. Similar explanations may be found to account for the structure and properties of most other fibrous, organic substances, such as silk and chitin, where the homopolar links extend in all three dimensions. H. Mark and G. v. Susich (Naturwiss. 1929, **17**, 803) have examined the process of cellulose mercerization with very intense X-rays, and found that two intermediate compounds are formed in the course of five minutes, from which it appears that the use of very short exposure times will probably prove of great value in the examination of intermediate phases which it is impossible to isolate.

The combination of numerous X-ray observations coupled with the recent concepts in the chemistry of compounds of high molecular weights, leads to the conclusion that the elongated submicroscopic crystallites which are the basis of fiber structure, are in reality no other than bundles of various thicknesses and varying degrees of relatively simple chemical units. Assuming cellulose molecules are long chains of *b*-glucose residues linked by primary valencies, it appears clear that such chains may be grouped together by operation of ordinary crystallographic forces to form bundles, long and of well defined periodicity *parallel* to the fiber axis, but thin and possibly of hazy-defined periodicity *perpendicular* to the fiber axis.

"fiber" is not a single crystal grain, nor is it an aggregate of small grains in random orientation, since this would produce a pattern of uniform rings. The fiber is constituted of many crystal grains (crystallites or colloidal micelles) which are orientated so that a common crystallographic direction in all tends to lie parallel in the direction of the fiber axis. A fiber diffraction pattern which characterizes cellulose, shows localized intensity maxima which are more or less disconnected arcs of the usual Debye-Scherrer rings. These intensity maxima also lie on layer line hyperbolas above and below the equatorial line of the pattern. Thus a very definite and large part of cellulose fibers is truly crystalline. Resins and disintegration products may be extracted and removed, leaving still the pure crystalline portion which yields a pattern essentially unchanged from that of the initial material.

Hence resins, hemicelluloses, lignin and other substances known to be present, may be designated as amorphous in the sense that they do not give interference with the crystalline pattern of true cellulose, and give little or no evidence of their presence as a cementing matrix. The crystalline part of cellulose fibers is remarkably persistent in that it can be mercerized, esterified or etherified or otherwise chemically treated in the solid form so that the resulting product is still a crystal fiber.

An interpretation of the spacings of the Debye-Scherrer rings, indexing of planes corresponding to the intensity maxima of the fiber pattern, straightforward measurement of the identity period along the fiber axis, and a careful analysis of intensities, have led H. Mark and K. Meyer to an analysis of crystalline cellulose which is now generally accepted as final in its fundamentals, and has been confirmed independently elsewhere.

First of all, therefore, X-rays select the smallest spacial unit or unit crystal cell which has the fundamental properties of cellulose:

Crystallographic system: monoclinic

Unit cell dimensions: $a = 8.3$, $b = 10.3$ (fiber axis), $c = 7.9$, $\beta = 84$ A.

Number of $C_6H_{10}O_5$ groups per cell: 4.

Space group: C_2^2.

Important intensity data: (200) missing, (002) very strong, (040) stronger than (020), (011) and (111) very weak, (021) and (031) relatively strong.

Since each unit cell contains at most important scattering centers 24 carbon and 20 oxygen atoms, direct calculation from intensity observations of atomic co-ordinates is practically impossible without constructing a model rationally related to chemical and physical properties, and comparing the intensity data calculated with that experimentally observed.

Upon the concept of long primary valence chains of dehydrated glucose residues backed by further chemical, physical and botanical facts, O. Sponsler has described in interesting fashion how cell wall increases in thickness. The ultimate layers indicated by X-ray data are only one glucose residue in thickness. No experimental evidence is available to show that anhydrous glucose units of the cell wall which constitutes cellulose are derived directly from glucose molecules which originate from photosynthesis.

X-ray data judiciously interpreted have led from the dehydrated glucose residue composed of C, O and H atoms to a pair, bound as a cellobiose residue, by 1-4 oxygen bridge and to a particular grouping in a small unit crystalline cell. An extension to a rational model depicts long, spiral, primary valence chains along the fiber axis with cross sections determined by the number of chains in a bundle. The question next arises as to how long are the chains, since it appears unlikely that they are as long as the entire fiber itself, and how many are grouped in a bundle. That is, does a spacial unit of structure larger than the ultimate cell exist, the dimensions of which are determinable from a diffraction pattern.

The measurement of particle size, particularly in the range 10^{-6} to 10^{-8} cm., is now well established in diffraction information. In the colloidal range, the smaller the particle and the fewer the diffracting parellel planes, the less perfect is the sharply unidirectional interference of secondary waves, and the broader will be the diffraction maxima which characterize a given crystalline structure. Hence a measurement of the breadths of diffraction lines or spots at points at half-maximum intensity leads to an evaluation of grain size in an aggregate. Numerous experiments have demonstrated the colloidal nature of cellulose, and the X-ray patterns prove that cellulose is an aggregate of grains, or crystallites or micelles (Gaegeli's notation).

A general summary of the numerical magnitudes involved in cellulose structure is as follows:

Unit	Weight	Volume	Surface
		Cc.	*Sq. cm.*
Glucose residue	162		
Cellobiose residue	324		
Unit cell	648	6.8×10^{-22}	
Micelle	$\sim 10^5 - 10^6$	$1\text{–}2 \times 10^{-18}$	$8\text{–}12 \times 10^{-12}$
1 grain		~ 0.6	$1\text{–}3 \times 10^7$

Unit	Glucoses	Cellobioses	Unit Cells	Micelles
Glucose residue	1			
Cellobiose residue	2	1		
Unit cell	4	2	1	
Micelle	6000–12,000	3000–6000	1500–3000	1
1 grain	3.7×10^{21}	1.85×10^{21}	$\sim 9 \times 10^{20}$	3.7×10^{17}

As applied to cellulose ethers, quantitative measurements in this field have always presented great difficulty, and the only agreed indisputable result available appears to be that the cellulose ethers or esters of the least degraded cellulose give the highest viscosity, other things being equal. Either, therefore, the micelle size affects the viscosity, or perhaps micelle detritus as degradation products has a lower absorptive capacity, because it may dissolve to form a true solution in the external phase, where it may also raise the external osmotic pressure and thus attract imbibed fluid away from the micelle.

W. Astbury and T. Marwick conclude from an examination of the available data in this field[1], that for cellulose and sugars, the 6-atom sugar ring is associated in the crystalline state with certain linear dimensions which are approximately constant, and that one dimension at least, corresponds with one of the axial lengths of the unit cell.

It has been determined by J. Strachan[2] that light passing through natural cellulose fibers deeply stained with iodine is completely polarized by absorption. Microscopic analysis of this phenomenon proves that the polarization is due to ultramicroscopic crystalline particles of iodine oriented on the lattice. These crystals are assumed to be rhombic.

As a result of the studies made in this field, the structure of the cellulose molecule may be regarded as each glucose residue of the cellulose appearing as a relatively flat ring which is connected to the next ring through 1-4 glucosidic oxygen linkages. Several glucose residues in this way form a chain, and from a series of such chains, lying parallel to one another and bound together by secondary valences, the micelle of the parent substance cellulose is constructed[3]. Such micelles produce crystal-like substance. A more complete insight into the structure of such micelles is obtained as the result of the recent investigations carried on by means of the X-ray analysis method by W. Abitz, O. Gerngross and K. Herrmann, whose studies, through improved photographic technic and an especially careful evaluation of the results, have led to surprising conclusions well suited to explain the major properties of a substance with micellar structure, and especially swelling and contraction phenomena and the alignment of micelles by stretching.

Their investigations were carried out with gelatin, but there is great probability that the knowledge so gained

1. Nature, 1931, **127**, 12; abst. C. A. 1931, **25**, 2349; J. S. C. I. 1931, **50**, 152-A.
2. Nature, 1930, **125**, 671; abst. C. A. 1930, **24**, 3149.
3. V. Bayerl and K. Roos, Cellulose, 1930, **1**, 261; abst. C. A. 1931, **25**, 4762. Kunstseide, 1930, **12**, 424; abst. C. A. 1931, **25**, 3826.

can be carried over with but slight changes into the system of cellulose micelles.

The most important result of these studies was the conclusion that the material of the micelle consists both of an amorphous and a crystalline part, both of which are present together at all times. This conclusion was reached as the result of a new crystalline ring in the X-ray diagram of the swollen gelatin.

Acetolysis. Cellobiose. Comparison of the yields of cellobiose octo-acetate, obtained by treating cellulose, cellobiose, methylcelloside, cellulose triacetate, cellobiose acetate and methylcelloside acetate with acetic anhydride and sulfuric acid under similar conditions[1] leads to the conclusion that cellulose must contain at least about 50%, and possibly more, of ready formed cellobiose complex, as against 33% of pre-formed cellobiose as reported by K. Hess and W. Wittelsbach[2]. Methylation of cellobiose by means of alkali and methyl sulfate gives unsatisfactory results, but methylation of methylcelloside in this way gives an almost quantitative yield of hexamethylmethylcelloside. The latter may be methylated by means of dry methyl iodide and silver oxide, to heptamethylmethylcelloside, and hydrolysis of this with boiling 5% HCl solution yields products from which *b*-tetramethylglucose may be isolated. Heptamethyl--*b*-methylcelloside prepared by methylating cellobiose, gives by cleavage tetramethyl- and trimethyl-glucose[3].

W. Haworth and E. Hirst[4] methylated cellobiose octo-acetate (m. pt. 224-227°, mol. wt. 685 ebullioscopically in

1. P. Karrer and F. Widmer, Helv. Chim. Acta. 1921, **4**, 174; abst. C. A. 1921, **15**, 2629; J. S. C. I. 1921, **40**, 342-A; J. C. S. 1921, **120**, i, 310; Chem. Zentr. 1921, I, 936.
2. Zts. Elektrochem. 1920, **26**, 232; abst. Paper, 1920, **27**, No. 13, 13; No. 26, 32; C. A. 1921, **15**, 1619; 1922, **16**, 2221; J. C. S. 1920, **118**, i, 532; J. C. S. Ann. Rep. 1920, **17**, 67; J. S. C. I. 1920, **39**, 512-A; Bull. Soc. Chim. 1921, **30**, 1332.
3. P. Karrer and F. Widmer, Helv. Chim. Acta. 1921, **4**, 295; abst. C. A. 1922, **16**, 63; Cellulosechem. 1921, **2**, 102; Chem. Zentr. 1921, III, 944.
4. J. C. S. 1921, **119**, 193; abst. C. A. 1921, **15**, 1505; Chem. Zentr. 1921, III, 29.

chloroform) in alkaline solution, isolated potassium cellobiosate and methylated with NaOH and methyl sulfate, obtaining a liquid distilling slightly below 200° at 0.2 mm. pressure, the analytical figures being in agreement with a hexamethylmethylcellobioside. This was subjected to a triple methylation with methyl iodide and silver oxide, a heptamethylmethylcellobioside resulting.

K. Freudenberg finds[1] that cellobiose octoacetate may be isolated in yield corresponding to 35-36% of cellobiose in the original material in a single operation when cellulose is treated with a mixture of acetic anhydride and concentrated sulfuric acid at a low temperature, the operation requiring about 4 days. He believes that an indirect estimation of the loss of octo-acetate which occurs during the change makes it highly probable that cellulose is composed of cellobiose to the extent of more than 60%.

Cellulose triacetate may be converted into methylglucoside by the formula of J. Irvine and E. Hirst[2] with a yield of 99.5% by digesting 4 gms. of the acetate with 15 parts methyl alcohol containing 0.75% HCl in a sealed tube. After 60-70 hrs. at 125° only a trace of solid matter remained. The yield of pure crystalline methylglucoside averaged 95.5%, so that the overall yield from the polysaccharide to the hexose is 95.1%. Although cellulose is quantitatively hydrolyzable into dextrose[3], and the graded hydrolysis undergone by cellulose may be arrested at a stage during acetolysis where the cellobiose is a definite product, it has been found that by substituting methoxyl groups for all the hydroxyl groups and subjecting the alkylated polysaccharide to hydrolysis, an equilibrium mixture is obtained containing *a*- and *b*-2.3.6-trimethylmethylglucosides (yield 91.5% of theory), which, when hydrolyzed in the usual

1. Ber. 1921, **54**, 767; abst. J. S. C. I. 1921, **40**, 342-A.
2. J. C. S. 1922, **121**, 1585; abst. C. A. 1922, **16**, 3468; Chem. Zentr. 1923, I, 1426.
3. J. Irvine and E. Hirst, J. C. S. 1923, **123**, 518; abst. C. A. 1923, **17**, 1956; J. S. C. I. 1923, **42**, 710-A; Chem. Zentr. 1923, III, 1603.

manner gives crystalline trimethylglucose alone (yield 86% of theory).

Treatment of trimethylglucose with methyl alcohol-HCl at 30° affords the heteromethylglucoside, containing the amylene oxide ring[1], while similar treatment at 100° produces the normal methylglucoside containing the butylene oxide ring[2]. By treating the hetero-methylglucoside with methyl alcohol-HCl at 100° it is quantitatively converted into the normal form which is the more stable, and cannot be made to undergo the reverse change. When trimethylglucose is dissolved in methyl alcohol-HCl, it is converted into a mixture of normal and hetero-forms, as is shown by the value for the initial specific rotation being 10-20° below normal. At 30° only the hetero form is converted into the glucoside. Methylation of the trimethylglucoside obtained from trimethylcellulose[3] yields a mixture of *a*- and *b*-tetramethylglucoside[4] which on methylation gives 2.3.5.6-tetra- original trimethylglucoside consist of a mixture of 65% *a*-form and 35% *b*-form. Their stability is suggested by the fact that octamethyl-lactose yields 2.3.6-trimethyl-*b*-methylglucoside[11] which on methylation gives 2.3.5.6-tetramethyl-*b*-methylglucoside, but hydrolysis of octamethyl-lactose results in the formation of tetramethylmethylgalactoside.

Two crystalline forms of the *a*-glucose penta-acetate have been isolated from the chloroform extract of the precipitation liquid from the acetolysis of cellulose without re-acetylation[5]. Further yields of glucose penta-acetate and of cellobiose octo-acetate have been obtained by the

1. H. Schlubach and H. von Bomhard, Ber. 1926, **59B**, 845; abst. J. S. C. I. 1926, **45**, 600-A.
2. J. Irvine and E. Hirst, J. C. S. 1922, **121**, 1213; abst. C. A. 1922, **16**, 3071.
3. F. Micheel and K. Hess, Ann. 1926, **449**, 146; abst. C. A. 1927, **21**, 173; J. S. C. I. 1926, **45**, 1230-A; Chem. Zentr. 1926, II, 2890.
4. H. Schlubach and K. Moog, Ber. 1923, **56B**, 1957; abst. J. C. S. 1923, **124**, i, 1063.
5. C. Webber, C. Staud and H. Gray, J. A. C. S. 1930, **52**, 1542; abst. C. A. 1930, **24**, 2433; Eastman Kodak Co. Abridge Sci. Pub. 1930, **14**, 69; Cellulose, 1930, **1**, 149; J. S. C. I. 1930, **49**, 749-A.

re-acetylation of the gum obtained after isolation of the crystalline glucose acetate above mentioned. α-Glucose penta-acetate has been isolated from the mother liquid of the crystallization of crude cellobiose octa-acetate obtained in the acetolysis of cellulose.

J. Chalmers and J. Earl[1] have found that boiling methanol containing 1% HCl does not form methylglucoside from cellulose triacetate, whereas 50 cc. containing 5% HCl dissolves 0.479-0.729 gm. from 1 gm. cellulose triacetate in 3-21 hrs., the dissolved portion showing α-methylglucoside. By re-acetylating the residue it was found to be a partially de-acetylated cellulose triacetate, the degradation of the latter being accompanied by a lowering of the specific rotation.

All the insoluble products of the degradation of cellulose acetate reduce alkaline iodine solution and the iodine consumption is stated to be an accurate and reproducible measure of the free aldehydic groups and the molecular weight of the compounds[2]. Technical cellulose acetate has been further degraded with hydrogen bromide in glacial acetic acid, and the product separated by hot methyl alcohol into two portions, acetylsaccharides A and B. The iodine numbers of the respective materials indicate the presence in them of mixtures of polysaccharides containing as an average 8 and 9-11 hexose units. The product obtained by the acetolysis of cellulose according to the method of K. Hess and H. Friese[3] has been separated into a number of fractions which appear to contain 8-13 hexose residues.

To the latter substance, the hexa-acetyl biosan considered by K. Hess and H. Friese to be a true dimetride of the fundamental cellulose molecule, a molecular weight of 554-

1. J. Proc. Roy. Soc. N. S. Wales, 1930, **63**, 155; abst. C. A. 1930, **24**, 6002; J. S. C. I. 1930, **49**, 1415-A.
2. M. Bergmann and H. Machemer, Ber. 1930, **63B**, 613; abst. J. S. C. I. 1930, **49**, 457-A; Ann. Rep. Chem. Soc. 1930, **27**, 112. See also R. Willstaetter and G. Schudel, Ber. 1918, **51**, 780; abst. J. C. S. 1918, **114**, ii, 461.
3. Ann. 1926, **450**, 40; abst. J. S. C. I. 1927, **46**, 44-A; Ann. Rep. Chem. Soc. 1930, **27**, 113.

587 has recently been assigned[1]; this value, determined in acetic acid, is considered to be a true one, although the behavior of the different samples of acetone-soluble cellulose acetate in acetic acid is irregular and the relationship of cellulose acetate to glacial acetic acid apparently complex. The value is rejected by other workers[2] on the grounds of the unsuitability of the cryoscopic method for determining the (very large) molecular weight of this substance and of the demonstrable non-homogeneity of the biosan acetate.

With regard to the more complex acetolysis products of cellulose, the terminal groups form so small a proportion of the molecule that their accurate determination by the iodine method is held to be impossible[3]; nevertheless, on the basis of iodine consumption, the chain in cellulose itself has been computed to contain 50 glucose residues on an average as against 25-30 such residues in the starch molecule[4].

The course of degradation of the cellulose molecule on heating with acetic acid and zinc chloride has been followed by viscosity measurements. Degradation of the initial cellulose molecule occurs very rapidly, but the simpler products are much more resistant. The initial, highly viscous solutions are computed to contain cellulose triacetates of average degree of polymerisation 60-100; after 20 hours action, the degree is reduced to 10. At the ordinary temperature, reaction proceeds extremely slowly, giving products of a degree of polymerisation, 150. After 7 days at 30°, the degree is 130 and after 10 days it is 100. Since

1. K. Hess, Ber. 1930, **63B**, 518; abst. J. S. C. I. 1930, **49**, 456-A; Ann. Rep. Chem. Soc. 1930, **27**, 113.

2. K. Freudenberg, E. Bruch and H. Rau, Ber. 1929, **62B**, 3078; abst. J. S. C. I. 1930, **49**, 198-A; Ann. Rep. Chem. Soc. 1930, **27**, 113. K. Freudenberg and E. Bruch, Ber. 1930, **63B**, 535; abst. J. S. C. I. 1930, **49**, 457-A. K. Meyer and H. Hopff, Ber. 1930, **63B**, 790; abst. J. S. C. I. 1930, **49**, 750-A; Ann. Rep. Chem. Soc. 1930, **27**, 113.

3. H. Staudinger and H. Freudenberger, Ber. 1930, **63B**, 2331; abst. J. S. C. I. 1930, **49**, 1416-A; Ann. Rep. Chem. Soc. 1930, **27**, 113.

4. K. Freudenberg, W. Kuhn, W. Durr, F. Bolz and C. Steinbrunn, Ber. 1930, **63B**, 1510; abst. J. S. C. I. 1930, **49**, 1025-A; Ann. Rep. Chem. Soc. 1930, **27**, 1025.

native cellulose is more highly polymerised than the most complex of its acetates, its molecular weight is considered to be above 24,000, and the cellulose molecule probably contains a chain of 500-1000 glucose residues, thus having dimensions similar to those of the caoutchouc molecule.

Details have been given[1] for the separation of decamethyl-*b*-methylcellotrioside (b. pt. 215-225° at 0.1 mm., m. pt. 118-119°) and tridecamethyl-*b*-methylcellotetraside (b. pt. 260-270° at 0.1 mm., m. pt. 139°), from the product obtained from methylation of the acetate mixture (partly freed from cellobiose octo-acetate) produced when cotton is acetylated with acetic acid, acetic anhydride and sulfuric acid at 0-30°[2]. Undecamethylmaltotriose (b. pt. 215-225° at 0.1 mm.) and tetradecamethylmaltotetraose (b. pt. 260-270° at 0.1 mm.) are obtained similarly from starch. Crude heptamethylcellobiose 1-chlorhydrin, prepared from heptamethylcellobiose by J. Allison and R. Hixon[3], and trimethyl-*b*-glucoside in presence of silver carbonate, give a mixture of products from which decamethyl-*b*-methylcellotrioside is isolated. From a mathematical elucidation, F. Klages[4] has shown that the differentiation between main valency chain molecules and small molecules cannot be effected by measurements of the rates of hydrolysis of polysaccharides.

Cellulose and Heat. When wood is destructively distilled[5], a large proportion of the acetic acid is given off in the neighborhood of the temperature of exothermic decomposition, i.e., about 280°, and it has been shown that with wet wood, 8-10% of the acetic acid may be driven off before

1. K. Freudenberg, C. Andersen, Y. Go, K. Friedrich and N. Richtmyer, Ber. 1930, **63B**, 1961; abst. J. S. C. I. 1930, **49**, 1412-A. K. Freudenberg and K. Friedrich, Naturwiss. 1930, **18**, 1114; abst. J. S. C. I. 1931, **50**, 337-A.
2. K. Freudenberg, K. Friedrich, I. Bumann and K. Soff, Ann. 1932, **494**, 41; abst. J. S. C. I. 1932, **51**, 501-A.
3. J. A. C. S. 1926, **48**, 406; abst. J. S. C. I. 1926, **45**, 386-A.
4. Ber. 1932, **65B**, 302; abst. J. S. C. I. 1932, **51**, 370-A.
5. L. Hawley and R. Palmer, Eighth Int. Cong. Appl. Chem. 1912, IV, **6**, 138; Bull. No. 129, U. S. Dept. Agric. Sept. 10, 1914; abst. J. S. C. I. 1912, **31**, 865.

decomposition commences[1]. P. Klason has demonstrated[2] that by distilling wood *in vacuo*, there is a small but definite increase in acetic acid. When cotton is heated to incipient decomposition[3], the products contain a small proportion of a dextrorotatory substance which reduces Fehling's solution, and forms a phenylosazone, m. pt. 202-203°. Further, when heated with water in an autoclave at 190-200°, cotton yields a reducing substance which probably is a sugar. J. Bain and G. Chute[4] have definitely established the presence of dextrose in cotton which has been heated at 200°, some formic acid and small amounts of acetic acid being formed.

A. Pictet and J. Sarasin[5] gradually heated cotton in a distillation apparatus under 12-15 mm. pressure. After the aqueous fractions there came over between 200-300° a thick, yellow oil which on cooling solidified to a semi-crystalline mass amounting to 45% of the original cellulose. Others have been unable to check this statement. The pasty mass on recrystallization from hot acetone or water, gave white, tabular anhydrous crystals, m. pt. 179.5°, strongly laevorotatory, and could not be distilled under atmospheric pressure without decomposition. It gave a triacetate, m. pt. 110°, and a tribenzoate, m. pt. 199.5°, and appears to be identical with the laevoglucosan of C. Tanret[6], obtained by the splitting of the glucosides picein, salicin and coniferin.

At ordinary temperatures cellulose appears to be stable for an indefinite period if kept dry, as evidenced by the paper found in sarcophagi which ante-date the Christ-

1. J. Bain, J. S. C. I. 1927, **46**, 193-T; abst. C. A. 1927, **21**, 2981.
2. Zts. ang. Chem. 1909, **25**, 1205; 1910, **27**, 1252. J. pr. Chem. 1914, **90**, 413.
3. J. Bain and G. Kay, Univ. Toronto, Sch. Eng. Res. Bull. 1925, **5**, 119; abst. J. S. C. I. 1925, **44**, 349-B. Trans. Roy. Soc. Can. 1924, **18**, Sec. III, 269; abst. C. A. 1925, **19**, 893.
4. Trans. Roy. Soc. Can. 1926, **20**, III, 189; abst. C. A. 1926, **20**, 2411; J. S. C. I. 1926, **45**, 660-B.
5. Compt. rend. 1918, **166**, 38; abst. J. S. C. I. 1918, **37**, 49-A.
6. Compt. rend. 1894, **119**, 158; abst. J. C. S. 1894, **66**, i, 564; Chem. Zentr. 1894, II, 360; Jahr. Chem. 1894, **47**, 1112; Chem. Ztg. Rep. 1894, **18**, 194; Ber. 1894, **27**, R, 665; Bull. Soc. Chem. 1894, (3), **11**, 949; Mon. Sci. 1894, **43**, 717; Rev. gen. sci. 1894, **5**, 552; Jahr. organ. Chem. 1894, **2**, 219; Chem. News, 1894, **70**, 72, 282.

ian Era. On heating cotton to 110° F. Cohn[1] and Kraut[2] found a rise of several degrees on the thermometer surrounded by a mass of fibers. W. Schramm[3] and A. Schweizer[4] found the rise to be 9°. According to A. Scheurer[5] decomposition of cellulose commences at 140-150°. C. Koechlin[6] has reported that cotton at 120-130° after several months becomes completely carbonized, and insoluble in all simple and mixed solvents. H. de Chardonnet in preparing cotton for nitration[7] specified a preliminary heating to 180° upon the assumption (and it was purely assumption) that this temperature leads to favorable changes in the molecule. According to P. Klason, G. v. Heidenstam and E. Norlin[8], no substantial amount of gases is evolved on heating cellulose between 100-260°, but the gas evolution becomes a substantial one at the real reaction temperature of 270°. J. Chorley and W. Ramsay[9] have found that the gases contain a small amount of free oxygen.

1. Ber. botan. Ges. 1893, **11**, 66.

2. Chem. Ztg. 1893, **17**, 1388.

3. Zts. ang. Chem. 1908, **21**, 254; abst. Chem. Zentr. 1908, I, 1217; J. S. C. I. 1908, **27**, 221; Bull. Soc. Chim. 1908, **4**, 634; Chem. Ztg. Rep. 1908, **32**, 137.

4. Leipziger Monatschrift. f. Text. Ind. 1908, **23**, 139; abst. Chem. Ztg. Rep. 1908, **32**, 436.

5. Bull. Soc. Mulhouse, 1883, **53**, 68; abst. Mon. Sci. 1883, **25**, 139. See also Dingl. Poly. 1885, **255**, 349; abst. J. S. C. I. 1885, **4**, 340.

6. Bull. Soc. Mulhouse, 1888, **55**, 547; abst. Mon. Sci. 1888, **31**, 509, 1385; J. S. C. I. 1888, **7**, 841; Chem. Ind. 1888, **11**, 400; 1889, **12**, 15; Chem. Tech. Rep. 1888, I, 37, 71; II, 60; Chem. Ztg. 1888, **12**, 375; Jahr. Chem. 1888, 2859.

7. D. R. P. 64031, 1891; abst. Wag. Jahr. 1892, **38**, 376; Ber. 1892, **25**, 699; Zts. ang. Chem. 1892, **5**, 499; Chem. Zentr. 1892, II, 1088; Meyer Jahr. Chem. 1892, **2**, 362; Tech. Chem. Jahr. 1892, **15**, 169; Chem. Ztg. 1892, **16**, 1432; 1893, **17**, 1004; Chem. Tech. Rep. 1892, II, 164; Chem. Ind. 1892, **15**, 485; Mon. Sci. 1892, **40**, 166; Indbl. 1892, 358.

8. Zts. ang. Chem. 1909, **22**, 1205; 1910, **23**, 1252; Arkiv. för Kemi. Min. Geol. 1908, **3**, No. 10, 1; abst. Chem. Zentr. 1909, I, 110; J. S. C. I. 1909, **28**, 132; see also abst. J. C. S. 1908, **94**, i, 717, 955; C. A. 1908, **2**, 3280; 1909, **3**, 1810; 1910, **4**, 1803, 3135; Chem. Ztg. Rep. 1909, **33**, 435.

9. J. S. C. I. 1892, **11**, 395, 872; abst. Jahr. Chem. 1892, 2897, 2898; Chem. Zentr. 1893, I, 189; Chem. Ztg. 1893, **17**, 653, 1709. See also Cross and Bevan, "Cellulose," page 69.

It has been shown by E. Justin-Mueller[1] that hydrocellulose caramellizes at a lower temperature than oxycellulose, and at a much lower temperature than normal cellulose. Upon submission to dry heat, it will assume a brown color at 130-150°, at which temperature oxycellulose shows at most only a pale yellow color and cellulose no change at all.

Action of Acids on Cellulose. Hydroxymethylfurfural is produced by heating cellulose with a 5% solution of oxalic acid 30 min. at 180°, and may be isolated by shaking the filtered solution with ethyl acetate[2]. The yields obtained were 0.82% from normal cellulose, 5.16% from viscose cellulose and 10.84% from hydrocellulose prepared from viscose cellulose by the method of E. Knoevenagel and H. Busch[3]. The hydroxymethylfurfural thus produced is identical with the isomeride prepared by J. Kiermayer from sucrose[4], and not with the normal aldehyde obtained by E. Erdman[5] from brommethylfurfural. The aldehyde of Erdman is converted into that of Kiermayer by prolonged heating with 0.3% oxalic acid in a sealed tube.

In the absence of water, cellulose is decomposed by HCl gas under pressure, into a mixture of anhydrides of low molecular weight. If the saturation pressure and temperature of 20-30° are used, the reaction time is 10 hrs.[6] The product can be separated into fractions of different optical rotations. There are present chiefly 1-, 2- and 3-mol. anhydrides capable of being split up by 1% HCl.

When cotton cellulose is treated at 10° with 100 times its weight of HCl of 40, 41, 43 and 45% strength and the

1. Bull. Soc. Chim. 1921, (iv), **29**, 987; abst. C. A. 1922, **16**, 1664; J. S. C. I. 1922, **41**, 9-A; J. C. S. 1922, **122**, i, 11.
2. E. Heuser and W. Schott, Cellulosechem. 1923, **4**, 84; abst. J. S. C. I. 1924, **43**, 89B.
3. Cellulosechem. 1922, **3**, 42; abst. C. A. 1922, **16**, 2779; J. S. C. I. 1922, **41**, 458-A; Chem. Zentr. 1922, III, 347.
4. Chem. Ztg. 1895, **19**, 1004; abst. J. C. S. 1896, **70**, i, 144; Jahr. Chem. 1895, **48**, 2220.
5. Ber. 1910, **43**, 2391; abst. C. A. 1910, **4**, 3223; J. S. C. I. 1910, **29**, 1198.
6. H. Schlubach, H. Elsner and V. Prochownick, Zts. ang. Chem. 1932, **45**, 245; abst. C. A. 1932, **26**, 3373.

course of hydrolysis followed by measurements of viscosity and rotatory power[1], it is found that increase in rotation is more rapid the higher the concentration of the acid, the rotation-time curves showing two points of inflection, the first after about 5 hrs. with 45% HCl, or 10 hrs. with 40%, and the second after 15 hrs. with 45%, or 30 hrs. with 40% acid. The viscosity falls rapidly along the first step of the specific rotation curve, and remains constant afterwards. The addition of 0.5% $CaCl_2$ suppresses the action of the HCl, the cellulose being disintegrated to a powdery form after a few days. The solution of cellulose is considered to take place by its association with the HCl, by virtue of its OH groups reacting with water so long as the concentration of the acid is such that it is still unsaturated with water of hydration; dispersion of the cellulose under these conditions being progressive.

In an investigation of the action of dry HBr on carbohydrates and polysaccharides, H. Hibbert and H. Hill have shown[2] that brommethylfurfural may be obtained from dextrose and its derivatives. The formation of this compound from cellulose is therefore not a criterion as to the presence of ketonic linkages in cellulose, contrary to the findings of H. Fenton and M. Gostling[3]. The solubility of cellulose in concentrated HCl has been made the basis of patent protection by R. Willstaetter[4] and by Z. Ostenberg[5].

1. K. Atsuki, Cellulose Ind. Tokyo, 1925, **1**, 53; abst. C. A. 1926, **20**, 2247; Pulp & Paper Mag. 1927, **25**, 286; J. S. C. I. 1926, **45**, 8-B.

2. J. A. C. S. 1923, **45**, 176; abst. C. A. 1923, **17**, 540; J. S. C. I. 1923, **42**, 219-A.

3. Proc. Chem. Soc. 1901, **17**, 119; J. C. S. 1901, **79**, 807; abst. Bull. Soc. Chim. 1901, **26**, 796; Rep. Chim. 1901, **1**, 424; Chem. Zentr. 1901, II, 123, 426; Jahr. Chem. 1901, 838, 1494; Zts. ang. Chem. 1901, **14**, 273; Chem. Ztg. 1901, **25**, 180, 507.

4. U. S. P. 1141510; abst. C. A. 1915, **9**, 2311; Kunst. 1915, **5**, 240. E. P. 10605, 1914; abst. C. A. 1915, **9**, 2980; J. S. C. I. 1914, **33**, 859. F. P. 471479; abst. J. S. C. I. 1915, **34**, 349. D. R. P. 273800; abst. C. A. 1914, **8**, 2948; Chem. Zentr. 1914, I, 1904; J. S. C. I. 1914, **33**, 746. Holl. P. 1848; abst. C. A. 1917, **11**, 1300. R. Willstaetter and L. Zechmeister, Ber. 1913, **46**, 2401; abst. C. A. 1913, **7**, 3412.

5. U. S. P. 1218954; abst. J. S. C. I. 1917, **36**, 450. U. S. P. 1242030; abst. C. A. 1918, **12**, 223; J. S. C. I. 1917, **36**, 1174 E. P.

Dry HCl converts cellulose into a mixture of low molecular glucose anhydrides, saturation pressure and 20-30° being the most favorable conditions, the process then being complete in 10 hrs. The decomposition also takes place in the presence of indifferent organic media as benzene, but requires a longer time, depending upon the nature of the liquid. The reddish-violet, powdery product does not show the original fiber structure. It contains much adsorbed HCl, of which 6-8% remains after leaving in vacuum. The action of HCl on cellulose is differentiable into three stages: depolymerization, hydrolysis and reversion.

T. Lieser[1] has shown that cellulose is quantitatively converted into alkali-soluble cellulose by means of supersaturated HCl at 0° without causing any apparent increase of reducing power, as measured by Schwalbe's copper number. The degradation is not due to hydrolysis, at least not to an extended degree.

Action of Salts upon Cellulose. Cellulose readily dissolves in the thiocyanates[2], and a process for artificial filament formation based upon this solubility has been granted patent protection[3]. Thiocyanates are also solvents of cellulose formate (p. 640), solvents (pp. 456, 567) and swelling agents (pp. 501, 1043) for acetated cellulose, and solvents (p. 97) and swelling agents (p. 264) for the cellulose ethers. Therefore by this means, it is possible to bring cellulose, acetated cellulose and etherized cellulose into solution together by the same solvent. According to H. Dem-

104173; abst. C. A. 1917, **11**, 1903; J. S. C. I. 1918, **37**, 146-A. F. P. 484442; abst. C. A. 1918, **12**, 1123. See U. S. P. 1315393; abst. C. A. 1919, **13**, 3035. U. S. P. 1348731.

1. Cellulosechem. 1926, **7**, 85; abst. C. A. 1927, **21**, 319.

2. A. Dubosc, Chem. Ztg. 1905, **29**, 823; abst. J. S. C. I. 1905, **24**, 901. Bull. Soc. Ind. Rouen, 1905, **33**, 318; abst. Faerb. Must. Ztg. **53**, 19. Bull. Soc. Ind. Rouen, 1908, **36**, 272; abst. C. A. 1908, **2**, 3283.

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.

ing[1] concentrated solutions of mercuric chloride and bismuth chloride dissolve cellulose with avidity, even in the cold.

L. Vignon found 1 gm. cotton capable of retaining up to 0.4% of the salt from a solution containing 1 gm. ammonium chloride in 250 cc. water, sodium chloride not being obtained under similar conditions[2]. E. Knecht claims cellulose has no affinity for calcium chloride[3]. Celluloses as cotton have the power of absorbing and fixing salts of iron[4], cerium[5], copper[6], lead[7] and titanium[8].

Distilled water in which purified cotton or other form of cellulose has been soaked at 35° for 24 hrs. readily gives a silver mirror and the characteristic aldehyde reaction with rosaniline[9], while if it is steeped in sodium acetate solution

1. J. A. C. S. 1911, **33**, 1515; abst. C. A. 1911, **5**, 3678; J. S. C. I. 1911, **30**, 1111; J. C. S. 1911, **99**, i, 771; Chem. Zentr. 1911, II, 1433; Koll. Zts. 1911, **9**, 200; Chem. Ind. Koll. 1912, **11**, 43.

2. Mansier, J. Pharm. Chim. 1902, (6), **16**, 60; abst. Chem. Zentr. 1902, II, 768, 769; J. C. S. 1903, **82**, ii, 690; J. S. C. I. 1902, **21**, 1098, 1155; Rep. Chim. 1902, **2**, 524; Jahr. Chem. 1902, 238; Zts. anal. Chem. 1904, **43**, 314.

3. Ber. 1888, **21**, 1557, 2804; abst. Chem. Ztg. 1888, **13**, 1173; Chem. Ztg. Rep. 1888, **13**, 170; J. C. S. 1888, **54**, 832; J. S. C. I. 1888, **7**, 621; J. Soc. Dyers. Col. 1888, 104; Bull. Soc. Chim. 1889, (3), **2**, 546; Mon. Sci. 1888, **32**, 1159; Chem. Ind. 1888, **11**, 400; Chem. Tech. Rep. 1888, II, 32; Jahr. Chem. 1888, 2865; Wag. Jahr. 1888, **34**, 1108; Zts. ang. Chem. 1888, **1**, 683; Tech. Chem. Jahr. 1888-1889, **11**, 234.

4. Schellen, Dissertation, Strassburg, 1905, 14.

5. G. Witz, Bull. soc. ind. Rouen, 1882, 416; 1883, **11**, 169; abst. J. S. C. I. 1883, **2**, 378; Faerb. Must. Ztg. **17**, 129; Mon. Sci. 1883, **25**, 517; 1884, **26**, 1161; Jahr. Chem. 1883, 1782; Wag. Jahr. 1883, **29**, 1068; Dingl. Poly. 1883, **250**, 271. See also G. Witz, D. R. P. 24173. H. Schmid, Dingl. Poly. 1883, **250**, 272.

6. Herzog. Zts. Farbenind. 1908, **1**, 281. v. Cochenhausen, Zts. ang. Chem. 1906, **19**, 1987, 2024; abst. Bull. Soc. Chim. 1907, (3), **37**, 491; Chem. Zentr. 1907, I, 188; Chem. Ztg. Rep. 1907, **31**, 11; Jahr. Chem. 1905-1908, I, 1397; Wag. Jahr. 1906, I, 539.

7. E. Knecht, Jour. Soc. Dyers Col. 1909, **25**, 47. See also Frerichs, Apoth. Ztg. 1902, 884.

8. E. Hibbert, Jour. Soc. Dyers Col. 1906, **22**, 278; Chem. Ztg. Repert. 1906, **30**, 394; C. A. 1907, **1**, 242; J. S. C. I. 1906, **25**, 880; Text. Col. **28**, 297.

9. J. Huebner and F. Kaye, J. S. C. I. 1922, **41**, 94-T; abst. J. C. S. 1922, **122**, i, 435; Chem. Tech. Uebers, 1923, **47**, 64; Bull. Soc. Chim. 1922, **32**, 1040.

under similar conditions, the amount of aldehyde produced is so considerable that it may be separated by distillation. If cellulose or starch remains for several days in contact with distilled water at 35° to which sodium acetate and resorcinol have been added, the solution becomes fluorescent and aldehydic substances may be obtained by distillation, while the addition of lead acetate to the residue after distillation causes a brown precipitation.

Hydrocellulose. Oxycellulose. Comparatively speaking, cellulose is unusually stable against oxidizing agents and hydrolytic treatment, yet due to its complexity of composition, it is profoundly changed upon prolonged exposure to oxidizing and reducing influences, especially at elevated temperatures. In general, chlorine acts but slowly upon the fiber in the *dry* state, the contrary observation by J. Kolb[1] on dyed cotton fibers being probably due to the fact that moisture was not rigidly excluded therefrom. Freshly generated chlorine (nascent state) in the presence of but small amounts of moisture is very effective[2], but on standing for some time becomes quite ineffective. A. Franchimont[3] found that bromine in the absence of moisture does not act upon cellulose, but in the presence of moisture HBr is formed and this in turn results in the formation of hydrocellulose and brom-methylfurfural. Iodine appears to be devoid of oxidizing action, although it is absorbed by cellulose, J. Huebner[4] recording that 10 gms. cotton absorbed 7.6 gms. iodine in 750 cc. KI solution, equivalent to 0.136 gm. iodine.

1. Bull. Soc. Ind. Mulhouse, 1868, **38**, 914; Compt. rend. 1868, **66**, 1024; **67**, 742; Instit. 1868, 329; Ann. Chim. Phys. 1868, (4), **14**, 348; Bull. Soc. Chim. 1868, **9**, 431; Dingl. Poly. 1868, **190**, 62; 1869, **191**, 321; Jahr. Chem. 1868, **21**, 981.

2. Leipziger Färberztg, 1886.

3. Rec. trav. Chim. Pays-Bas, 1883, **2**, 91; abst. Ber. 1883, **16**, 1872; Jahr. Chem. 1883, **36**, 1366.

4. J. C. S. 1907, **91**, 1072; Proc. Chem. Soc. 1907, **23**, 144; Chem. News, 1907, **95**, 273; abst. J. S. C. I. 1907, **26**, 866; Bull. Soc. Chim. 1908, (4), **4**, 165; Rep. Chim. 1907, **7**, 355; Chem. Zentr. 1907, II, 752; Chem. Ztg. 1907, **31**, 716; Jahr. Chem. 1905-1908, II, 3171.

Both ozone[1] and hydrogen dioxide[2] in high concentration exert a profound oxidizing action, which is intensified by the presence of metallic salts as chromium oxide[3]. Nitric acid may either form hydrocellulose, oxycellulose, mercerize or nitrate, depending upon concentration, temperature and hygroscopic-absorbing agents. Oxycellulose results upon the treatment of cellulose with chromic acid, as attested to by the work of P. Jeanmaire[4], G. Witz[5], and C. Brandt[6]. Hypochlorous acid is an energetic oxidizing agent of cellulose, in energy depending upon the concentration of the bleaching liquor and exposure to the atmosphere. Weakening of the fiber is given as 0.2% by G. Witz[7], and 0.8% by A. Nastjukoff[8], CO_2 accelerating this action[9]. Alkaline bromine solutions attack cellulose[10], carbon tetrabromide and bromoform being formed. Although potassium permanga-

1. J. Kolb, Bull. Soc. Ind. Mulhouse, 1868, **38**, 914; Compt. rend. 1868, **66**, 1024; **67**, 742; Ann. Chim. Phys. 1868, (4), **14**, 348; Bull. Soc. Chim. 1869, **11**, 431; abst. Dingl. Poly. 1868, **190**, 62; 1869, **191**, 321; Jahr. Chem. 1868, **21**, 981. Bull. Soc. Ind. Rouen, 1883, **11**, 198; abst. J. S. C. I. 1883, **2**, 378; Jahr. Chem. 1883, **36**, 1782; Wag. Jahr. 1883, **29**, 1068.

2. 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, II, 752; Jahr. Chem. 1899, **52**, 1290; Meyer Jahr. Chem. 1899, **9**, 300.

3. E. Knecht, J. Soc. Dyers Col. 1897, **13**, 109, 131; abst. J. S. C. I. 1897, **16**, 534; Jahr. Chem. 1897, **50**, 1511. See also Persoz, Bull. Soc. Ind. Rouen, 1882, **10**, 466; Bull. Soc. Chim. 1883, **39**, 620; Chem. Ind. 1884, **7**, 162; Chem. Tech. Rep. 1884, **23**, I, 26.

4. Bull. Soc. Ind. Mulhouse, 1873, **43**, 334; abst. Chem. News, 1874, **29**, 174; J. C. S. 1874, **27**, 931; Chem. Zentr. 1874, **45**, 207; Chem. Tech. Rep. 1874, **13**, I, 70; Dingl. Poly. 1874, **211**, 403; Jahr. Chem. 1874, **27**, 1199; Wag. Jahr. 1874, **20**, 852; Indbl. 1874, 133; Poly. Centr. 1874, **40**, 144; Deutsche Ind. Ztg. 1874, 96; Poly. Notizbl. 1874, **29**, 85.

5. Bull. Soc. Ind. Rouen, 1883, **11**, 208.

6. Bull. Soc. Ind. Mulhouse, 1891, **61**, 496; abst. Reiman's Faerberztg. 1891, 3, 61, 62; Deutsche Chem. Ztg. 1891, 417; J. S. C. I. 1892, **11**, 33; Chem. Ind. 1892, **15**, 172; Chem. Tech. Rep. 1891, **30**, 63; Wag. Jahr. 1891, **37**, 1138.

7. Bull. Soc. Ind. Rouen, 1882, **10**, 416.

8. Bull. Soc. Ind. Mulhouse, 1892, **62**, 500.

9. A. Girard, Ann. Chim. Phys. 1881, (5), **24**, 337, 382; abst. Jahr. Chem. 1881, **34**, 985; J. C. S. 1882, **42**, 378.

10. J. Collie, J. C. S. 1894, **65**, 262; abst. Bull. Soc. Chim. 1894, **12**, 448; Jahr. Chem. 1894, **47**, 758.

nate[1], potassium bichromate[2] and potassium ferrocyanide oxidize cellulose, bleaching is very noticeable, brilliant white effects being produced.

When powerful inorganic oxidizing agents as chlorine, permanganate, chromic acid, chlorates, perchlorates and persulfates are allowed to act upon cellulose, especially in the presence of oxygen, the latter is readily attacked and is converted into a brittle modification almost devoid of tensile strength and with augmented affinity for dyestuffs. Ammonium persulfate under certain condition may cause considerable diminution in the strength of cotton, A. Scheurer[3] reporting losses up to 40%. According to L. Vignon[4], oxycellulose may be prepared by treating cotton with a boling solution of 1% KOH, then 1% HCl in the cold, followed by treatment in the cold with 1% sodium carbonate solution as an ant-acid. I. Frankenburg and C. Weber[5] prepare oxycellulose by immersion of cellulose in bleaching solution of sp. gr. 1.03, and A. Nastjukoff[6] by oxidizing

1. G. Witz, Bull. Soc. Ind. Rouen, 1883, **11**, 211.

2. E. Berl and R. Klaye, Zts. Schiess u. Sprengw. 1907, **2**, 403; abst. C. A. 1908, **2**, 184; J. C. S. 1908, **94**, i, 504; J. S. C. I. 1907, **26**, 1157; Chem. Zentr. 1908, I, 1381; Chem. Ztg. Rep. 1908, **32**, 43; Jahr. Chem. 1905-1908, II, 976.

3. Bull. Soc. Ind. Mulhouse, 1890, **60**, 311. Bull. Soc. Ind. Mulhouse, 1901, **71**, 182; abst. J. S. C. I. 1901, **20**, 891; Meyer Jahr. Chem. 1901, **11**, 447.

4. Compt. rend. 1897, **125**, 448; Bull. Soc. Chim. 1898, **19**, 790; abst. Chem. News, 1897, **76**, 194; J. C. S. 1898, **74**, i, 8; J. S. C. I. 1897, **16**, 908; 1898, **17**, 917; Mon. Sci. 1897, **49**, 859; Rev. Phys. Chim. 1897-1898, **2**, 21; Chem. Zentr. 1897, II, 843; Chem. Ztg. 1897, **21**, 811; Jahr. Chem. 1897, **50**, 1506.

5. E. P. 12367, 1893; abst. J. S. C. I. 1894, **13**, 725. D. R. P. 77826; abst. Chem. Ztg. 1894, **18**, 2044; Wag. Jahr. 1894, **40**, 1096. R. Alder (Can. P. 154062, 1914; abst. C. A. 1914, **8**, 2269) has described a plastic composite of ammonia, an albuminous substance and oxycellulose.

6. J. Russ. Phys. Chem. Soc. 1900, **32**, 543; 1901, **33**, 310, 678; Ber. 1900, **33**, 2239; 1901, **34**, 719, 3589; abst. Chem. News, 1902, **86**, 306; J. C. S. 1900, 78, i, 540; J. S. C. I. 1900, **19**, 733; 1901, **20**, 63, 573; J. Soc. Dyers Col. 1901, **17**, 122; Bull. Soc. Chim. 1901, **26**, 123, 557; 1902, **28**, 130, 481; Rep. Chem. 1901, **1**, 414; 1902, **2**, 189; Chem. Zentr. 1900, II, 430; 1901, I, 99, 932, II, 335, 1263; Chem. Ztg. Rep. 1900, **24**, 258; 1901, **25**, 122, 353; Jahr. Chem. 1900, **53**, 844; 1901, **54**, 897, 898; Meyer Jahr. Chem. 1901, **11**, 441; Zts. ang. Chem. 1900, **13**, 1083.

Swedish filter paper with calcium hypochlorite solution or[1] permanganate solution, followed after 36 hrs. by introduction of SO_2 gas, and finally by dilute sulfuric acid. R. Oertel[2] has prepared oxycellulose by treating cellulose with 15% KCl, which was subsequently subjected to electrolysis.

When saccharified by 70% sulfuric acid according to the method of H. Ost and L. Wilkening[3] oxycellulose yields a maximum of 90% of dextrose obtainable from cellulose. R. Mueller has found[4] that immersion in an alkaline aqueous solution through which a current of oxygen is passed and in conjunction with 0.5% cobalt oxide, fibrous cellulose is convertible to structureless cellulose. To remove stains from textiles caused by oxycellulose, A. Benjamin and R. Huebner[5] boil the fabric 20 min. in a dilute solution of titanous chloride.

1. H. Moore (J. Soc. Dyers Col. 1915, **31**, 180; abst. J. S. C. I. 1915, **34**, 1008; C. A. 1915, **9**, 3365) has also studied the action of calcium and sodium hypochlorite of varying concentration upon cotton yarn, methylene blue being employed to estimate the amount of oxycellulose formed. The effect of moderate additions of acid was to decrease the amount of oxycellulose and not increase it, as might reasonably be expected. Upon addition of alkali to the bleach, a minimum amount of oxycellulose is produced at a definite concentration of caustic soda. Permanganate solutions give similar results.

2. Chem. Ztg. 1911, **35**, 713; abst. J. C. S. 1911, **100**, i, 607; J. S. C. I. 1911, **30**, 887; Chem. Zentr. 1911, II, 855. Zts. ang. Chem. 1913, **26**, I, 246; abst. C. A. 1913, **7**, 2302; J. C. S. 1913, **104**, i, 594; J. S. C. I. 1913, **32**, 595; Chem. Zentr. 1913, I, 2110; Chem. Ztg. Rep. 1913, **37**, 273; Kunst. 1913, **3**, 330; Wag. Jahr. 1913, **59**, II, 543.

3. Chem. Ztg. 1910, **34**, 461; abst. C. A. 1910, **4**, 1888; J. C. S. 1910, **98**, i, 365; J. S. C. I. 1910, **29**, 688; Bull. Soc. Chim. 1911, **10**, 61; Chem. Zentr. 1910, I, 2074; Jahr. Chem. 1910, **63**, II, 420; Meyer Jahr. Chem. 1910, **20**, 318; Wag. Jahr. 1910, **56**, II, 392; Ztg. ang. Chem. 1910, **23**, 1534. See E. Nölting and Rosenthal, Bull. soc. ind. Rouen, 1883, **10**, 170, 239. C. Kurz, Zts. Farb. Textilchem. 1902, **1**, 46; J. S. C. I. 1902, **21**, 405; Rep. Chim. 1902, **2**, 15; Chem. Zentr. 1902, I, 956; Chem. Ztg. Rep. 1902, **26**, 79; Jahr. Chem. 1902, **55**, 1600; Wag. Jahr. 1902, **48**, II, 562.

4. E. P. 9369, 1910; abst. J. S. C. I. 1911, **30**, 82; see also F. P. 414821, 1910; abst. J. S. C. I. 1910, **19**, 1200.

5. E. P. 17653, 1902; abst. J. S. C. I. 1902, **31**, 1328; Chem. Ztg. 1903, **27**, 1259.

In connection with the work of G. Witz[1], A. Nastjukoff[2], E. Berl and R. Klaye[3], and O. v. Faber and B. Tollens[4], it is claimed by W. Harrison[5] that it is impossible to distinguish between oxycellulose and hydrocellulose by the tests which have been proposed, the evidence indicating that both are absorption compounds of peptized cellulose and the products of cellulose hydrolysis.

At first, oxycellulose was regarded as a definite compound, C. Cross and E. Bevan[6] having found cotton treated with boiling 60% nitric acid was converted to oxalic acid and an insoluble product—oxidized cellulose. G. Witz and F. Osmund[7] showed oxidized cellulose is able to absorb vanadium from weak solutions of its salts. When distilled with HCl, sp. gr. 1.06, O. v. Faber and B. Tollens found

1. Bull. soc. ind. Rouen, 1883, **11**, 188; abst. J. S. C. I. 1883, **2**, 378; Mon. Sci. 1883, **25**, 517; 1884, **26**, 116; Dingl. Poly. 1883, **250**, 271; Jahr. Chem. 1883, **36**, 1782; Wag. Jahr. 1883, **29**, 1068. Färb. Must. Ztg. **17**, 129; Tech. Chem. Jahr. 1884-1885, 473.

2. J. Russ. Phys. Chem. Soc. 1900, **32**, 543; 1901, **33**, 310, 678; Ber. 1900, **33**, 2239; 1901, **34**, 719, 3589; abst. Chem. News, 1902, **86**, 306; J. C. S. 1900, **78**, i, 540; J. S. C. I. 1900, **19**, 733; 1901, **20**, 63, 573; J. Soc. Dyers Col. 1901, **17**, 122; Bull. Soc. Chim. 1901, **26**, 123, 557; 1902, **28**, 130, 481; Rep. Chim. 1901, **1**, 414; 1902, **2**, 189; Chem. Zentr. 1900, II, 430; 1901, I, 99, 932; II, 335, 1263; Chem. Ztg. Rep. 1900, **24**, 258; 1901, **25**, 122, 353; Jahr. Chem. 1900, **53**, 844; 1901, **54**, 897, 898; Meyer Jahr. Chem. 1901, **11**, 441; Zts. ang. Chem. 1900, **13**, 1083.

3. Zts. Schiess-Spreng. 1907, **2**, 381, 403; abst. C. A. 1908, **2**, 184; J. C. S. 1908, **94**, i, 504; J. S. C. I. 1907, **26**, 1157; Chem. Zentr. 1908, I, 1381; Chem. Ztg. Rep. 1908, **32**, 43; Jahr. Chem. 1905-1908, II, 976.

4. Ber. 1899, **32**, 2589; abst. J. S. C. I. 1899, **28**, 1014; J. C. S. 1899, **76**, i, 854; Chem. Zentr. 1899, II, 901; Jahr. Chem. 1899, **52**, 1292; Chem. Ztg. Rep. 1899, **23**, 321; Chem. Tech. Rep. 1899, **38**, 550; Bull. Soc. Chim. 1900, **24**, 621.

5. J. Soc. Dyers Col. 1912, **28**, 359; abst. J. S. C. I. 1913, **32**, 17; Meyer Jahr. Chem. 1912, **22**, 508. A process for the manufacture of salts-free oxycellulose has been described by R. Adler in D. R. Anm. A-25211; Chem. Zentr. 1919, II, 387.

6. J. C. S. 1883, **43**, 22; Chem. News, 1882, **46**, 240; abst. J. S. C. I. 1884, **3**, 206, 291; Bull. Soc. Chim. 1883, **39**, 671; Chem. Ind. 1883, **6**, 353; Chem. Tech. Rep. 1883, **22**, II, 94; Ding. Poly. 1883, **250**, 280; Jahr. Chem. 1883, **36**, 1366, 1777; Mon. prod. chim. 1883, 242.

7. Bull. Soc. Chim. 1886, **45**, 309; abst. J. C. S. 1886, **50**, 923; Bull. Soc. Ind. Rouen, 1886, **14**, 30; J. S. C. I. 1886, **5**, 546; Ber. 1886, **19**, 318; Jahr. Chem. 1886, **39**, 1493; Wag. Jahr. 1886, **37**, 362.

oxidized products which yielded 1.4-1.8% furfural. In 1922 P. Clifford and R. Fargher summarized the literature of oxycellulose and its formation[1], and the next year, P. Clifford that of hydrocellulose[2].

According to P. Karrer[3] oxycellulose presents a greater enigma than does hydrocellulose for the reason that the first is applied to cellulose when attacked under all conditions by any oxidant[4]. E. Knecht and E. Mueller[5] reported that mercerized cotton is more readily attacked by acid permanganate than by hypochlorites, whereas in an earlier study E. Knecht and J. Egan[6] reported substantially the reverse. According to D. Clibbens and B. Ridge[7] mercerized cotton is attacked much more readily by hypochlorite solutions than unmercerized cotton. P. Karrer and T. Lieser[8] have prepared a hydrocellulose by action of phosphoric acid which possessed a very low copper number, and completely soluble in 10% NaOH, not yielding isosaccharinic acid with calcium hydroxide.

Ordinary oxidized cellulose is divisable into three fractions, (1) the alkali-insoluble portion, similar to if not identical with normal cellulose; (2) alkali-soluble portion precipitable by acids; and (3) alkali-soluble fraction not precipitated by acids. The lowest degraded and acid-forming substances are inferred to be in the last fraction. H. Hibbert and J. Parsons[9] have shown that solubility of oxidized celluloses in alkali varies both with the volume of alkali so-

1. Trans. Text. Inst. 1922, **13**, 189; abst. J. C. S. 1922, **122**, i, 1121.
2. J. Text. Inst. 1923, **14**, 69-T; abst. C. A. 1923, **17**, 2049; J. C. S. 1923, **124**, i, 541.
3. "Polymere Kohlenhydrate" 1925, p. 198.
4. J. Parsons, I. E. C. 1928, **20**, 491; abst. C. A. 1928, **22**, 2054; Pulp and Paper Mag. 1928, Oct. 11, p. 1423.
5. J. Soc. Dyers Col. 1926, **42**, 46; abst. Papier. Fabr. 1926, **24**, 476; C. A. 1926, **20**, 1326.
6. J. Soc. Dyers. Col. 1923, **39**, 67; abst. C. A. 1923, **17**, 2194.
7. J. Text. Inst. 1927, **18**, 135-T; abst. C. A. 1927, **21**, 2192; J. S. C. I. 1927, **46**, 471-B.
8. Cellulosechem. 1926, **7**, 1; abst. C. A. 1926, **20**, 1515.
9. J. S. C. I. 1925, **44**, 473-T; abst. C. A. 1926, **20**, 283; Chem. Zentr. 1926, II, 883.

lution and its concentration. A colloidal solution of oxidized cellulose has been prepared by dialyzing its alkaline solution in a parchment or collodion sac until free from alkali, a stiff jelly remaining partly soluble in distilled water. Salts and acids precipitate the oxidized cellulose from solution, transference experiments indicating migration of particles to the anode. E. Heuser and W. Niethammer[1] find alkali absorption by cellulose and its degradation products is a measure of the degree of depolymerization. Using the direct method of Gladstone, they found the following NaOH percent retained: purified cellulose 11.75, Girard's hydrocellulose 17.25, cuprammonium regenerated cellulose 17.98, hydrogen dioxide oxidized cellulose 21.7, permanganate oxidized cellulose 24.12, and the alkali-soluble hydrocellulose of E. Knoevenagel and H. Busch 25[2].

Further evidence of the depolymerization of the cellulose structure has been recorded by R. Herzog[3], as the result of X-ray analysis of cellulose preparations, the position and probable size of the crystallites in oxidized cellulose varying but slightly from normal cellulose. Using the Debye-Scherrer crystal analysis method and a tube with copper target, E. Ott[4] observed that the reflection angles for cellulose precipitated from a phosphoric acid solution, hydrocellulose, and oxidized cellulose are identical.

1. Cellulosechem. 1925, **6**, 13; abst. C. A. 1925, **19**, 2272; J. S. C. I. 1925, **44**, 311-B; Chem. Zentr. 1925, I, 1862.

2. Cellulosechem. 1922, **3**, 42; abst. J. S. C. I. 1922, **41**, 458-A. They produced a hydrocellulose, which even after drying, is completely soluble in 8% NaOH solution by hydrolyzing viscose cellulose with acids. The hydrolysis was effected by steeping viscose solution in 3% HCl, pressing out until the weight of acid is equal to that of the cellulose, drying in the air, and heating in a closed vessel at 70° for 4 hrs. With viscose cellulose of normal humidity (11%) the reaction at the ordinary temperature requires about 12 hrs. Conversion into alkali-soluble product does not take place if the cellulose is completely dried. With cellulose regenerated from cellulose acetate, the solubility of the product in alkali is only about one-tenth that of the product from viscose cellulose.

3. Papier-Fabr. 1925, **23**, 121; abst. C. A. 1925, **19**, 2128; J. S. C. I. 1925, **44**, 349-B. See R. Herzog, Cellulosechem. 1925, **6**, 39; abst. C. A. 1925, **19**, 2272.

4. Helv. chim. Acta. 1926, **9**, 31; abst. C. A. 1926, **20**, 1222; J. S. C. I. 1926, **45**, 387-A.

The evidence of E. Heuser and F. Stoeckigt that oxidized cellulose contains a glucuronic group has been repeatedly confirmed, C. Schwalbe and G. Feldtmann[1] succeeding in isolating *d*-glucuronic acid salt from bleached straw pulp, and J. Marcusson[2] obtaining it in healthy, slightly decayed pine wood to the extent of 4.4-12.5%. K. Atsuki[3] has shown the relation between the copper number of oxidized cellulose and its nitrate varies inversely with the yield, nitrogen content and viscosity of the latter. H. Hibbert and J. Parsons believe oxidized cellulose to be a mixture of a comparatively large number of unattacked and possibly depolymerized celluloses, with small quantities of aldehydic and acidic oxidation products. According to K. Hess[4] it is chiefly a mixture of cellulose and cellulose A with small amounts of other substances, while P. Karrer considers the mixture to be an adsorption system similar to hydrocellulose of the slightly changed cellulose and its degradation products.

O. Sponsler and W. Dore[5] have attempted to reconcile their concept of cellulose structure with the physical properties of the fiber, and believe the latter is stabilized longitudinally by primary valence forces which unite the glucose units alternately in the 1-1 and 4-4 linkages, the structure being stabilized laterally by secondary valence forces of oxygen atoms. Then, breakdown of fibrous structure begins with the separation of the longitudinal chains, as a result of which, the possibilities for rearrangement appear almost limitless.

E. Heuser and F. Stoeckigt[6] find that pure cellulose

1. Ber. 1925, **58**, 1534; abst. C. A. 1926, **20**, 45; J. S. C. I. 1925, **44**, 911-B; Chem. Zentr. 1925, IV, 2280.
2. Zts. ang. Chem. 1926, **39**, 898; abst. C. A. 1926, **20**, 3348; J. S. C. I. 1926, **45**, 809-B; Chem. Zentr. 1926, II, 1526.
3. J. Faculty Eng. Tokyo Imp. Univ. 1924, **15**, 55; abst. C. A. 1925, **19**, 727; J. S. C. I. 1925, **44**, 36-B; Chem. Zentr. 1925, I, 1252.
4. Papier-Fabr. 1925, **23**, 122, 164; abst. C. A. 1925, **19**, 2127; J. S. C. I. 1925, **44**, 349-B; Chem. Zentr. 1925, III, 17.
5. Fourth Colloid Symposium Monograph, 1926, **4**, 174; abst. C. A. 1927, **21**, 3268.
6. Cellulosechem. 1922, **3**, 61; abst. C. A. 1922, **16**, 2988; J. C. S. 1922, **122**, i, 719; J. S. C. I. 1922, **41**, 583-B; Chem. Zentr. 1922, IV, 558.

and hydrocellulose split off only oxymethylfurfural, oxycellulose gives furfural but no methylfurfural, oxymethylfurfural being present in very small amounts as an impurity. They found the comparative yields of glucose to be: cellulose 94.1%, hydrocellulose 93%, oxycellulose by chromic acid 83.8%. Long fiber cotton has been oxidized with two oxygen equivalents per $C_6H_{10}O_5$ group, using potassium permanganate in orthophosphoric acid at 53°, the oxidized celluloses obtained extracted with 18.5% NaOH and the optical rotations determined[1]. T. Nakashima[2] claims that when cellulose (biosan acetate) is treated with NaOH solution, the iodine number decreases and the acid number increases because of oxidation of the aldehyde to carboxyl groups. If only the original aldehyde groups are oxidized, the sum of the iodine and acid numbers should be constant, but this sum increases because the carboxyl-containing terminal glucose residues break down to lower molecular weight acids, thus forming new aldehyde groups which are oxidized, the viscosity of the cellulose solution decreasing with oxidation.

J. Lehalleur[3] has described a process for obtaining from cotton a hydrocellulose suitable for the preparation of smokeless powders, the cotton being treated 30 min. with HCl sp. gr. 1.14. The hydrocellulose is washed with water and finally with dilute sodium carbonate solution. 83.5% of the acid is recovered. F. Klages[4] has described the formation from cellulose fibers of a crystalline carbohydrate soluble in water and giving the Roentgen diagram of hydrocellulose.

Cotton Linters. In addition to wood pulp as a source of cellulose ethers, the one other source is the short hairs obtained from the seed after the longer filaments have been removed therefrom and known as "linters." It is

1. T. Murray, C. Staud and H. Gray, J. A. C. S. 1931, **53**, 4027.
2. J. S. C. I. (Japan), 1931, **34**, 414 (Suppl.); abst. C. A. 1932, **26**, 2487.
3. Ann. Acad. Brasil. Sci. 1929, **1**, 79; abst. J. S. C. I. 1930, **49**, 96-B.
4. Ber. 1931, **64B**, 1193; abst. C. A. 1932, **26**, 1115.

the least expensive form of cotton of comparatively high purity. The strength of fiber produced in any specified locality depends on the variety planted, soil, climatic conditions and cultural methods.

Physically, linters comprises the bases of the longer fibers and the shorter or immature filaments, all being tubular and hollow, the average length being one-fourth inch, varying somewhat with the closeness of setting the knife in ginning the filament bases from the cotton seed. There are about 8,000 of these filaments attached to each seed[1]. Linters is obtained as a second treatment of cotton, the fiber on the seed which has escaped the first ginning treatment is removed by a second process, usually at the oil mills in cleaning, this short fiber or fuzz, when purified and sheeted constituting the cotton used in esterification and etherification processes[2].

There are certain growths of staple cotton that will produce linters measuring 0.75-1 inch in length, but the quantity of these lengths is negligible. The length of the fiber is also partly dependable upon the time of the year the seed is ginned. The early picked seed almost invariably yields a longer staple than that picked later in the season, for when the cotton is ginned from the early pickings a larger percentage of longer fibers remains on the seed after it leaves the gin.

Under the microscope linters shows the same characteristics as ordinary cotton fibers. They are colorless, practically transparent, and present a flattened, ribbon-like appearance. The fibers are hollow, the lumen showing plainly in unstained preparations[3]. The slight yellowish caste to pulp sheets of linters is usually due to traces of iron, and may be removed by digesting in hydrochloric acid. Percentage of iron is minimized by the use of chromium-iron

1. H. Skinner, I. E. C. 1932, **24**, 694.
2. A. Angelasto, U. S. Dept. Agric. Department Circ. #175, May, 1921.
3. W. Henderson, I. E. C. 1923, **15**, 819; abst. C. A. 1923, **17**, 2963; J. S. C. I. 1923, **42**, 922-A.

alloys for the purifying apparatus, as detailed by E. Partridge[1]. Linters are hygroscopic, retaining 5-6% moisture in the air-dry condition. It is essential that linters sheets used for etherification purposes should be of minimum moisture content (bone dry) for most uniform results, air-dry linters in the presence of saturated air containing about 14-15%. Linters ready for etherification or esterification (as produced in the United States) gives about 0.3% water extractive, 0.4% chloroform extract and 0.6% ether-alcohol extract when Soxhleted to exhaustion.

The ash should not exceed 0.3%, and is usually under 0.2%, although C. Schwalbe gives 0.5% for bleached cotton[2]. The copper number of suitable linters usually is very close to 1% for total copper and 0.6% for reduced copper (by difference). By treating cotton with strong acids the copper number is increased considerably as long as the acid concentrations are low, but rapidly when the acid concentration is high. When linters are treated with alkalis, the copper number remains practically constant. The nitrogen content[3] ranges from 0.2-0.35%, that of Egyptian and American cottons being somewhat lower[4]. A typical analysis of the ash of linters shows potassium carbonate 44.8%, potassium chloride 9.9%, potassium sulfate 9.3%, calcium phosphate 9%, calcium carbonate 10.6%, magnesium phosphate 8.4%, iron oxide 3% and aluminum oxide and loss 5%. The phosphorus fluctuates between 0.06-0.13% P_2O_5.

Methods of preparation of a standard cellulose have been given by A. Corey and H. Gray[5], in which a specified

1. E. Partridge, I. E. C. 1929, **21**, 1044; abst. C. A. 1930, **24**, 727.
2. C. Schwalbe, "Chemie de Cellulose," 1911, p. 34.
3. B. Ridge, J. Text. Inst. 1924, **15**, 94.
4. E. Knecht and W. Hall, J. Soc. Dyers. 1918, **34**, 220; abst. C. A. 1919, **13**, 909. S. Higgins, J. Soc. Dyers. 1919, **35**, 169; abst. C. A. 1919, **13**, 2604. J. Hebden, I. E. C. 1914, **6**, 714.
5. I. E. C. 1924, **16**, 853, 1130; abst. C. A. 1924, **18**, 2805; 1925, **19**, 575; Paper, 1924, **35**, #1, 25; J. S. C. I. 1924, **43**, 1008-B. For exhaustive paper on the constituents of the benzene extract of American cotton accompanied by a bibliography, see R. Fargher and M. Probert, J. Text. Inst. 1923, **14**, T-49. In Trans. Text. Inst. 1922, **13**, 1; abst. J. C. S. 1922, **122**, i, 615, R. Fargher and J. Withers

cellulose is Soxhlet extracted 6 hrs. with 95% alcohol, then for 6 hrs. with ether. It is then boiled in a nickel-gauze basket 6 hrs. with 1% NaOH solution, then with distilled water, washed and dried. Composition, alphacellulose 99.74-99.8%, ash 0.26%, copper number 0.13-0.21%, cellulose number 0.24-0.28%. The effect of oxidation of cotton linters has been detailed by R. Haller[1]; apparatus for cleaning linters by K. Van Rensselaer and H. Swanson[2]; for dewatering linters by Gebr. Bellmer Maschinenfabrik[3]; and for purification by W. Chase[4] and C. Stark[5].

S. Seaman[6] has given the method of linters purification used by the Stamscott Co., W. Munson[7] that used by the U. S. Department of Agriculture, and J. Clerc[8] that by the De Vains chlorination process. They follow in general the method of F. Olsen and H. Aaronson[9], that of steeping the cellulose in an acid bath, washing, boiling in the absence of air as far as possible with weak alkali solution, a light bleach, and thorough washing. In a recently described process[10] linters is beaten 1 hr. at 85-90° with 0.15% soap solution to open up the fiber and emulsify the fats, then with 0.6% NaOH solution for 1 hr. at 130° (3.5 kgm. per sq. cm. pressure), followed by washing and beating, then bleaching with 0.1% available chlorine with the stock completely submerged. In order to ensure as nearly as possible absolute uniformity, huge amounts are blended in one batch

give an exhaustive review of our knowledge of the ash, wax, protein, pigments and cellulose in raw cotton, with more than 100 literature references cited.

1. Helv. Chim. Acta, 1931, **14**, 578; abst. J. S. C. I. 1931, **50**, 828-A.
2. U. S. P. 1805117; abst. C. A. 1931, **25**, 3850.
3. D. R. P. 496059; abst. C. A. 1930, **24**, 3139.
4. Textile World, 1925, **68**, 1479; abst. C. A. 1926, **20**, 295.
5. C. Stark, Kunst. 1931, **21**, 125; abst. C. A. 1931, **25**, 5556.
6. Paper Trade J. 1922, **74**, No. 15, 265; Paper, 1922, **30**, No. 7, 88; Paper Ind. **4**, No. 2, 277, 279, 281; World's Paper Trade Rev. 1922, **77**, #23, 1836, 1838, 1840; abst. C. A. 1922, **16**, 3391.
7. I. E. C. 1930, **22**, 467; abst. C. A. 1930, **24**, 3111.
8. Papierfabr, 1923, **21**, 201; abst. J. S. C. I. 1923, **42**, 710-A.
9. U. S. P. 1615343; abst. C. A. 1927, **21**, 822.
10. P. B., Russa, 1930, **5**, 743, 745; Rev. gen. Mat. Plastiques, 1930, **6**, 259, 261; abst. C. A. 1930, **24**, 4148.

before sheeting, one firm to our knowledge blending hundred ton (dry weight) batches in a single charge. J. Wiesel[1] has described and illustrated in a very comprehensive manner the steps required from raw linters to finished cellulose ester. The Wiesel symposium is especially authoritative. According to O. Kress and S. Wells[2] linters may be properly purified for esterification and etherification purposes with 10 lb. NaOH and 2 lb. 35% bleaching powder per 100 lb. cotton.

The methods of cotton purification at the Government explosive plant, Nitro, Va., have been detailed by J. Wallace[3], and the chemical analysis of cotton with special reference to the phosphorus content, by A. Geake[4]. According to W. Stark[5], from 50 lb. raw linters, about 35 lb. purified product are obtained. In another purification method[6], low-grade cotton waste, cotton flocks or linters are boiled under pressure with NaOH solution, bleached with hypochloride liquor and boiled again with NaOH. Hemicellulose by this treatment, it is claimed, is all removed. The H. Bassett process[7] boils cotton linters with NaOH solution at a pressure up to 50 lb. per sq. in., for 1-6 hrs., then boils with 3-10 lb. NaOH per 100 lb. linters at 50-120 lb. per sq. in. for 3-10 hrs., and finally washes to neutrality and dries.

A standard cotton cellulose has been prepared by K. Kanamaru[8] by taking samples of American, Egyptian and

1. The Labors of a Modern Hercules, 1929, page 7. M. Fanjat (Paper, 1923, **26**, 73; abst. C. A. 1923, **17**, 1715) has published a symposium on the treatment of raw cotton as a material for esterification and etherification, including the purification, sorting, dusting, cutting, defibering, boiling, bleaching and drying, both on a laboratory and a commercial scale. See E. Schmidt, D. R. P. 546104. Aust. P. 125698; abst. C. A. 1932, **26**, 1437, 3376.
2. Paper, 1920, **26**, 320; abst. C. A. 1920, **14**, 2082.
3. Paper, 1919, **23**, No. 23, 634; abst. C. A. 1919, **13**, 1016.
4. J. Text. Inst. 1924, **15**, 81; abst. J. S. C. I. 1924, **43**, 371-B.
5. Chem. Met. Eng. 1922, **26**, 167; abst. C. A. 1922, **16**, 1014.
6. W. Kershaw, F. Barrett and Bleacher's Assoc., Ltd., E. P. 277722; abst. J. S. C. I. 1927, **46**, 935-B.
7. Can. P. 314709.
8. J. Cellulose Inst. Tokyo, 1931, **7**, 149; abst. C. A. 1931, **25**, 5284; J. S. C. I. 1931, **50**, 798-B.

Indian cotton, cleaning by hand-picking, extracting with ethyl alcohol, then with ether, scouring with NaOH solutions under various conditions, the purification process being followed by determination of tensile strength, elongation, copper number, methylene blue value and viscosity of 1% solution in cuprammonium. It is concluded that there are three types of non-cellulosic impurities in the raw cotton difficult to remove, differing in the manner in which they are progressingly dissolved, viz., the material causing decrease in viscosity, that causing high copper number and that having a high methylene blue absorption. H. Levinstein[1] in 1930 gave a resume of our knowledge of cotton and other celluloses[2].

L. Lecomber and M. Probert[3] have determined the waxes of cotton of different origins and their characteristics, their summary being given under seven headings as follows: American (12 samples), Egyptian (7), Sea Island (2), S. American (5), Australian (1), mean of these 27 samples, and Indian (6); Fat and wax, 0.435%, 0.39, 0.51, 0.29-0.54, 0.42, —, 0.34; Acid value, 25, 27, 21.5, 30, 29, 26, 38; Saponification values, 66, 78, 61, 71, 58, 70, 121; Unsaponifiable matter, 64, 54, 61.5, 60, 68, 61, 45; Iodine value, 22, 23, 23, 25, 19, 23, 32. The specific volume of cotton cellulose has been reported upon by G. Davidson[4].

As the culmination of his investigations, C. Schwalbe[5] concludes that the chemical reactivity of cotton cellulose is influenced by the incrustations present, the life age and the

1. J. S. C. I. 1930, **49**, 55-T, 78-T; abst. C. A. 1930, **24**, 1737; Chem. Trade J. 1930, **86**, 127.

2. On page 56-T an error has crept in (probably typographical) which in the interest of accuracy should be corrected. The statement there appears that the first useful cellulose acetate was prepared by G. Miles is a *fact*. The statement that this acetate was prepared in the laboratory of A. Little is an *error*. Miles prepared his "useful" or partially hydrated cellulose acetate several years after severing all connection with the Little Laboratory.

3. J. Text. Inst. 1926, **16**, 338-T; abst. C. A. 1926, **20**, 699; J. S. C. I. 1926, **45**, 150-B.

4. J. Text. Inst. 1927, **18**, 175-T; abst. C. A. 1927, **21**, 2988; J. S. C. I. 1927, **46**, 615-A.

5. Papierfabr. 1926, **24**, 769; abst. C. A. 1927, **21**, 1705.

period of the storage of the fiber. In 1932 R. Titus, C. Staud and H. Gray[1] gave a review of the growth process by which the cottonseed hair is formed.

E. Darling[2] prepares high α-cellulose from corn stalks by pulping and bleaching the stalks, then subjecting to 4-6% NaOH solution near the freezing point of water.

Processes have received patent protection for the utilization of linters in the manufacture of an amber substitute[3], storage battery separator[4], cellulose ether and ester manufacture[5], fiber board fabrication[6], and for other uses[7].

Starch[8]. As yet, starch has not been synthesized, and notwithstanding the multitude of researches which have appeared in the last decade, especially in connection with attempts to elucidate its inner structure, but comparatively little is definitely known as to its constitution. Only those fundamental points are briefly considered here which deal with the general problem of starch etherification, or as shedding light on the mechanics of hydroxyl

1. J. Chem. Ed. 1932, **9**, 114.
2. U. S. P. 1838367. For suitability of "Cotton Hull Fibre for Pulp and Paper Manufacture" see O. Kress, Cotton Oil Press, 1920, **3**, #12, 33; abst. C. A. 1920, **14**, 2706. O. Kress and S. Wells, Paper Industry, July, 1919.
3. U. S. P. 1502945.
4. U. S. P. 1500220.
5. U. S. P. 1425580, 1425581, 1502945, 1503604, 1507330.
6. U. S. P. 1514655.
7. U. S. P. 1143487, 1198142, 1209964, 1229181, 1236578, 1236579, 1246379, 1249726, 1249734, 1251261, 1273536, 1286502, 1286503, 1379590, 1385033, 1385034, 1390689, 1398378, 1471699, 1495789, 1501111, 1519311. E. Opfermann, O. Merlau and G. Feldtmann (D. R. P. 539938, 546344; abst. C. A. 1932, **26**, 2319, 3666) have described a method for preparing pentosan-free cellulose from cellulose waste of cotton origin.
8. For recent advances in the chemistry and manufacture of starch, see H. Crown, Proc. Am. Assoc. Textile Chem. Col. 1930, 59; Am. Dyestuff Reporter, 1930, **19**, 83; abst. C. A. 1930, **24**, 3127. W. Ekhard, Zts. Spiritusind, 1927, **50**, 172; abst. C. A. 1927, **21**, 4088. H. Ellis, Textile Recorder, 1931, **49**, #578, 23; abst. C. A. 1931, **25**, 3867. H. Gray and C. Staud, Chem. Reviews, 1927, **4**, 355; abst. C. A. 1928, **22**, 1038. J. McLachlan, J. South African Chem. Inst. 1929, **12**, 3; abst. C. A. 1929, **23**, 2595. H. Pringsheim, Aceta Chem. Fennica, 1930, **3**, 1; abst. C. A. 1930, **24**, 4951. M. Schoen, Bull. Soc. Chim. Biol. 1930, **12**, 1033; abst. C. A. 1931, **25**, 2873. A. Williams, Ind. Chemist, 1930, **6**, 495.

substitution in starch by alkyl, aryl and aralkyl radicals. Starch is an individual substance except for about 1% of impurity contained in the outer wall of the grains[1], and appears not to be a definite mixture of amylose and amylopectin[2], starches from different plants having different constitutions[3].

Starches may be divided into two types, transitory starch present in foliage leaves and germinating seed embryos, and reserve starch which occurs in roots, tubers and stems of plants in granular form, which is the starch used for etherification purposes. The substance forming the inner portion of the granule of starch is termed amylose, and the outer portion amylopectin, the former being present in the granule partly in combination with the latter, so that but about half of the amylose present is extractable by dilute alkalis. Extraction of starch paste with barley diastase solution is preferable for separation of amylose from amylopectin, the former being hydrolyzed to maltose, and the latter depolymerized to *ab*-hexa-amylose, a non-reducing polysaccharide obtained first by J. Baker[4] and called by him *a*-amylodextrin, but A. Ling and D. Nanji[5] have shown that the polysaccharide contained both *a*- and *b*-linkages.

Inasmuch as amylose is converted to maltose by barley diastase, and amylopectin forms a non-reducing substance, it became possible to determine the ratio of amylose to amylopectin in starches from the relative reducing power of the mixed products of hydrolysis of barley diastase[6], this ratio being 2 (of amylose) to 1. S. Schryver and E. Thomas

1. E. Peiser, Zts. physiol. Chem. 1926, **161**, 210; abst. C. A. 1927, **21**, 668.
2. J. Effront, Ann. Soc. Zymol, 1930, **2**, 27; abst. C. A. 1931, **25**, 2735.
3. M. Philia, Bull. soc. botan. Geneve, 1924, (2), **16**, 519; abst. Rev. Intern. Reseign. Agr. 1926, **4**, 437; abst. C. A. 1927, **21**, 1723.
4. J. C. S. 1902, **81**, 1177; abst. J. S. C. I. 1902, **21**, 1087.
5. J. C. S. 1923, **123**, 2666; abst. C. A. 1924, **17**, 79; Chem. Zentr. 1924, II, 313. J. C. S. 1925, **127**, 636; abst. C. A. 1925, **19**, 1698; Chem. Zentr. 1925, II, 647.
6. A. Ling, J. S. C. I. 1927, **46**, 279-T.

have shown that another substance is present in the starch granules of some plants[1], of the nature of a hemicellulose, which has been termed amylohemicellulose, and which seems to be a compound of a calcium and magnesium salt of a silicic and phosphoric ester of *a*-amylose.

The physical condition of starches in their commercially purified state have a great influence upon their chemical and physico-chemical properties[2], especially for esterification and etherification purposes. Likewise the size of the granules, E. Szego[3] having shown, for instance, that the best quality of potato starch contains 1.5-6% granules by weight below 20 microns in diameter, and 43-44% above 40 microns. Albumins may be removed by treatment with dilute solutions of hypochlorites[4], oil by extraction by hydrogenated hydrocarbons as cyclohexane[5], the granules being bleached by treatment with aldehydes or materials liberating aldehydes in admixture with acid halides[6], and dried by displacing the water with a non-aqueous, water-miscible liquid as ethyl alcohol or acetone[7].

Action of anhydrous hydrofluoric acid on dry starch yields 85% crude amylan; maltose giving maltan[8]. Ethylene at 21° partially changes starch into a reducing sugar, the action being slow and accompanied by change in color to a pale yellow[9]. A readily pulverizable starch adapted to swell in cold water is prepared by mixing starch with a

1. Biochemical J. 1923, **17**, 497; abst. C. A. 1924, **18**, 402; Chem. Zentr. 1923, III, 1622.
2. P. Karrer and E. v. Krauss, Helv. chim. Acta. 1929, **12**, 1144; abst. C. A. 1930, **24**, 1538.
3. Bull. assoc. chim. sucr. dist. 1931, **48**, 268; abst. C. A. 1932, **26**, 1149.
4. W. Uhland, F. P. 641277; abst. C. A. 1929, **23**, 1301.
5. Syndicate d'Etudes des Matieres Organiques, F. P. 638909; abst. C. A. 1929, **23**, 2843.
6. S. Schotz, E. P. 345985; abst. C. A. 1931, **25**, 5477.
7. W. Campbell, E. P. 359641; abst. J. S. C. I. 1932, **51**, 16-B.
8. B. Helferich, A. Staerker and O. Peters, Ann. 1930, **482**, 183; abst. C. A. 1931, **25**, 88.
9. H. Rea and R. Mullinx, J. A. C. S. 1927, **49**, 2116; abst. C. A. 1927, **21**, 3046.

small proportion of cyclohexanone or methylcyclohexanone, adding an alkali and then dilute oxalic acid to neutrality[1].

Corn starch is obtained by steeping and disintegrating the germs, separation of bran and fiber, tabled to remove gluten and water[2], and washed until the water comes away clear[3]. The recent G. Moffatt[4], R. McCoy[5], and O. Sjostrom[6] processes are basically similar. The starch may be purified by the addition of a lyophilic colloid while in suspension[7], or by submitting a suspension of the granules to a centrifugal separation of a type such that the suspension is divided into a fraction practically free from granules[8]. R. Carr has recently discussed the relationship between structure and solubility of carbohydrates[9], and H. Pringsheim[10] a review of molecular weight determinations of complex polysaccharides, with 55 bibliographic references. Calcium starch compounds may be prepared[11] and are found very reactive. They may be rendered completely soluble in water by the addition of 2% borax thereto[12]. A. William[13] in 1932 reviewed the modern methods of potato starch manufacture, and O. Riemann[14] described apparatus for separating starch from its impurities.

For etherification purposes, there seems to be little to choose between the various starches from potato, corn or

1. O. Meyer, E. P. 286377; abst. C. A. 1929, **23**, 302.
2. Corn Products Refining Co., E. P. 277572; abst. C. A. 1928, **22**, 2681. F. P. 632712; abst. C. A. 1928, **22**, 3549.
3. R. McCoy, E. P. 288546; abst. C. A. 1929, **23**, 728. Corn Products Co., Ltd., F. P. 652360; abst. C. A. 1929, **23**, 3592.
4. U. S. P. 1655395; abst. C. A. 1928, **22**, 1054.
5. U. S. P. 1651611; abst. C. A. 1928, **22**, 881. U. S. P. 1832229; abst. C. A. 1932, **26**, 869.
6. R. McCoy and O. Sjostrom, U. S. P. 1828334; abst. C. A. 1932, **26**, 869.
7. G. VanNes, Holl. P. 19937; abst. C. A. 1930, **24**, 4951.
8. Aktiebolaget Separator, F. P. 715822; abst. C. A. 1932, **26**, 2077.
9. Science, 1929, **69**, 407; abst. C. A. 1929, **23**, 2869.
10. Dixieme Conference de l'Union Internationale de Chimie, 1930, 154; abst. C. A. 1931, **25**, 3970.
11. E. Ritsert, D. R. P. 308616; abst. Chem. Zentr. 1918, II, 880.
12. Henkel and Cie, Ges., E. P. 244708; abst. C. A. 1927, **21**, 339.
13. Chem. Trade J. 1932, **90**, 29; abst. C. A. 1932, **26**, 2341.
14. U. S. P. 1798811; abst. J. S. C. I. 1932, **51**, 42-B.

rice. All have been employed in etherification investigations. It is essential that the starch be as finely divided as possible, substantially anhydrous, and of low ash content. Freedom from gluten and all water-soluble or ether extractable matter should be insisted upon.

Inulin is widely distributed as a reserve material in tubers or tuberous root plants, as in Jerusalem artichoke, chicory, dahlia and elecampane[1]. It may be prepared by washing the tubers and soaking in water with calcium carbonate[2], the juice being then boiled, clarified with lead acetate, decolorized with charcoal and evaporated to dryness *in vacuo*. W. Arsem[3] treats the juice from dahlia bulbs with a mixture of calcium hydroxide and chloride, decolorizes and then with sodium carbonate to precipitate the calcium, leaving purified inulin in solution. The mineral content of inulin, mannan and glycogen is said to be greatly reduced by electrolysis[4]. A method of purification has been described in which fermentation with Schizosaccharomyces is resorted to[5], inulin remaining unattacked and the impurities rendered water-soluble. Commercial inulin may be further purified by dissolving in hot, 40% alcohol, adding norite, filtering, and evaporating the filtrate in a vacuum at 95°[6].

Inulin precipitated from alcohol is a colorless powder resembling starch, and probably consists of chains of fructose-furanose or fructose rings, the molecule containing at least 20-24 such rings[7]. Inulin is convertible into fructose[8]

1. H. Colin, Rev. gen. bot. 1919, **31**, 70, 179, 229, 277. Expt. Sta. Rec. **42**, 226; abst. C. A. 1920, **14**, 3449. Cf. C. A. 1920, **14**, 1134.
2. J. Willaman, J. Biol. Chem. 1922, **51**, 275; abst. C. A. 1922, **16**, 2314.
3. W. Arsem, U. S. P. 1616167; abst. C. A. 1927, **21**, 1026.
4. J. Reilly and D. McSweeney, Sci. Proc. Roy. Dublin Soc. 1930, **19**, 451; abst. C. A. 1930, **24**, 3763.
5. J. Wolff and B. Geslin, Pasteur Inst. Ann. Chim. anal. 1917, **22**, 241; abst. C. A. 1918, **12**, 461.
6. T. Harding, Sugar, 1923, **25**, 583; abst. C. A. 1924, **18**, 1274. Cf. C. A. 1923, **17**, 636.
7. H. Drew and W. Haworth, J. C. S. 1928, **131**, 2690; abst. C. A. 1929, **23**, 818.
8. W. Arsem, U. S. P. 1616169; abst. C. A. 1927, **21**, 1026.

by the action of tartaric acid, may readily be hydrolyzed[1], and has the composition of a hexose anhydride[2]. The results of J. Reilly and P. Donovan[3] point to a difructose anhydride as the structural unit of inulin.

In attempts to determine the molecular weight of inulin[4], fractional distillation of the acetate has been found more efficient than crystallization, but the molecular weight is uncertain, as results obtained by unimpeachable investigators do not agree. P. Karrer[5], H. Pringsheim[6] and H. Staudinger and O. Schweitzer[7] have detailed the physical constants of inulin.

Inulin has been patented for the manufacture of celluloid substitutes[8], and in cellulose ether compositions[9].

Inulin Esters. The acetic esters have been most exhaustively studied, primarily in connection with attempts to elucidate the structure of inulin and other carbohydrates. Following the precautions of keeping the length of undercooling in both solvent and solution the same[10], the molecular weight of inulin triacetate in 0.807 dilution in acetic acid, is given by H. Pringsheim and W. Hensel[11] as 594, corresponding to a difructose anhydride acetate. K. Hess

1. J. Wolff and B. Geslin, Bull. Soc. Chim. Biol. 1920, **2**, 19; abst. C. A. 1920, **14**, 3430.
2. H. Schlubach and H. Elsner, Ber. 1929, **62B**, 1493; abst. J. S. C. I. 1929, **48**, 915-A.
3. J. Reilly and P. Donovan, Sci. Proc. Roy. Dublin Soc. 1930, **19**, 409; abst. C. A. 1930, **24**, 2729. Cf. C. A. 1930, **24**, 831.
4. K. Hess, Ber. 1930, **63B**, 518; abst. C. A. 1930, **24**, 2360.
5. P. Karrer, Z. Angew. Chem. 1922, **35**, 85; abst. C. A. 1922, **16**, 1745.
6. H. Pringsheim, Z. Angew. Chem. 1922, **35**, 345; abst. C. A. 1923, **17**, 223.
7. H. Staudinger and O. Schweitzer, Ber. 1930, **63B**, 2317; abst. J. S. C. I. 1930, **49**, 1414-A; C. A. 1931, **25**, 280.
8. Can. P. 150646. Belg. P. 255253. Nor. P. 24818. Ital. P. 133188. Span. P. 55263. Hung. P. 59446.
9. E. P. 6387, 1913; 3370, 1914. F. P. 459972. D. R. P. 357707. Dan. P. 28835. Aust. P. 61055. U. S. P. 1217027, 1217028.
10. K. Freudenberg, E. Bruch and H. Rau, Ber. 1929, **62B**, 3078; abst. C. A. 1930, **24**, 1846; J. S. C. I. 1930, **49**, 198-A.
11. Ber. 1929, **62B**, 1096; abst. C. A. 1930, **24**, 3997. See M. Bergmann, E. Knehe and E. Von Lippmann, Ann. 1927, **458**, 93; abst. C. A. 1928, **22**, 392; J. S. C. I. 1927, **46**, 1173-A.

and R. Stahn[1] claim triacetylinulin dissolves in acetic acid to triacetylfructose. By keeping mixtures of inulin, acetic acid and pyridine for some days at temperatures between 20-60°, 80% inulin hexa-acetate, m. pt. 135° is obtained[2], or[3] inulin acetate may be prepared by boiling for 15 min. 1 part each of inulin and acetic anhydride and 2 parts glacial acetic acid. Inulin acetate may be depolymerized by heating for 40 min. at 250-290° in the presence of 20% of tetralin[4], and is converted by treatment with benzenesulfonic acid in boiling toluene and subsequently with alcoholic KOH into inulan[5], identical with inulin in specific rotation, but having the molecular weight of a disaccharide anhydride. The following heats of combustion have been obtained: inulin 4190, starch 4182, cellulose 4185, inulin triacetate 4522, starch hexa-acetate 4499, and cellulose hexa-acetate 4496[6]. The heats of combustion of the acetates are calculated from those of the parent substances on the assumption that the heat of esterification (known to be small) may be neglected. Inulin acetate is fluorescent[7].

1. Ann. 1927, **455**, 104; abst. C. A. 1927, **21**, 2881.

2. M. Bergmann and E. Knehe, Ann. 1926, **449**, 302; abst. C. A. 1927, **21**, 2881. According to W. Haworth and H. Streight (Helv. Chim. Acta, 1932, **15**, 609) inulin triacetate is converted by methyl sulfate and 30% NaOH solution at 55° into trimethylinulin, m. pt. 140°, (a) —54° to —55° in chloroform, which on hydrolysis gives 3.4.6-trimethylfructofuranose. Impure trimethylinulin may be purified by deposition from hot ethyl alcohol.

3. Ferrouillet and Savigny, Compt. rend. 1869, **68**, 1571; abst. Bull. Soc. Chim. 1869, **12**, 209; J. prakt. Chim. 1869, **107**, 434; Jahr. Chem. 1869, 748. See also P. Schuetzenberger, Ann. 1871, **160**, 82. W. Hagenbuch (Helv. Chim. Acta, 1932, **15**, 616; abst. J. S. C. I. 1932, **51**, 725-A) prepares inulin triacetate rapidly by adding inulin in aqueous pyridine to mixtures of pyridine and acetic anhydride and purifying the product by precipitation from methyl alcohol or acetic acid.

4. H. Pringsheim and I. Fellner, Ann. 1928, **462**, 231; abst. Bull. Soc. Chim. 1928, **44**, 1235; J. S. C. I. 1928, **48**, 742-A.

5. H. Pringsheim and J. Reilly, Ber. 1928, **61B**, 2018; abst. J. S. C. I. 1928, **47**, 1225-A.

6. P. Karrer and W. Fioroni, Ber. 1922, **55B**, 2854.

7. H. Pringsheim and O. Gerngross, Ber. 1928, **61B**, 2009; abst. C. A. 1929, **23**, 565.

H. Pringsheim and A. Aronowsky[1] have found that a non-reducing inulin acetate may be prepared whose molecular weight can be determined, and which on saponification with alcoholic KOH regenerates the original inulin[2], the ester being soluble in acetone. Inulin tripalmitate, sintering at 45°, melting at 52.5°, and inulin tristearate, m. pt. 60-63° have been described[3]. When triacetylinulin (inulin triacetate) is treated with nitric acid in chloroform for 30 min., the major portion of the material is transformed into triacetylfructose dinitrate, from which triacetylanhydrofructose may be isolated, and which, on methylation, yields a trimethyl derivative, density 1.473, and soluble in chloroform[4]. Acetylbrominulin has been described[5].

The inulin esters up to the present time, insofar as aware, have no technical applications.

Inulin Ethers. Methylation of inulin by means of methyl sulfate in the presence of sodium hydroxide[6] yields a product containing 39-39.7% methoxyl, the proportions required for the di- and tri-methyl derivatives being 32.7% and 45% respectively. The ether is soluble in alcohol, chloroform, acetone or ether. Its aqueous solution, which is turbid, and becomes more so when heated, becomes clear and optically inactive when subjected to ultrafiltration, but is rendered turbid again, even when evaporated at as low a temperature as 30°. In phenol, the ester has a mol. wt. of 1650-1890. The above methylated product, when heated with dry methyl iodide and silver oxide is converted into trimethylinulin, a pulverulent solid, m. pt. 102-107°, mol.

1. Ber. 1921, **54B**, 1281; abst. C. A. 1920, **15**, 3463.
2. K. Hess, Ber. 1930, **63B**, 518; abst. C. A. 1930, **24**, 2360. See also K. Freudenberg and E. Bruch, Ber. 1930, **63B**, 535; abst. J. S. C. I. 1930, **49**, 457-A; Chem. Zentr. 1930, I, 1981; Bull. Soc. Chim. 1930, **48**, 1404.
3. P. Karrer and Z. Zega, Helv. Chim. Acta, 1923, **6**, 822; abst. C. A. 1924, **18**, 80.
4. J. Irvine and J. Stevenson, J. A. C. S. 1929, **51**, 2197; abst. C. A. 1929, **23**, 3907.
5. S. Born and J. Nelson, J. A. C. S. 1915, **37**, 1763.
6. P. Karrer and L. Lang, Helv. Chim. Acta. 1921, **4**, 249; abst. J. C. S. 1921, **120**, i, 312; C. A. 1921, **15**, 2631; Chem. Zentr. 1921, I, 935.

wt. in freezing phenol, 1892. The methylated product of J. Irvine and E. Steele is described as an oil[1], its purity depending in a large measure upon the quality of the charcoal used in purification, they claiming to have produced at least three forms of methylated inulin of properties varying with the experimental procedure used in its preparation[2]. All were soluble in ethyl alcohol[3].

A trimethyl inulin of m. pt. 138-140° which does not reduce Fehling's solution[4] may be prepared by the method of W. Haworth and A. Learner, which consists in etherifying inulin with 35% aqueous NaOH and methyl sulfate, then with methyl iodide. In order to methylate inulin as mildly as possible, diazomethane has been used[5], the methyl ether formed being very easily soluble in alcohol and water, less soluble in hot than in cold water, does not reduce Fehling's solution, of 25.24% methoxyl content, corresponding to trimethylinulin for 2 $C_6H_{10}O_5$ complexes[6].

Ethyl-inulin forms a viscous mass, insoluble in cold or hot water[7], stable on heating and in the presence of acids and alkalis. Solutions in organic solvents leave on evaporation transparent films, resistant to moisture. Dextrin ethyl ether has similar properties, while tragacanth ethyl ether is a white or gray powder, insoluble in both hot or cold water[8]. L. Lilienfeld[9] has described general methods for the preparation of ethyl-inulin.

By the action of monochloracetic acid on inulin in 40% NaOH[10], the maxima of molecules introduced are 2.5 per glucose residue. Inulin may be benzylated in a manner sim-

1. J. C. S. 1920, **117**, 1474; abst. C. A. 1921, **15**, 1017.
2. J. Irvine, E. Steele and M. Shannon, J. C. S. 1922, **121**, 1060; abst. C. A. 1922, **16**, 2850.
3. H. Pringsheim, Zts. ang. Chem. 1922, **35**, 345; abst. C. A. 1923, **17**, 223.
4. J. C. S. 1928, **131**, 619; abst. C. A. 1928, **22**, 1959.
5. L. Schmid, Ber. 1925, **58B**, 1963; abst. C. A. 1926, **20**, 743.
6. L. Schmid and B. Becker, Ber. 1925, **58B**, 1966; abst. C. A. 1926, **20**, 744.
7. L. Lilienfeld, Aust. P. 82866; abst. C. A. 1923, **17**, 1803.
8. H. Schlubach and W. Floersheim, Ber. 1929, **62B**, 1491; abst. C. A. 1929, **23**, 4934.
9. See p. 44, n. 1.
10. See p. 56, n. 1.

ilar to that of the starches, the benzylinulin described by M. Gomberg and C. Buchler[1], "analyzed a little short of the formula $C_{12}H_{19}O_{10}(C_7H_7)$", benzyl chloride being used as the etherifying agent.

The inulin ethers have been proposed as components in cosmetics, soaps, salves and detergents[2], on account of their property of swelling in cold water.

Lichenin. About 200 different compounds have been extracted from various species of lichens[3], and which have not been found in any other group of plants, but the constitution of very few of them are known[4]. Lichenin is obtained from the cell-wall of Iceland moss, from which it was first isolated by J. Berzelius[5], and recognized as a membrane material by A. Payen[6]. Notwithstanding statements to the contrary, lichenin does not appear to be widely distributed among the lichens. It has been isolated from the hot water extract of *Ramalina fraxinea*[7], from *Cetraria islandica*[8], and *Evernia vulpina*[9], the general method being to obtain an aqueous extract, from which the lichenin is precipitated by alcohol and/or ether[10].

Lichenin is gelatinous, slightly soluble in cold water, and substantially insoluble in alcohol, chloroform and ether.

1. J. A. C. S. 1921, **43**, 1909; abst. C. A. 1922, **16**, 59; J. S. C. I. 1922, **41**, 71-A; J. C. S. 1922, **122**, i, 112; Chem. Zentr. 1922, I, 1396.

2. L. Lilienfeld, Aust. P. 87803; abst. Chem. Zentr. 1922, IV, 904. See p. 87, n. 2. W. Haworth and H. Streight (Helv. Chim. Acta, 1932, **15**, 609; abst. J. S. C. I. 1932, **51**, 724-A) obtain inulin triacetate in 95% yield on theory, by swelling inulin in pyridine at 80° and then digesting with acetic anhydride at room temperature. With acetyl chloride instead of acetic anhydride, a poorer yield of a degraded product is obtained.

3. As indicative, see Thorpe, Dict. Appl. Chem. 1922, **4**, 117.

4. G. Bergellini and C. Moncada, Univ. Rome Gazz. chim. Ital. 1921, **51**, II, 173; abst. C. A. 1922, **16**, 561.

5. Schw. **7**, 336. Scher. Ann. **3**, 288.

6. N. Ann. Sc. nat. Bot. 1840, **14**, 85; Inst. **206**, 128, 145.

7. K. Mueller, Zts. physik. Chem. 1905, **45**, 284, 286.

8. P. Karrer and B. Joos, Biochem. Zts. 1923, **136**, 537; abst. C. A. 1923, **17**, 3323.

9. P. Karrer, M. and J. Staub, Helv. Chim. Acta. 1924, **7**, 159; abst. C. A. 1924, **18**, 1275.

10. M. Hönig and S. Schubert, Monats. 1887, **8**, 460; abst. J. C. S. 1888, **54**, 127.

Does not react blue with iodine and sulfuric acid, but dissolves in HCl from which solution it is precipitated in flocks by alcohol. It becomes depolymerized when heated in glycerol to 240° to lichosan, which, from the molecular weight of its triacetate[1], should be regarded as a glucose anhydride. Both lichenin and lichosan are optically inactive, the former being converted by methylation into a trimethylglucose. With HCl a yield of less than 1% furfural results[2]. Lichenin is closely identified with reserve cellulose[3], and on distillation *in vacuo* (12 min.) gives levoglucosan[4]. Similar to cellulose in many respects, differences have been noted, as in the interference positions[5], reflection angles[6], and ready precipitation with tannin[7]. Lichenin contains about 2.64% ash, mostly silica[8], and a small amount of phosphorus as phosphate. It contains small amounts of oils and fats readily extractable by turpentine oil[9], and upon fermentation with lichenase (6 days at 35°) gives 96% glucose, fructose and galactose not being present[10]. It appears that lichenin is a polymeric anhydrocellobiose[11].

1. H. Pringsheim, W. Knoll and E. Kasten, Ber. 1925, **58**, 2135; abst. J. S. C. I. 1925, **44**, 954-B.
2. P. Karrer, B. Joos and M. Staub, Helv. Chim. Acta, 1923, **6**, 800; abst. C. A. 1924, **18**, 81.
3. P. Karrer, M. Staub, A. Weinhagen and B. Joos, Helv. Chim. Acta, 1924, **7**, 144; abst. J. S. C. I. 1924, **43**, 249-B. H. Pringsheim, W. Knoll and E. Kasten, Ber. 1925, **58B**, 2135; abst. C. A. 1926, **20**, 902. P. Karrer, M. and J. Staub, Helv. Chim. Acta, 1924, **7**, 159; abst. J. S. C. I. 1924, -**4**, 250-B.
4. P. Karrer and M. Staub, Helv. Chim. Acta, 1924, **7**, 916; abst. C. A. 1925, **19**, 661.
5. R. Herzog and H. Gonell, Zts. physiol. Chem. 1924, **141**, 63; abst. C. A. 1925, **19**, 1583. K. Hess, Zts. ang. Chem. 1924, **37**, 993; abst. C. A. 1925, **19**, 1196.
6. E. Ott, Helv. Chim. Acta. 1926, **9**, 31; abst. C. A. 1926, **20**, 1222.
7. A. v. Lingelsheim, Pharm. Zentr. 1928, **69**, 355; abst. C. A. 1928, **22**, 2809.
8. H. Pringsheim and W. Kusenack, Zts. physiol. Chem. 1924, **137**, 265; abst. C. A. 1924, **18**, 3064.
9. K. von Porat, E. P. 133989; abst. C. A. 1920, **14**, 808.
10. P. Karrer and M. Staub, Helv. Chim. Acta, 1924, **7**, 518; abst. C. A. 1924, **18**, 2134.
11. H. Pringsheim and J. Leibowitz, Zts. physiol. Chem. 1923, **131**, 262; abst. C. A. 1924, **18**, 2347.

In the preparation of lichenin, it is important to guard against the presence of *iso*lichenin which is soluble in cold water, and is colored blue with iodine. Separation is best effected by repeated reprecipitation from water by alcohol or ether. A lichen-stearic acid[1] has been described[2].

Acetylated Lichenin. Lichenin with glacial acetic acid yields an amorphous triacetate, but gives lower yields on acetylation than does cellulose[3]. Both acetylated products have the same rotatory power and yield some aceto-1.61 dibromglucose when treated with phosphorous pentabromide. The optical activity of lichenin acetate[4] is from —17.7° to 23°, and when heated to 235° in naphthalene gives 60% of lichosan acetate of 391-445 mol. wt. in phenol. M. Bergmann and E. Knehe[5] have prepared the pure acetates of lichenin and lichohexosan, and have shown differences in physical constants, especially optical behavior. They acetylated with acetic anhydride and pyridine, and acetic anhydride and sulfuric acid. Lichenin triacetate produces a transparent film from solvents[6]. From purified lichenin triacetate, a pentanitrate has been prepared[7], similar in properties to cellulose nitrate. When gelatinized with a solvent, this ester gives a product resembling horn.

By heating lichenin acetate to 235° in glycerol or naphthalene, carbohydrate preparations soluble in cold water have been obtained. Chemical differences between

1. O. Tunmann, Apoth. Ztg. 1913, **28**, 892; abst. C. A. 1914, **8**, 201.
2. In this connection see H. Pringsheim and H. Braun, Ann. 1928, **460**, 42; abst. C. A. 1928, **22**, 1575. Zts. physiol. Chem. 1928, **173**, 188; abst. C. A. 1928, **22**, 1368. E. Fischer, Sitz. kgl. preuss. Akad. 1918, 1100; abst. C. A. 1919, **13**, 1304. P. Karrer, Inst. Inter. Chimie Solvay 3me conseil 1928, 533; abst. C. A. 1930, **24**, 3224.
3. P. Karrer, Zts. ang. Chem. 1924, **37**, 1003; abst. C. A. 1925, **19**, 1196.
4. H. Pringsheim and O. Routala, Ann. 1926, **450**, 255; abst. C. A. 1927, **21**, 1448.
5. M. Bergmann and E. Knehe, Ann. 1927, **452**, 151; abst. C. A. 1927, **21**, 1448.
6. K. Hess and H. Friese, Ann. 1927, **455**, 199; abst. C. A. 1927, **21**, 2881.
7. J. Reilly, M. Hayes and P. Drumm, Proc. Roy. Irish Acad. 1931, **40B**, 102; abst. J. S. C. I. 1931, **50**, 1401-A; C. A. 1932, **26**, 433.

cellulose and lichenin are best shown by the variations in rotatory power of their respective acetates in chloroform solution.

Lichenin Ethers. The methyl-lichenin of P. Karrer and K. Nishida[1] is prepared by the usual treatment of lichenin with methyl sulfate and NaOH, a product being obtained with 41.9% methoxyl, which was not further increased by treatment with methyl iodide and silver oxide. The lichenin ether obtained dissolves to a clear, colloidal solution in water and many organic solvents, and gives no freezing point depression in water or tribrommethane. Hydrolysis with methyl-alcoholic HCl gives dimethyl- and trimethyl-methylglucosides, in proportions similar to the treatment of methylated cellulose of maximum etherification.

L. Schmid and R. Becker[2] etherified lichenin with diazomethane to a monomethyl compound, and Y. Asahina and N. Kutani[3] methylated in like manner, gyrophoric acid, a component of lichens.

The technical uses of lichenin esters and ethers are, as yet, not developed. L. Lilienfeld has patented methods of forming ethylated lichenin[4], and the use of the product for artificial filament formation[5] and for the preparation of colloidal suspensions[6].

Peat. A widely distributed and abundant source of cellulose, has been limited in its industrial utilization by the cost required to remove the 80-90% of water it usually contains, and possesses the drawback chemically in that it usually contains 5-15% ash on a dry basis. As a possible source for cellulose for esterifying and etherifying purposes, the subject has been brought into prominence by the

1. Helv. Chim. Acta, 1924, **7**, 363; abst. J. S. C. I. 1924, **43**, 373-B.
2. Ber. 1925, **56B**, 1966; abst. C. A. 1926, **20**, 744.
3. J. Pharm. Soc. Japan, 1925, No. 519, 423; abst. C. A. 1926, **20**, 594.
4. U. S. P. 1350820.
5. U. S. P. 1217028.
6. U. S. P. 1444257.

disclosures of A. Bosse[1] who proposes to boil peat with dilute ammonia solution, acidify, wash until neutral, then treat with alkali and wash when the cellulose after drying is suitable for use in the arts. It is claimed that an acetylcellulose may be prepared from this peat cellulose, by first mechanically disintegrating, then immersing 250 of the cellulose in a bath of acetic anhydride 1350, glacial acetic acid 350, sulfuric acid 17.5, maintaining a temperature of 48-49° for about 6 hrs., at a pressure of 20 atms.

The cellulose from peat has also been proposed as an ingredient in plastics[2], combined with rubber[3], for paper manufacture[4], as a tanning component[5], liquid air absorbent[6], ammonia absorbent[7], bowling ball production[8], briquetting[9], decolorizing purposes[10], distillation processes[11], fertilizer component[12], insulating constituent[13], and for the production of methane[14] and methyl alcohol[15]. The wood substitute of H. Lieber[16] combines peat and viscose.

1. E. P. 337360. Can. P. 319755. D. R. P. 531221. F. P. 677749.
2. S. Kislitzuin, Russ. P. 3713. I. Mellanoff, U. S. P. 1681155. F. P. 661354. See U. S. P. 698856, 699713, 749224, 1213115, 1384037, 1397144. E. P. 156137. D. R. P. 337960. Swiss P. 97589.
3. L. Hamon, E. P. 247712; abst. C. A. 1927, **21**, 674.
4. C. Roth, U. S. P. 1721974. Cf. U. S. P. 1420303.
5. K. Gustavsson, Tek. Tid. Kemi, 1929, **59**, 68; abst. C. A. 1929, **23**, 5347.
6. U. S. P. 1473994.
7. U. S. P. 1145095, 1459703.
8. U. S. P. 1203747.
9. U. S. P. 1139315, 1205007, 1487764, 1501101.
10. U. S. P. 1195720, 1286187, 1287592, 1289053, 1314203, 1314204, 1359094, 1501321, 1502592, 1510284.
11. U. S. P. 1143319, 1196470, 1229367, 1336264, 1365128, 1376582, 1422496, 1423527, 1437292, 1473641, 1488055, 1504385.
12. U. S. P. 1205829, 1212196, Re-14686, 1212573, 1218678, 1221979, 1228587, 1252332, 1254365, 1254366, 1257591, 1260103, 1261025, 1269795, 1277155, 1309723, 1320701, 1355732, 1434749, 1456332. E. P. 148190. D. R. P. 219305, 299386.
13. U. S. P. 1183694, 1213115, 1397144.
14. U. S. P. 1445423, 1490357, 1495461.
15. U. S. P. 1143319, 1504385, 1510284.
16. U. S. P. 1213115; abst. C. A. 1917, **11**, 881. The moldable material of R. Armenault, J. Malet and Fabriques de Produits de Chimie Organique de Laire, (E. P. 344086; abst. C. A. 1932, **26**, 3344), and suitable for the manufacture of buttons, is made from peat containing 1% or more of tarry components mixed with synthetic resins and powdered blood.

Wood Pulp. There are but two forms of cellulose used in the cellulose ether industry, wood pulp and cotton cellulose, the latter in the linters form, and both usually in sheet form for ease of manipulation when subjected to caustic soda treatment. While cotton cellulose is superior to that obtained from wood in alphacellulose content (cotton about 98%, wood about 89%, both bone dry basis), the latter is materially cheaper, and in general easier of manipulation, more readily soluble in cellulose ether form, and of lower viscosity. The earlier methods of cellulose utilization for etherification purposes gave inadequate thought to the necessity for meticulous care in the purification of the cellulose, and also to the extreme care required in the formation of alkalicellulose therefrom, as preliminary to the etherification process. Due primarily to researches in the viscose rayon art, the necessity for careful supervision of raw materials intended for etherification purposes—and in this connection alkalicellulose is regarded as a raw material—has led to a more proper appreciation of the necessity for extreme care in the preparation and use of the cellulosic source, freedom from hemicellulose and other non-alphacellulosic bodies, as governing the desirable properties of the finished cellulose ether.

Of course, the amount of wood pulp expressed in percentage, employed for etherification purposes as compared to that utilized in the paper industry is very small, but due to the higher price of wood pulp suitable for esterification and etherification, the incentive is furnished for research aiming at the production of a pulp of most highly desirable properties for cellulose derivatives formation. In general, a wood pulp which will produce the highest grade of viscose rayon or cellulose acetate filaments is equally suitable for etherification purposes. A. Herzog[1] has summarized the literature on the microscopy of wood cellulose, and given tables showing the various physical and chemical char-

1. Kunstseide, 1931, **13**, 203, 239, 275, 311; abst. C. A. 1932, **26**, 1773.

acteristics of cellulose from different types of wood, while E. Jahn[1] has published data on the suitability of wood cellulose for etherification purposes.

In a comparison of wood cellulose and cotton cellulose made by S. Mahood and D. Cable[2], it was found that wood cellulose most nearly approaching cotton from the viewpoint of suitability for esterification and etherification purposes is obtained by re-cooking "easy bleaching" sulfite pulp with soda, and treating with 2% bleach, such treatment, however, being uneconomic from the low yield. To produce wood pulp suitable for etherification they recommend an acid cooking, followed by bleaching lightly to remove non-cellulosic material. D. Krueger[3] has discussed the fundamental morphological, chemical and colloidal differences between wood pulp and cotton linters as to relative suitability for the preparation of cellulose derivatives.

The following methods for the practical production of wood pulp suitable for etherification purposes are in general based upon the endeavor to produce a pulp with the maximum of alphacellulose, maximum solubility of *b*-cellulose and hemicellulosic bodies in NaOH solutions ranging between 17-20% strength at 15-25°, and minimum of ash, especially in iron and silica content, and are indicative of the most recent tendencies in this direction. It is a fact, exploited by the wood pulp industry, and not admitted in the cotton trade, that advancement in chemical control in production of wood pulp for ester and ether production is rapidly narrowing the gap between these two sources of cellulose from a price standpoint and from the viewpoint of suitability, as judged by the strength, elasticity, resiliency and uniformity when tested in filament and film form.

1. *Processes of A. Richter.* The long fiber portion of raw pulp is separated and treated with chlorine water or

1. Paper Trade J. Dec. 10, 1931, **93**, 24.
2. J. I. E. C. 1922, **14**, 727; abst. C. A. 1922, **16**, 3203; J. S. C. I. 1922, **41**, 664-A.
3. Papier Fabrikant, 1931, **29**, 509; abst. C. A. 1932, **26**, 592.

hypochlorite solution[1] to just beyond the point at which further consumption of chlorine is accompanied by a marked decrease in alphacellulose content and increase in copper number. It is then cooked with NaOH or sodium sulfide, further bleached and separated into long and short fibers, the former being used for etherification purposes. He proposes to insure the maximum *a*-cellulose content in wood pulp with the minimum of hemicellulose, by depolymerizing[2] the cellulose by treatment with NaOH solution in which the hemicelluloses are soluble, ageing the alkalicellulose thus formed, washing and alkaline digesting the fiber to remove oxycelluose and other undesirable water-insoluble components, then drying at a low temperature. This treatment, it is claimed, produces an alphacellulose content of better than 95%, a 1% solubility in 3% NaOH and a copper number of 2.

If the raw cellulosic material is first cooked in a NaOH solution short of effecting fiber liberation, and then in a sodium sulfide solution to the point of ready fiber liberation[3], minimum of degradation of the cellulose takes place with a corresponding rise in *a*-cellulose content. To diminish the pentosan percentage to the minimum[4], the wood is first cooked in a liquor containing substantially only acid as sulfuric or sulfurous, and then in a liquor of strong NaOH and/or sodium sulfide, pentosans being reduced to less than 1%, the *a*-cellulose rising to about 96%. However, there is no wood pulp on the American market at the present time insofar as we are aware, which assays as high as 96% *a*-cellulose.

To raise the *a*-cellulose content by reduction of the hemicellulose bodies to a negligible percentage, the cellulose

1. G. Richter and M. Schur, U. S. P. 1599489, 1602553, 1632802, 1635637, 1639704, 1640853, 1643355, 1801782, 1802575, 1809312; abst. J. S. C. I. 1932, **51**, 142-B; Chem. Zentr. 1931, II, 1516. See G. Richter, U. S. P. 1860431, 1870650.
2. U. S. P. 1821321. Can. P. 299299.
3. U. S. P. 1828848. Can. P. 315641. See Can. P. 300945, 313720.
4. U. S. P. 1838326. See U. S. P. 1802984.

is treated with mercerizing liquor, then cooked to complete fiber liberation[1] in a sulfurous acid solution, washed, sheeted and dried. In order to produce a wood pulp fiber of low viscosity when etherified or esterified[2], the fiber in the form of aqueous pulp of 2-10% fiber concentration, is treated with ferric compounds (hydroxide, basic chloride, basic nitrate or citrate), in comparatively small amount (as 0.25% based on the weight of the fiber), afterwards removing the iron by treatment with weak oxalic acid solution, or acid permanganate. Digestion with weak NaOH solution under 100 lb. air pressure in a digester[3] accomplishes the same purpose.

Treating wood pulp with a copper-ammonia solution containing less ammonia and far less copper value than that necessary to dissolve the pulp is said to extract nearly all of the non-alphacellulosic portion and should result in the formation of a wood pulp excellent for etherification purposes, if the cost is not commercially prohibitive[4]. The preparation of wood pulp under great pressure[5], by decreasing the absorptive pulp by treatment with hydrated cellulose[6], or by splitting into strip form[7], is more applicable to the preparation of pulp for nitration purposes.

2. *Processes of H. Dreyfus.* A high quality wood cellulose particularly amenable to acetylation or alkylation[8], and giving products of high quality and satisfactory viscosity, is prepared by first treating with 5-10% NaOH solution, washing to neutrality, then with dilute formic or acetic acids. The pentosan content is said to be materially

1. U. S. P. 1848662. Can. P. 315640, 315642.
2. U. S. P. 1860431. Cf. C. Bouvier, G. Fouche and E. Seguin, F. P. 719400.
3. U. S. P. 1860432. Can. P. 319635.
4. Can. P. 319801. See U. S. P. 1774403, 1790169, 1790170.
5. G. Richter, M. Schur and R. Rasch, U. S. P. 1859889.
6. *Ibid.* U. S. P. 1729628; abst. C. A. 1929, **23**, 5593; J. S. C. I. 1930, **49**, 184-B.
7. *Ibid.* U. S. P. 1826825; abst. C. A. 1932, **26**, 598. M. Schur and B. Hoos, Can. P. 315865.
8. U. S. P. 1711110, 1711111; abst. C. A. 1929, **23**, 3098; J. S. C. I. 1929, **48**, 514-B. E. P. 249173, 263939; abst. J. S. C. I. 1926, **45**, 436-B; 1927, **46**, 247-B. Ital. P. 242635, 255928.

reduced and the alphacellulose percentage correspondingly raised.

3. *Procedure of Eastern Manufacturing Co.* Raw wood chips are heated at 140-160° at 70 lb. per sq. inch pressure, first with sulfite liquor containing alkaline bisulfite and free sulfuric acid, and, after washing, the product is transferred to a rotary boiler and heated with a mixture of sodium hydroxide, sulfide and sulfite, the cellulose being finally washed, sheeted and dried[1]. The *α*-cellulose content of this pulp averages over 90%. Or[2], the wood pulp is treated with an alkaline solution containing sodium sulfite, washed, bleached, freed from excess of water and passed through a succession of picker rolls to form cellulose fiber aggregates of about 1 mgm. in weight containing some 40,000 individual fibers, the idea being to insure maximum uniformity in esterification and etherification. In focussing their inventive ingenuity on this problem[3], H. Hanson and S. Seaman have evolved a method of preparing high *α*-cellulose especially desirable for the formation of cellulose ethers typified by ethylcellulose, by taking the matted, interlaced, intertwined and interwoven fibers and subjecting them to impact attrition in an attrition mill at 1400-1800 r. p. m., where fine subdivision and uniformity in blending is assured.

4. *I. G. Farbenindustrie Wood Pulp Purification.* A cellulose nearly free from resins and containing a high percentage of *α*-cellulose[4] is obtained from pine wood shavings by "opening up" the material by treatment with nitric acid, then treating with boiling NaOH solution, bleaching with chlorine, again treating with dilute NaOH solution and finally gently bleaching again. The wood may initially

1. C. Blodgett and H. Hanson, U. S. P. 1822126; abst. J. S. C. I. 1932, **51**, 543-B. Cf. C. Blodgett, U. S. P. 1855332.
2. S. Seaman, U. S. P. 1822174; abst. J. S. C. I. 1932, **51**, 543-B.
3. U. S. P. 1851008; abst. C. A. 1932, **26**, 3112.
4. H. Heimann, E. Opfermann, I. Petersen, K. Bitterfeld and A. Bayerl, U. S. P. 1840162; abst. C. A. 1932, **26**, 1437. Beech wood (F. P. 712260; abst. C. A. 1932, **26**, 2056) is said to be especially applicable.

be deresinified and dewaxed by extraction with solvents[1], then treated with steam to vaporize last traces of solvent.

5. *Other Wood Pulp Processes.* The characteristic feature of the E. Schmidt method[2] is to digest with a normal sulfite lye, and then treat with a water-soluble sulfate as aluminum, nickel or zinc in the ratio of 20-100 k. per 100 cu. m. of lye, or[3] the bleached wood pulp is subjected to an additional treatment of at least 5% alkali hydroxide or carbonate in the presence of an oxidizing bleaching agent, and then washed with water and sheeted[4]. The essence of another process[5] is to grind the purified pulp in water to an almost indistinguishable fineness for blending, then run into sheet form and dry at a low temperature[6].

A. Thiriet[7] claims to be able to produce a wood pulp of 97-98% α-cellulose content—higher than any sample ever examined by us—by adding the step of a physical purification of the pulp as it flows down an inclined gauze by means of jets of water under pressure, then treatment with dilute hydrochloric or sulfuric acid, finally washing with alkali hydroxide free from carbonate, and pressing into sheet form. In another method[8], the cellulose otherwise purified, is subjected to a treatment with a solution of nitrogen dioxide, preferably as a saturated solution in acetic or other aliphatic acid.

1. I. G. Farbenindustrie, E. P. 336969; abst. C. A. 1931, **25**, 1996; Brit. Plas. 1931, **2**, 530. Can. P. 298014.
2. U. S. P. 1840413. Aust. P. 125698; abst. C. A. 1932, **26**, 1437. F. P. 689291; abst. C. A. 1931, **25**, 1081.
3. Zellstofffabrik Waldhof, H. Muller-Clemm and W. Leopold, F. P. 709229; abst. C. A. 1932, **26**, 1437. Zellstofffabrik Waldhof and A. Bernstein, D. R. P. 537846; abst. C. A. 1932, **26**, 1437.
4. Wolff & Co., Holl. P. 21150, 1929.
5. J. Schaub, E. P. 322997; abst. J. S. C. I. 1930, **49**, 184-B.
6. See A. de Vains, India P. 8900, 8901, 9285, 9932, 10457, 10458. Australian P. 18855.
7. E. P. 318868. See Papeteries Navarre, Belg. P. 349525.
8. C. Staud and C. Webber, E. P. 345235; abst. C. A. 1932, **26**, 303; J. S. C. I. 1931, **50**, 582-B; Silk J. and Rayon World, 1931, **8**, 52.

A. Pollard and J. Whincop[1] have given directions for the use of purified, decorticated fibers from caroa, and E. Worden[2] the utilization of purified Musa fibers for the manufacture of cellulose derivatives, but the processes, as yet, insofar as aware, have not been commercialized.

M. Schur and R. Webber[3] have found upon close examination of wood pulp, that the shorter fiber lengths—so-called fines—are higher in impurities, lower in alphacellulose, and when dried on a steam drum under temperature conditions normal in pulp and paper mill practice, are sufficiently more sensitive to heat so that they are prone to yellow. They propose to prepare wood pulp for etherification and esterification purposes for removal of the fines mechanically in any suitable stage of the chemical treatment, but preferably from the unbleached pulp in order to obviate their chemical processing. Where the pulp is to be refined to a high alphacellulose content by a series of chemical treatments including chlorination of the unbleached pulp, followed by alkaline digestion and bleaching, it is preferable to remove the fines before the first chemical treatment.

The short fibers may be removed by washing the wood pulp against a 50-mesh Fourdrinier wire, or against thin plates provided with perforations of about 0.02 inches in diameter, or by passing edge-presenting members capable of picking up the long fibers, through the pulp suspension, and then washing off and recovering the long fibers picked up from the edge-presenting members.

Or[4], the cellulose pulp may be broken down at any desired stage by chemical reactions which give rise to depolymerization of the cellulose molecule to a "copper viscosity" of less than 6 units, and immediately after the

1. E. P. 315902; abst. Cellulose, 1930, **1**, 150. See Wolff & Co. and R. Weingand, E. P. 288997; abst. C. A. 1929, **23**, 703. E. Schmidt, U. S. P. 1840413; abst. C. A. 1932, **26**, 1785. O. Mueller, E. P. 340164.
2. U. S. P. 1814106; abst. J. S. C. I. 1932, **51**, 499-B. Can. P. 298172.
3. U. S. P. 1806421; abst. J. S. C. I. 1932, **51**, 224-B.
4. Vereinigte Glanzstoff-Fabriken A. G. E. P. 345208.

breaking-down treatment, the pulp is freed from hemicellulose by alkaline reagents, until an alphacellulose of 90-93% or better is obtained.

A. Hooker[1] prepares high percentage alphacellulose by treatment of sulfite fiber with dilute NaOH solution, the concentration of the effluent liquor restored, and the liquor then used for conversion of wood fiber into soda pulp; the effluent from the soda pulp preparation is purified and regenerated and the purified liquor used for production of high *a*-cellulose, the cycle being then repeated. In order to convert incrusting substances into water-soluble bodies[2], L. Durchman treats chemical wood pulp 4-6 hrs. at 20-60 lb. pressure, with a solution containing 2-5% NaOH and 1-3% sodium sulfite.

A. Schorger[3] has given the following as the average composition of cotton, sulfite pulp and *a*-cellulose pulp, as of 1930: *a*-cellulose %, 94-98, 83-86, 93.5-96; beta-cellulose, 2-3%, 7-9, 2-4; gamma-cellulose, 2-3%, 7-8, 2-2.5; lignin, 0.3%, 0.5-0.3, 0.3; resins, etc., 0.3%, 0.5-1.0, 0.2-0.4; pentosans, 0.5-1.0%, 3.5-5.5, 1-2.4; solubility in boiling 3% NaOH, 1-20%, 15-30, not over 9.

The present composition of the wood pulp manufactured in the United States for etherification and esterification purposes, on a bone dry basis, may be represented by *a*-cellulose 93%, hemicelluloses 3%, ash 0.2%, unaccounted for 3.8%.

Lignin. *Lignose.* The non-carbohydrate portion of lignified tissues after having been freed from resins, fats, tannins and similar extractives, is classified as lignin, the study of which is exceedingly complex due to the impossibility of isolating it unchanged. Attempts to elucidate

1. U. S. P. 1847111; abst. C. A. 1932, **26**, 2593.
2. L. Durchman, U. S. P. 1780347, 1781449; abst. Cellulose, 1930, **1**, 294. Can. P. 307798, 307799; abst. C. A. 1931, **25**, 1081.
3. Cellulose, 1930, **1**, 248. D. Krueger, Papier Fabrikant, 1931, **29**, 509. J. Rossman, Paper Trade J. 1928, **86**, 59; Tech. Assoc. Papers, 1928, IX, 187; abst. C. A. 1928, **22**, 3292; Pulp & Paper Mag. 1928, 1734.

the structure of lignin have been many, but the results obtained are at great variance. There are fundamental differences in the acetyl and methoxyl content of lignin from different species of the same wood, particularly between softwoods and hardwoods, and lignins obtained from the same woods vary due to soil, climatic conditions of growth, and the particular portion of the tree from which the lignin is obtained.

The lignin content of woody tissue appears to be far from a fixed figure. P. Klason[1], investigating 222 samples of spruce wood from 12 localities in Sweden, obtained an average content of 28.1% lignin, varying from 27.8-28.4. A very tall tree throughout its length contained from 27.1% to 27.9%. Ordinarily, when ether extracted pine wood is treated with 43% HCl, the lignin residue amounts to about 28%[2], but W. Fuchs[3] has shown that this figure is susceptible to considerable variation.

The structure of lignin is uncertain, in many of its reactions resembling the tannins, although incontrovertible evidence of a cyclic structure has not been forthcoming. The conifers and the Cycadaceae contain a lignin which seems to be a polymer of coniferaldehyde, $C_{10}H_{10}O_3$, while other growths contain a lignin which appears to be a polymer of an oxyconiferaldehyde[4]. Recent results indicate that the 17% methoxyl in isolated lignin is present in a system of the vanillin type[5], the behavior of lignin towards acid hydrolysis indicating that the formaldehyde group is present as a methylenedioxy-group attached to the pyro-

1. Cellulosechem. 1931, **12**, 36; abst. C. A. 1931, **25**, 5761.
2. E. Haegglund, Arkiv Kemi, Min. och Geol. 1918, **7**, 1; abst. Chem. Zentr. 1919, III, 186.
3. Z. Angew. Chem. 1931, **44**, 111; abst. C. A. 1931, **25**, 2123. Kolloid-Z. 1930, **52**, 248, 350; abst. C. A. 1931, **25**, 761.
4. P. Klason, Svensk Pappers-Tid. 1930, **33**, 16; abst. C. A. 1930, **24**, 3358.
5. K. Freudenberg, W. Belz and C. Niemann, Ber. 1929, **62B**, 1554; abst. C. A. 1929, **23**, 5038; Chem. Zentr. 1929, II, 554; J. S. C. I. 1929, **48**, 915-A.

catechol nucleus[1]. T. Pavolini[2] regards lignin as a tetramer of special aromatic hydroxyaldehydes.

On fusion with KOH and a little water, lignin yields lignic acid, protocatechuic acid, catechol and oxalic acid[3]. Below 240° the product is mainly lignic acid, but between 240-280°, the melt becomes fluid, froths strongly, the lignic acid being further decomposed. The formation of oxalic acid, which under ordinary circumstances may amount to 20%, may be entirely suppressed by fusing in an atmosphere of hydrogen or nitrogen, the yield of phenolic products being correspondingly increased.

The relative viscosity of lignin derivatives in acetone and chloroform at low concentrations is approximately proportional to the concentration[4]; at higher concentrations the viscosity-concentration curve is no longer linear. From the fact that alkali lignin isolated from corn cobs, when distilled with zinc dust in a hydrogen atmosphere at a maximum temperature of 400° yields guaiacol and 1-propyl-3-methoxy-4-hydroxybenzene[5], is indicative that the lignin molecule has at least two aromatic nuclei, or groups that are convertible into aromatic nuclei.

Lignin may be prepared from straw by treatment with alkali carbonate, precipitation of the extract with acid, and purified by repeated solution in alkali and re-precipitation with acid[6], and may be separated from xylan[7] by subjecting such material as cornstalks to the action of dilute NaOH solution (about 1%) so that when the lignin has been substantially dissolved, insufficient free NaOH will remain in

1. K. Freudenberg, M. Harder and L. Market, Ber. 1928, **61B**, 1760; abst. C. A. 1929, **23**, 276; J. S. C. I. 1928, **47**, 1227-A. L. Kalb and T. Lieser, Ber., 1928, **61B**, 1007; abst. J. S. C. I. 1928, **47**, 743-A.
2. Ind. Chim, 1931, **6**, 1367; abst. C. A. 1932, **26**, 2173.
3. E. Heuser and A. Winsvold, Cellulosechem. 1923, **4**, 49, 62.
4. E. Wederkind, O. Engel, K. Storch and L. Tauber, Cellulosechem. 1931, **12**, 163; abst. C. A. 1932, **26**, 298.
5. M. Phillips and M. Goes, J. Am. Chem. Soc. 1932, **54**, 1518; abst. C. A. 1932, **26**, 2711. See M. Harlow, Ind. Eng. Chem. 1931, **23**, 419; abst. C. A. 1931, **25**, 4020.
6. F. Paschke, Zts. ang. Chem. 1921, **34**, 465; abst. J. S. C. I 1921, **40**, 732-A.
7. E. Darling, U. S. P. 1825307; abst. C. A. 1932, **26**, 305.

the solution to materially affect the residual xylan. The chemical composition of red beechwood has been exhaustively investigated by R. Runkel and G. Lange[1].

Lignin is usually prepared by the methods of R. Willstaetter and L. Zechmeister[2], R. Willstaetter and L. Kalb[3], H. Urban[4], K. Kuerschner[5], and A. Friedrich[6], which depend upon the solution of cellulose by concentrated HCl, leaving the lignin insoluble but in a more or less modified condition. Dilute HCl is advocated by J. Greuss[7] as being less drastic on the lignin. Considerable research has been published on the isolation of lignin with alkalis (alkali lignin), as in the disclosures of E. Beckmann and O. Liesche[8], extended by W. Powell and H. Whittaker[9], but the lignin obtained in this way appears to be different from the HCl or the sulfite lignin.

Lignin is characterized by a number of well defined groups (methoxyl, acetyl, hydroxyl), while the existence of aldehydic groups and an unsaturated linkage also appears probable. Inasmuch as lignin contains hydroxyl groups, it may be nitrated, acetylated, benzoylated, and ethers prepared by the usual alkylation methods (see topic "Alkyl Lignin"). Lignin tribenzoate[10], toluenesulfonate[11], lignin nitrate (nitrolignin)[12], and acetyl-lignin (see p. 664, n. 12) are examples of lignin esters that have been described.

Lignin as such has been patented for use in formalde-

1. Cellulosechem. 1931, **12**, 185; abst. C. A. 1932, **26**, 299.
2. Ber. 1913, **46**, 2401; abst. C. A. 1913, **7**, 3414; J. C. S. 1913, **104**, i, 955; J. S. C. I. 1913, **32**, 822; Bull. Soc. Chim. 1914, **14**, 1354; Chem. Zentr. 1913, II, 1209.
3. Ber. 1922, **55**, 2637; abst. J. S. C. I. 1922, **41**, 893-A.
4. Cellulosechem. 1926, **7**, 23.
5. Chemie der Ligninkoerper, Stuttgart, 1925.
6. Zts. f. physiolog. Chem. 1928, **176**, 127.
7. Ber. botan. Ges. 1923, **41**, 48; abst. C. A. 1923, **17**, 3168.
8. Zts. ang. Chem. 1921, **34**, 285. 9. J. C. S. 1924, **125**, 357.
10. A. Friedrich and J. Diwald, Monats. Chem. 1925, **46**, 31.
11. K. Freudenberg and H. Hess, Ann. 1926, **448**, 121.
12. E. P. 2693, 1872. U. S. P. 994273, 1410037, 1497600.

hyde-phenol condensates[1], and as an asphalt substitute[2], and for the production of ligneous acetates[3].

Flax. The bast fibers of flax consist of cells composed of pure cellulose and an intercellular material containing a furfural-yielding component[4]. The glucose residues appear to be joined together in positions 1 and 4 by glucoside linkages, as are those of cotton. Cellobiose is obtained from flax cellulose in yields equivalent to those from cotton. Acetates of a trisaccharide and of an anhydrosaccharide may be obtained from flax cellulose, which results point to the chemical identity with cotton cellulose, without reference to the relative states of polymerization.

According to D. Andersen[5] the fibers originate in the meristematic region of the stem tip. The middle lamella is of pectose, and the secondary wall of cellulose, somewhat modified by pectose in the region of the middle lamella. Fiber elongation is the result of both a slipping action of the cells past each other, and an elongation of the fiber in harmony with the adjoining tissues. Tertiary deposition occurs through the periodic deposition of complete layers within the secondary wall, the amount of which varies, often amounting to 90% of the area of the cell in cross section. Alternate layers of spiral fibrils run in opposite directions. Flax fibers are partially lignified when seen in the stem, lignification being a change of pectic compounds, and there is evidence that some change of cellulose to pectose occurs previous to lignification. Retting is accomplished not by dissolution of the middle lamella, but by the destruction of the entire secondary wall. Lignification interferes with retting, the degree of lignification being one

1. R. Hartmuth, D. R. P. 326705.

2. J. Stokes, E. P. 208193. For other uses of lignin, see U. S. P. 1141510, 1148104, 1218638, 1298476, 1298477, 1303176, 1303177, 1392047, 1394241, 1440566, 1456540, 1472322, 1505990.

3. V. Drewsen, U. S. P. 1298479, 1298480, 1298481.

4. G. Rigby, J. A. C. S. 1928, **50**, 3364; abst. C. A. 1929, **23**, 699.

5. Amer. J. Botany, 1927, **14**, 187; abst. C. A. 1928, **22**, 2489.

of the determining factors in the success of the retting process.

A study of the progress of the reactions taking place during digestion of flax straw with mixtures of NaOH and Na_2S has shown the solution of the lignin to be much slower than the solution of those portions of the material known as "other than lignin"[1]. When small quantities of lignin are removed for a given degree of delignification[2], less cellulose is destroyed with sodium sulfite than with either NaOH or Na_2S. Fiber obtained by A. Cashmore[3] from unretted flax was treated with 0.5% soap solution at 80° for 1 hr., washed with water, leached with soap solution 90-120 min., the loss in weight being 25-30%. After drying, the fiber was extracted with ethyl alcohol-benzene 6 hrs., then with 0.5% ammonium oxalate solution to remove pectin. It was then washed, soaked 24 hrs. in 4% NaOH, washed and dried. From the NaOH extract, hemicellulose showing the presence of "uronic anhydride" was isolated to 1% of the weight of the fiber; α-cellulose 82-83%. Barium hydroxide extract of the fiber contained 9.8% galactose. From hydrolysis of 25 gms. fiber with 5% sulfuric acid at 130-140°, 4.8 gms. of a syrup were obtained containing 6.1% free pentose, 6.2% methylpentose, 11.5% galactose and 47% total reducing sugars as glucose. The non-cellulosic portion of flax fiber is made up (in part) of a hemicellulose bound to the cellulose.

W. Kind[4] found in Irish water-retted, Courtrai, Russian and Peufaillit-retted flax, 7.02, 4.46, 6.45 and 5.78% of pectins respectively, a brown powder containing 84.67% pectin being obtained by extracting flax stalks with 1% ammonium oxalate[5]. The average regain of water-retted

1. E. Schafer and C. Peterson, Paper Trade J. 1928, **86**, #3, 51; abst. C. A. 1928, **22**, 1681.
2. M. Bray and C. Peterson, Pulp and Paper Mag. Can. 1928, **26**, 37; Paper Trade J. 1928, **86**, #3, 48; abst. C. A. 1928, **22**, 1681.
3. J. C. S. 1927, **130**, 718; abst. C. A. 1927, **21**, 2988.
4. Spär-u.Wirtsch, 1926, **17**, 12; Melliand's Textilber. 1926, **7**, 872; abst. C. A. 1927, **21**, 2803.
5. F. Norris, Biochem. J. 1929, **23**, 195; abst. C. A. 1929, **23**, 4242.

flax has been stated[1] as 14.15%. A. Frey[2] has determined the refractive index of flax and other natural fibers, and J. Katz and K. Hess[3] the swelling and mercerizing action of 61% nitric acid. H. Mark[4] has reviewed the development of X-ray analysis to fibrous materials, giving diagrams for ramie, flax, cotton, mercerized cellulose, viscose and cellulose acetate, extending the work of J. Trillat[5].

Flax may be degummed and purified by treatment with NaOH and potassium bichromate[6]; potassium permanganate[7]; by washing with wool suint[8] with an aqueous solution containing over 12% SO_2[9]; cuprammonium solution[10]; chlorine gas[11]; ammonium tartrate, citrate, oxalate, sulfate or phosphate[12]; or alkyl naphthalenesulfonates[13]. The retting of flax with an extract prepared from stalks of *Urtica*[14], an enzyme[15], or a specific bacillus[16] have also been recommended[17].

1. W. Schaposchnikoff, Melliand Textilber. 1928, **9**, 844; abst. C. A. 1929, **23**, 1273.
2. Kolloidchem. Beihefte, 1926, **23**, 40; abst. C. A. 1927, **21**, 500.
3. Zts. phys. Chem. 1927, **122**, 126; abst. C. A. 1927, **21**, 1358.
4. Kunstseide, 1930, **12**, 214; Jentgen Rayon Review, 1930, **2**, 196; abst. C. A. 1931, **25**, 211.
5. Rev. Gen. Colloides, 1928, **6**, 57, 89; abst. Pulp and Paper Mag. 1929, Jan. 3, p. 16.
6. L. Gillis, U. S. P. 1619111; abst. C. A. 1927, **21**, 1355. E. P. 279302; abst. C. A. 1928, **22**, 2847.
7. T. Haughey, U. S. P. 1814155; abst. C. A. 1931, **25**, 5300.
8. E. Duhamel and Comp. Gen. des Industries Textiles, D. R. P. 530149; abst. C. A. 1931, **25**, 5300.
9. R. Wolf, R. Hill and R. Hatch, U. S. P. 1804967; abst. C. A. 1931, **25**, 3832.
10. O. Lucas, U. S. P. 1733742; abst. C. A. 1930, **24**, 510. E. P. 298178; abst. C. A. 1929, **23**, 2838.
11. L. De Pestele and A. Dujardin, F. P. 678837; abst. C. A. 1930, **24**, 3646. Belg. P. 353112; abst. C. A. 1929, **23**, 3098.
12. Abbey Syndicate, Ltd., and D. Nanji, E. P. 296333; abst. C. A. 1929, **23**, 2581.
13. British Dyestuff Corp., Ltd., C. Hollins and E. Chapman, E. P. 279583.
14. E. Fitzner and N. Zuirin, Russ. P. 15593, 36464; abst. C. A. 1931, **25**, 1103.
15. E. Schafer and C. Peterson, Paper Mill, 1928, **51**, #41, 2, 10, 35; abst. C. A. 1928, **22**, 4808.
16. V. Omelyanskii and M. Kononova, Compt. rend. 1926, **183**, 919; abst. C. A. 1927, **21**, 3132.
17. A. Aksipetrov and G. Rioumin, Izvestiya Tekstilnoi Prom. i. Torgovli, 1930, **9**, #3, 89; Chim. Ind. 1930, **24**, 948; abst. C. A. 1931,

L. Lilienfeld[1] has described flax as a raw material for benzylation, and for general cellulose etherification purposes[2].

Esparto Grass Cellulose. From the work of J. Irvine and E. Hirst[3] it appears this cellulose is a mixture or solid solution containing about 18.5% xylan, which may be completely removed by alkali extraction. The residue coincides fairly well with the chemical properties of cotton cellulose. It yields cellobiose octoacetate on acetolysis, forms a trimethyl ether which upon hydrolysis yields 2.3.6-trimethylglucose, and upon acetylation of the partially

25, 1388. G. Bredemann, Faserforschung, 1930, **8**, 123; abst. C. A. 1930, **24**, 1986. W. Gibson, Trans. Inst. Eng. Advance copy, Mar. 5-6, 1931, 3-6; abst. C. A. 1931, **25**, 3860. S. Henderson, J. C. S. 1928, **131**, 2117; abst. C. A. 1929, **23**, 118. B. Lotarev, Niti (Suppl. to Izvestiya Tekstilnoi Prom. i. Torgovli) 1930, **1**, #1-2, 17; Chim. et Ind. 1930, **24**, 942; abst. C. A. 1931, **25**, 1389. A. Meyer-Sansboeuf Ges., E. P. 263102; abst. C. A. 1927, **21**, 4077. B. von Ehrenthal and K. Scholz, D. R. P. 471103; abst. C. A. 1929, **23**, 2307. G. Rice, Tex. Color. 1930, **52**, 550; abst. C. A. 1931, **25**, 597. J. Stanley, E. P. 292801; abst. C. A. 1929, **23**, 1515. P. Waentig, Zts. ang. Chem. 1927, **39**, 1237; abst. C. A. 1927, **21**, 654. A. Zakochtchikov, I. Kohyeniov and E. Ykiouchkin, Izvestiya Tekstilnoi Prom. i. Torgovli, 1930, **9**, #3, 91; Chim. et Ind. 1930, **24**, 949; abst. C. A. 1931, **25**, 1388.

1. U. S. P. 1800944; abst. C. A. 1931, **25**, 3498.

2. L. Lilienfeld, U. S. P. 1188376, 1916; applied for June 26, 1912; abst. C. A. 1916, **10**, 2145; J. S. C. I. 1916, **35**, 887; Mon. Sci. 1917, **84**, 28; Chem. Ztg. 1916, **14**, 805; Kunstoffe, 1916, **6**, 282. E. P. 6035, 1913, date applied for March 16, 1912, claimed from the date of first foreign application; abst. C. A. 1914, **8**, 2947; J. S. C. I. 1914, **33**, 417; Chem. Ztg. 1913, **37**, 472; 1914, **38**, 419; Chem. Ztg. Rept. 1914, **38**, 490; Kunstoffe, 1914, **4**, 435. E. P. 12854, 1912; applied for May 31, 1912; abst. C. A. 1913, **7**, 3839; J. S. C. I. 1913, **32**, 940; Chem. Ztg. 1913, **37**, 1205; 1914, **38**, 419; Chem. Ztg. Rept. 1914, **38**, 490. F. P. 447974, applied for July 17, 1912; claims Austrian application dated March 16, 1912; abst. J. S. C. I. 1913, **32**, 420; Mon. Sci. 1914, **80**, 3; Chem. Ztg., 1913, **37**, 122; Kunst. 1913, **3**, 195. Belg. P. 254591; abst. Chem. Ztg. 1913, **37**, 567; Kunst. 1913, **3**, 355. F. P. 459972; abst. J. S. C. I. 1913, **32**, 1153. Hung. P. L-3451; abst. Chem. Ztg. 1919, **43**, 753. Ital. P. 132825; abst. Chem. Ztg. 1913, **37**, 1334. Aust. 63526; abst. J. C. S. 1914, **106**, i, 919. Aust. P. 73001; abst. Kunstoffe, 1917, **7**, 222; Meyers Jahr. Chem. 1918, **28**, 219; Aust. P. 78217. Span. P. 55104; abst. Chem. Ztg. 1913, **37**, 728. Swiss P. 66512; abst. Chem. Ztg. 1914, **38**, 1034; Kunstoffe, 1915, **5**, 70. Norw. P. 27507; abst. C. A. 1917, **11**, 1748. D. R. P. 477154; abst. C. A. 1929, **23**, 4071. D. R. P. 470142; abst. Chem. Zentr. 1929, I, 1528. Dan. P. 18285. Swed. P. 38905. Ital. P. 140506.

3. Jour. Chem. Soc. 1924, **125**, 15.

purified pulp, a mixture of cellulose triacetate and xylan diacetate results.

Esparto cellulose does not appear in the market as a pulp, but solely in the form of manufactured paper, and is an industry primarily associated with Edinburg and Central Scotland. The grass is first mechanically cleaned, then cooked with caustic soda under pressure, the pulp after washing being bleached with calcium hypochlorite.

E. Hirst[1] has acetylated esparto cellulose and obtained almost quantitative yields of ester without loss of the pentose residue, while F. Greening[2] has described the nitration of esparto cellulose. Methylation of esparto has been reported upon by J. Irvine and E. Hirst[3], the ethylation of esparto by L. Lilienfeld[4] and by K. Ott and H. Schuessler[5]. A benzyl ether of esparto has also been described[6]. So far as aware, esparto cellulose is not being commercially etherified at the present time.

Hemicellulose is of interest in the cellulose ether art in the negative sense that its absence must be assured if products of the most desirable characteristics are to be obtained, and in this respect resembles the viscose industry wherein the presence of notable amounts of hemicellulose in the alkalicellulose is contraindicated[7]. The hemicelluloses may be defined as those constituents of the cell membrane which are more easily attacked than the cellulose. Hemicelluloses are easily dissolved by hot, dilute mineral acids and are hydrolyzed; also soluble in hot, dilute alkalis, and almost entirely by 18% NaOH solution at room temperature[8]. Therefore the best commercial way to insure the

1. Rept. Brit. Assoc. Advancement Sci. 1922, 358.
2. E. P. 5344, 1899. See S. Mackie, C. Faure and G. Trench, E. P. 2472, 1876. L. Trigos, F. P. 480606.
3. J. C. S. 1924, **125**, 15.
4. E. P. 12854, 1912; 6035, 1913.
5. U. S. P. 1806703.
6. I. G. Farbenindustrie, E. P. 343147.
7. H. Gisdakis, Silk J. 1930, **7**, #74, 46; #75, 41; abst. C. A. 1930, **24**, 6006.
8. E. Heuser, Papierfabr. 1927, **25**, 238; abst. Pulp and Paper Mag. 1927, 1662; J. S. C. I. 1927, **46**, 545-A.

minimum of hemicellulosic bodies present is to use approximately an 18% NaOH solution for alkalicellulose formation, circulating the alkali during the mercerizing period, and pressing the alkali at the close of the process so that the minimum of alkali (containing hemicellulose in solution) remains in the alkalicellulose mass.

It appears that hemicellulose is formed by conjugation of sugars and sugar acids (uronic acids, i.e., glycuronic and galacturonic acids)[1]. Non-lignified plant tissues contain relatively large amounts of hemicellulose. According to M. O'Dwyer[2] hemicellulose contains a certain percentage of methoxyl, of which about half exists in the form of an ester. Although hemicellulose is not a true carbohydrate[3], acid groups are present. It may be regarded more as a reserve carbohydrate[4]. Methods for the intentional production of hemicellulose have been patented[5], and it has been proposed for use in a baking compound[6], as an explosive component[7], for the addition to starch[8], and in the treatment of textiles[9].

1. E. Candlin and S. Schryver, Proc. Roy. Soc. 1928, **103B**, 365; abst. C. A. 1928, **22**, 4576.
2. Biochem. J. 1928, **22**, 381; abst. C. A. 1928, **22**, 2463.
3. M. O'Dwyer, Biochem. J. 1926, **20**, 656; abst. C. A. 1927, **21**, 174. See also Biochem. J. 1923, **17**, 493; 1925, **19**, 694; abst. C. A. 1924, **18**, 402; 1925, **19**, 3289.
4. A. Murneek, Plant Physiology, 1929, **4**, 251; abst. C. A. 1929, **23**, 5217. R. Malhotra, J. Biochem. (Japan), 1930, **12**, 341; abst. C. A. 1931, **25**, 1553.
5. J. Aktschourin, U. S. P. 1169592. T. and E. Kittelsen, U. S. P. 1365039.
6. A. Clark, U. S. P. 1491380.
7. C. Stine, U. S. P. 1143330, 1313650.
8. W. Snelling, U. S. P. 1430035.
9. E. Bloch-Pimentel, U. S. P. 1044434, E. P. 7893, 1912.

CHAPTER IV

ALKALICELLULOSE THEORY AND MANUFACTURE

In the etherification of cellulose, alkalicellulse may properly be regarded as a raw material, because the commercial processes which have been developed beyond the academic stage, use alkalicellulose as the initial cellulosic material, and it is not exaggeration to say that the *proper* manipulation of this step in cellulose ether production is probably the most important, and one which until comparatively recently has not been given the attention which its importance merits. While this does not necessarily mean that the limitations in steps of alkalicellulose manufacture are the same in different plants, it *should* be daily duplicated within very close limits, and the succeeding steps of the process should be founded upon and governed by the nature and reactivity of the alkalicellulose formed, rather than to regard the etherification step as of premier importance, for irrespective of the care exercised in the subsequent operations, if the manufacture of alkalicellulose has not been carried on under strictly governable conditions and with strict analytical control, it is almost impossible to produce cellulose ethers uninterruptedly of maximum desirable physical constants and hence of technical superiority.

Insofar as alkalicellulose of maximum suitability for etherification purposes is concerned, it is theoretically desired to bring 2 to 2.2 molecules NaOH into contact with one molecule of cellulose of the highest α-cellulose content under such conditions that maximum etherification will result, and in which the steps of formation, expression of excess alkali, comminution and ageing are carried out under as nearly as possible duplicable conditions. The literature on the mercerization of cellulose, especially cotton cellulose, is most voluminous, and since the initial discovery of John Mercer, the Lancashire calico printer, in 1844, has abounded in polemics from investigators of undisputable integrity.

The factors of alkali concentration, temperature and time of steeping of the cellulose, degree of removal of exhausted alkali, period and degree of comminution, temperature and desirable time of ageing, all these factors have introduced variables, thereby greatly complicating the subject.

The mercerization reaction practically takes place when cellulose in the form of pulp, usually in sheet form, is brought in contact with sodium hydroxide solutions above 16% in strength at temperatures around that of the room. Below this strength, the reaction becomes reversible, and the progress increases with lowered temperatures and higher alkali concentrations up to a certain point. On account of the fact—not perfectly appreciated as yet—that this reaction controls the quality and uniformity of alkalicellulose produced, or rather the reverse way of stating the proposition, which is, that if the alkalicellulose is not properly prepared in this step of the process, errors cannot be entirely counteracted in subsequent treatment steps, and exerts a prime effect upon the quality and degree of subsequent etherification, the step of alkalicellulose formation is herein dealt with in detail commeasurate with its importance.

A major portion of the older theories and work in this field has been supplanted by later and more accurate data, and for this reason the salient facts disclosed in this art are taken up substantially chronologically, and covering the period of the past fifteen years only.

While it is true that successful products can and have been made under widely differing conditions of alkalicellulose formation and treatment, there is a surprising uniformity of conditions adopted by the viscose rayon industry at present, along which lines the major portion of intensive investigation in the past decade has been carried on. An adjustment is also possible between time of mercerization and strength of sodium hydroxide, but due to the fact that in the major number of disclosed cellulose ether manufacturing processes, additional alkali hydroxide is added to

the alkalicellulose after maturation, the total alkalinity per molecule original cellulose, is one which is dependent upon the course of the steps initial to aged alkalicellulose formation. Also, another variable factor in alkali consumption is the ratio of alkyl or aralkyl to the haloid or sulfate in combination to form the alkylating or aralkylating agent, for a portion of the free alkali present is neutralized incident to combining with the liberated acid radical. For instance, in the methylating step, 35.5 parts acid radical are liberated to 15 parts methyl in methyl chloride, as against 48 parts acid radical per 15 parts methyl in methyl sulfate. If ethyl chloride or ethyl sulfate is used, the 15 is changed to 29, and in benzylation, the 15 is substituted by 91 (all parts by weight).

The amount of caustic soda combined with the cellulose as evidenced by non-removal by washing with alcohol (a very laborious process) increases with the concentration of NaOH used. Thus, 100 gms. cotton cellulose takes up 4.1 gms. NaOH from a 10% NaOH solution and 16.7% from a 20% NaOH solution, time and temperature being the same in both instances. The lower the temperature, the greater the amount of NaOH combined with the cellulose, and the lower the viscosity of the etherified cellulose in a named volatile solvent. Other conditions being equal, mercerization at 20° gives rise to cellulose ethers of maximum viscosity—not always a desirable feature. With high alkali concentration but at substantially lower mercerizing temperatures, either a longer alkylation or an increased temperature is necessary to introduce the maximum of etherifying group. Above the optimum time, the longer the cellulose remains in the alkali solution, the lower is the viscosity of the cellulose ether produced therefrom, and the lower is the tensile strength of the same in film or filament form.

It is also a fact that ageing of the alkalicellulose at too high a temperature or beyond the optimum period results in cellulose ethers of increased solubility in a named solvent

or solvent combination, diminished viscosity and less tensile strength. Furthermore, if alkylation is to be carried on with a gaseous alkylating agent as methyl chloride or ethyl chloride in contradistinction to methyl sulfate or ethyl sulfate, the concentration of alkali in mercerization, time of mercerization and period of ageing of the formed alkalicellulose may be carried further without danger of lessening the strength of the finished cellulose ether, in comparison to where an alkyl chloride as used as etherifiant as against the corresponding alkyl sulfate. The greater the excess of caustic soda allowed to remain in the alkalicellulose, the larger the proportion of hemicellulose present, and the lower will be the viscosity of the cellulose ether obtained therefrom. These facts are of fundamental importance, and the value of one process over another, as judged by the wet and dry tensile strength of films and filaments made from the etherized cellulose, comprises a careful adjustment and balancing of one step in respect to the others, coupled with an etherifying step which results in the finished ether showing a maximum range of solubility in the cheaper solvents and solvent mixtures, a maximum water resistivity, and a diminished viscosity which is not attained at the expense of cellulose degradation at some step in the process sufficiently pronounced to show unfavorably in the tensile strength of the finished product.

For the purposes of subsequent etherification, it is immaterial whether the system cellulose-sodium hydroxide-water is a physical admixture or a chemical compound. One group of supporters maintains that the changes are almost entirely due to physical causes, while the other school holds that chemical interaction between alkali and cellulose takes place, and this is the cause of the ultimate effects. The present sum total of information supports the view that the action of alkali metals on cellulose is a primary chemical interaction.

The most pronounced visible effect of the action of NaOH in mercerizing concentration upon unmodified cel-

lulose is distension or swelling, but this is accompanied by a simultaneous contraction in area, this contraction being about 7% with cotton pulp sheets when 17.5% NaOH solution is used and allowed to act upon the cellulose about 2 hrs. at 18°. If regenerated cellulose be acted upon, a much less concentrated alkali solution is required to induce the maximum contraction effect. These macroscopic changes observable with cellulose in presence of alkali hydroxide solutions are accompanied by changes in structure observable microscopically. T. Barratt and J. Lewis[1] have shown that heat is evolved when cotton cellulose is treated with NaOH, the curve plotted from alkali concentration and heat calories evolved indicating a gradual increase until the solution used is about 40% concentration, then remaining stationary with solutions up to about 60% concentration. Although two distinct inflections take place in the curve, corresponding to 10-12% and 30% NaOH respectively, they appear to be of little significance apart from the fact that the first occurs at a point where the cellulose net-work appears fully opened up. S. Neale[2] has corroborated these results up to 40% alkali concentration, but he finds the temperature does not remain stationary with solutions above 40% concentration, but that a well discernible rise takes place.

According to I. Kolthoff[3] cellulose does not absorb sodium and potassium hydroxides in the physical sense; they are taken up by it from solutions, and with concentrations

1. Trans. Text. Inst. 1922, **13**, 113; abst. J. C. S. 1922, **122**, i, 526. They measured the heat developed when well-scoured Egyptian cotton is immersed in NaOH solutions of varying concentrations, the maximum rise in temperature being 0.5°, equilibrium being reached only after several minutes. This "heat of mercerization" increases with NaOH concentration, but is not proportional to it. The curve shows an inflection corresponding with a rapid increase in the heat produced when the concentration of alkali is between 10-15%. A second inflection, corresponding with a decrease, occurs at about 30%, which is near the upper limit of solutions used in mercerization. The rate of heat development is greatest between 10% and 18%, equilibrium being reached in solutions within these concentrations in about 2 min.

2. J. Text. Inst. 1929, **20**, 373; abst. C. A. 1930, **24**, 3110.

3. Pharm. Weekblad, 1921, **58**, 46; Analyst, 1921, **46**, 257; abst. Paper Trade J. 1922, **74**, 55.

up to 4*N*, the amounts are proportional to the concentration. Thus from NaOH solutions of 4*N*, 2*N*, 0.5*N*, 0.1*N*, 0.05*N* and 0.01*N* strength, undried cellulose removed 3.2, 1.4, 0.65, 0.35, 0.085, 0.04 and 0.011 molecular-equivalents per gram respectively. With dried cellulose the following figures were obtained: from 4*N*, 2.1; 2*N*, 1.1; *N*, 0.58; 0.5*N*, 0.3; 0.1*N*, 0.055; and 0.05*N*, 0.03. Ammonia is taken up only in the presence of other alkalis. P. Karrer[1] has shown that cellulose in 30% NaOH forms a complex represented by 10.69% NaOH, and cotton under similar conditions, absorbs about 13% NaOH.

Cellulose takes up more alkali from an alcoholic than from an aqueous solution[2], and therefore removal of alkali by washing with ethyl alcohol is excluded. P. Karrer and K. Nishida incorporated 2-6 gm. samples of purified cotton previously dried at 100° *in vacuo*, in 40-50 cc. NaOH solution varying in concentration from 20.5 to 45.5%, carbon dioxide being excluded. The solution was expressed and 5 cc. titrated in each case. The retention of NaOH by the cotton was calculated, the most consistent results being obtained with 4 gm. samples, amounts of NaOH taken up varying from 12.5 to 151.1 gms. per 100 gms. cotton. The amounts of alkali taken up do not regularly increase with increasing concentration, and no evidence was obtained indicating the formation of a compound $C_6H_{10}O_5$.NaOH.

W. Vieweg[3] holds there is no experimental evidence that cellulose combines with NaOH in the presence of aqueous ethyl alcohol to form a definite compound (alkali-cellulose), because the higher the concentration of NaOH, or the higher the ratio ethyl alcohol-water in the solution, the higher NaOH% absorbed; in 50% ethyl alcohol 5 times

1. Cellulosechem. 1921, **2**, 125; abst. C. A. 1922, **16**, 644; J. S. C. I. 1922, **41**, 170-A; J. C. S. 1922, **122**, i, 231. See E. Knoevenagel and H. Busch, Cellulosechem. 1922, **3**, 42; abst. C. A. 1922, **16**, 2779.

2. P. Karrer and K. Nishida, Cellulosechem. 1924, **5**, 69; abst. C. A. 1925, **19**, 1051.

3. Ber. 1924, **57B**, 1917; abst. C. A. 1925, **19**, 1050. Zts. ang. Chem. 1924, **37**, 1008; abst. C. A. 1925, **19**, 1050. See W. Vieweg, Papier Ztg. 1907, **32**, 130, 174; Wochbl. Papierfabr. 1907, **38**, 545, 625, 703; abst. C. A. 1907, **1**, 1320, 2488.

as much NaOH is absorbed from an 18% NaOH solution as from a 2% NaOH solution.

Eliminating analytical errors, E. Heuser[1] finds the absorption of NaOH from solutions of 16-24% concentration, corresponds with the formation of a compound $C_{12}H_{20}O_{10}$.NaOH, the experiments being carried out with 4 gms. finely powdered cotton and 50 cc. NaOH solution, and the liquid being pressed out as completely as possible. Titrations were then made. At higher concentrations evidence points to the absorption of NaOH by alkalicellulose, adsorption being reduced by working at higher temperatures[2]. E. Heuser and W. Niethammer[3] find a similar compound with KOH is formed. With 16% NaOH a definite alkalicellulose results, which at much higher concentrations adsorbs additional NaOH. If 45% NaOH acts upon cellulose at 80° the compound $(C_6H_{10}O_5)_2$ NaOH results, but at lower concentrations at this temperature, the compound is partially hydrolyzed. With 35% NaOH at 80°, cellulose retains only 9.4% NaOH, instead of the theoretical 12.3% NaOH required by alkalicellulose. The maximum swelling of dry cellulose in 18% NaOH is 78%[4]. The swelling action of NaOH is reduced by the presence of alcohol[5].

F. Dehnert and W. Koenig[6] have investigated the interaction of cellulose with NaOH, KOH and LiOH in rising concentrations at 20°, care being taken to exclude CO_2. They found mercerization of cellulose is caused by tetramethylammonium hydroxide, phenyltrimethylammonium hydroxide, and diphenylmethyleneammonium hydroxide, and that repeated mercerization with different alkalis pro-

1. Zts. ang. Chem. 1924, **37**, 1010; abst. C. A. 1925, **19**, 1051; J. S. C. I. 1925, **44**, 94-B.
2. E. Heuser, Cellulosechem. 1927, **8**, 31; abst. C. A. 1927, **21**, 1705.
3. Cellulosechem. 1925, **6**, 13; abst. C. A. 1925, **19**, 2272; J. S. C. I. 1925, **44**, 311-B.
4. E. Heuser and R. Bartunek, Cellulosechem. 1925, **6**, 19; abst. C. A. 1925, **19**, 2272; J. S. C. I. 1925, **44**, 311-B.
5. *Ibid.* Cellulosechem. 1926, **7**, 169; abst. C. A. 1927, **21**, 3127.
6. Cellulosechem. 1924, **5**, 107; 1925, **6**, 1; abst. C. A. 1925, **19**, 1050; J. S. C. I. 1925, **44**, 200-B.

duces no change in the relations established between cellulose and strong bases.

By measurement of the change in concentration produced by immersion of cotton yarn in a solution of NaOH, it is shown[1] that cotton absorbs rapidly increasing amount of alkali with increasing strength of NaOH solution, but with a solution of 1.2-1.47 density, the amount of alkali absorbed remains nearly constant at 12.28%, thereby indicating the formation of the compound $(C_6H_{10}O_5).NaOH$[2]. T. Katayama has found[3] that an alkaline solution of cellulose takes up oxygen from the air, but not H or N, the amount of O absorbed increasing as the temperature increases, the amount being exceedingly small below 10°. The degree of oxygen absorption is also a function of alkali concentration, 20-30% alkali solution producing the maximum absorption. The more the original cellulose is hydrolyzed, the greater the oxygen absorption. When oxygen is absorbed by alkalicellulose acid substances are formed, even in the cold, oxalic and other organic acids being formed. The copper value of alkalicellulose is not changed after oxygen absorption.

J. Huebner and E. Wootton[4] have studied the action of NaOH solutions of varying strengths up to 1.5 density upon the shrinkage, strength, iodine absorption, water content and the copper number of cotton yarns and fabrics. Lightly scoured Sea Island cotton fabric treated with NaOH solutions up to 1.25 density shows increasing shrinkage with increasing concentration, the greatest degree of shrinkage being from solutions between 1.1-1.15 density. Treatment with NaOH solutions increases the hygroscopic

1. E. Knecht and J. Platt, J. Soc. Dyers. Col. 1925, **41**, 53; abst. C. A. 1925, **19**, 1945; J. S. C. I. 1925, **44**, 200-B.

2. R. Lorenz, Wochenbl. Papierfabr. (Sondernummer) 1925, **56**, 23; abst. C. A. 1925, **19**, 3016.

3. Report Osaka Ind. Research Lab. (Japan) 1925, **6**, #1, 1; abst. C. A. 1926, **20**, 2745.

4. J. Soc. Dyers Col. 1925, **41**, 10; abst. C. A. 1925, **19**, 1350; J. S. C. I. 1925, **44**, 167-B.

moisture present. V. Sharkov[1] finds potassium thiocyanate is capable of mercerizing cellulose, when a mixture with KOH is used, the effect on cellulose at lower temperatures being far greater than that of either of the two components used separately. At higher temperatures, however, the swelling decreases. Likewise, aqueous lithium hydroxide has a powerful swelling effect upon cellulose.

It has been found that absorption of sodium or potassium hydroxide remains constant although swelling decreases[2] when methyl alcohol is present with the alkali, and in direct ratio to increase in methyl alcohol present. With 50% alcohol, absorption of KOH is reduced to one-third. Absorption of KOH by pure methyl alcohol depends on the moisture content of the cellulose, the latter (originally containing 5.51% water), dried for 15 hrs. at 120-130° adsorbed practically none, while after drying 4 hrs. at 100-150°, 1.7% of its weight of KOH was absorbed in 1 hr. from a 0.414% solution.

When the medium is a mixture of water and alcohol and not water alone as the NaOH solvent[3] in the treatment of cellulose, with increasing NaOH concentration up to 16%, the cellulose spectrum persists with that of the alkalicellulose, and at a definite NaOH concentration, a definite number of cellulose crystallites which have been converted into alkalicellulose are in equilibrium with the unchanged crystallites remaining. The state of homogeneous equilibrium is determinable by means of Roentgen spectrographic methods.

In studying the effect of temperature on the swelling of sulfite pulp in NaOH and KOH solutions, O. Faust[4] found that by taking 1 gm. sheets of pulp, soaking in excess NaOH solution for 1.5 hrs., allowing to drain to constant

1. J. Chem. Ind. (Moscow), 1926, **3**, 1148; 1927, **4**, 666; abst. C. A. 1928, **22**, 2837, 3525.
2. V. Sharkov, J. Appl. Chem. (Russia), 1929, **3**, 579; abst. C. A. 1930, **24**, 956; J. S. C. I. 1930, **49**, 367-B.
3. J. Katz, Zts. Elektrochem. 1926, **32**, 125; abst. C. A. 1926, **20**, 3565.
4. Cellulosechem. 1926, **7**, 153; abst. C. A. 1927, **21**, 821.

weight and taking the increase in weight as a measure of the swelling, bleached sulfite pulp (α-cellulose 89%, copper number 1.15%) gave a decided maximum swelling in 10% NaOH, which concentration also has the greatest solvent action on the pulp. In agreement with the solubility behavior, the swelling in KOH is much less. In both solutions the maximum swelling is less at 20° than at 0°. In KOH there is no true maximum at 0°, the swelling increasing with concentration up to 16.8%, and thereafter remaining constant. At 20° the swelling is constant from 5.6% to 14%, and above 28% concentration increasing in two steps.

The oxidation of alkalicellulose by gaseous oxygen has been studied[1]. When cotton or hydrated cellulose is immersed in NaOH solution of different concentrations, and the products squeezed and exposed to the action of oxygen at 60°, the NaOH is partly in combination with the cellulose, and partly adherent to the fiber (swelling hydroxide). With increasing concentration of alkali in the bath up to 30%, the absorption of oxygen increases considerably, and attains remarkably high values, reaction being complete within 15 days. With higher concentration the absorption is smaller but less rapidly completed. If the primary oxidation consists in the conversion of a carbonyl group into a carboxyl group which is neutralized by the alkali, or in the complete combustion of the cellulose, the absorption of one atom of oxygen is causative of the neutralization of one mol. NaOH, and the established, practical cessation of the reaction when the greater part of the alkali has been neutralized becomes understandable. The rate of oxygen absorption depends on the alkali concentration and attains a maximum of 23.8%. With hydrated cellulose, due to the presence of greater amounts of "swelling alkali," the

1. W. Weltzien and G. zum Tobel, Ber. 1927, **60**, 2024; abst. C. A. 1928, **22**, 4795; Chem. Zentr. 1928, I, 31; J. S. C. I. 1927, **46**, 962-B. Papierfabr. 1926, **24**, 413; abst. C. A. 1926, **20**, 3806; J. S. C. I. 1926, **45**, 911-B. Cellulose Ind. 1928, **4**, 1; Seide, 1928, **32**, 371, 414; abst. Chem. Zentr. 1928, I, 2080; C. A. 1929, **23**, 5571.

rate of absorption and the amount of oxygen absorbed are higher than with cotton.

In a study of the action of NaOH on cellulose under high pressure[1], cotton was treated with about 7 times its weight of 3.5*N* NaOH and slowly heated in an autoclave to 372°, being maintained at that temperature for some hours. After removal of gaseous reaction products, the residual, transparent yellow-brown solution was fractionated to recover methyl alcohol, acetone and light oil, evaporated to dryness, and ether extracted to remove pitch. The residue, consisting of alkali salts of organic acids, was then steam-distilled at 110-125°. Ultimate analysis of the products reveals losses equivalent to 3.25% of the original cellulose.

According to A. Lottermoser and H. Radestock[2] on the action of NaOH on cellulose, with increasing concentration of alkali, loss in weight of cellulose rises to a maximum at a concentration of 3.2 mols/liter, but the value of this loss is least for the cellulose which has been most carefully treated in preparation (e.g. unbleached and coarsely ground). Loss increases with the time of steeping up to 12-16 hrs., then remains constant for about 8 hrs., and finally falls to its initial value after 20-24 hrs. The loss at 100° is not appreciably greater than twice that at 20°.

W. Ermen and S. Jenkins[3] have repeated the work of E. Knecht and J. Platt[4] on the action of caustic soda on cellulose, and have found that with NaOH up to 27° Tw. there is no evidence of chemical action between the NaOH and cotton. They believe the NaOH suffers a constant partition between water and cellulose. At 27° Tw. a marked increase occurs in the absorption of NaOH by cellulose, which rises rapidly to a constant at 15 parts NaOH per 100 of cellulose, over a range of 27-50° Tw. of NaOH. Above

1. S. Oden and S. Lindberg, Ind. Eng. Chem. 1927, **19**, 132; abst. J. S. C. I. 1927, **46**, 406-B; Pulp & Paper Mag. 1927, **25**, 743.
2. Zts. ang. Chem. 1927, **40**, 1506; abst. C. A. 1928, **22**, 1234; J. S. C. I. 1928, **47**, 189-B.
3. J. Soc. Dyers Col. 1927, **43**, 9; abst. C. A. 1927, **21**, 820; J. S. C. I. 1927, **46**, 103-B.
4. J. Soc. Dyers Col. 1925, **41**, 53; abst. C. A. 1925, **19**, 1945.

50° Tw. the NaOH taken up by cellulose increases to a maximum of 25 parts to 100 of cellulose, or equimolecular proportions of cellulose and alkali. The rate of absorption of NaOH by cellulose is extremely rapid with alkali of mercerizing concentration. Thus, in 3 min. the absorption was 12 gms. NaOH per 100 gms. cellulose, which gradually rose to 15.1 gms. in 30 min.

In studying the action of strong caustic solutions on cellulose, P. Waentig[1] found that alkalicellulose aged in a closed flask 40-50 days takes up about 1.3% O, but the decomposition product is not oxycellulose, since the copper number is but slightly increased. There is a small decrease in *a*-cellulose. When the cellulose is both mercerized and aged in a vacuum, there is an actual increase of about 1% in the *a*-cellulose value, and preparations obtained therefrom are highly viscous.

Alkalicellulose prepared by the method of A. Pringsheim and A. Aronowsky[2], after careful washing with alcohol and drying to constant weight at 110°, contained 13.11% NaOH, as compared with 12.92% NaOH required by the formula $(C_6H_{10}O_5)_2$.NaOH. In the opinion of V. Sharkov[3], this discrepancy is due to the difficulty of washing out the last traces of sodium ethylate[4]. This formula has ben checked by B. Rassow and K. Schwarze[5], who found that when alkalicellulose is washed with 92.4% ethyl alcohol to phenolphthalein neutrality, a 2:1 molecular ratio of glucose residue to caustic is obtained in the residue when NaOH of 35 vol./% concentration is used; when alizarin yellow R is used as indicator, a 39% mercerizing solution is required. The swelling of cellulose and the electric con-

1. Papier Fabr, (Fest and Auslands-Heft) 1928, **26**, 64; abst. C. A. 1928, **22**, 3292; J. S. C. I. 1928, **47**, 564-B.
2. Ber. 1922, **55B**, 1414; abst. C. A. 1922, **16**, 3878.
3. Zhur. Prikladnoi Khim. 1929, **2**, 775; abst. C. A. 1930, **24**, 1972.
4. B. Rassow and L. Wolf, Ber. 1929, **62B**, 2949; abst. C. A. 1930, **24**, 1737; J. S. C. I. 1930, **49**, 198-A.
5. Papier-Fabr. (Tech. Wiss Teil) 1930, **28**, 693, 746, 832, 869; 1931, **29**, 34, 56; abst. C. A. 1931, **25**, 5018; J. S. C. I. 1931, **50**, 390-B.

ductivity of the solution are at a maximum in the solutions giving the 2:1 cellulose-alkali ratio.

The relation between NaOH concentration and its absorption by cotton[1] is expressed by a stepped curve; in the case of tissue paper and wood cellulose the curve exhibits no sharp breaks. Yields of over 90% regenerated cellulose may be obtained provided the NaOH absorption is over 0.17 gm. per gm. cellulose, and this requires the use of a solution containing more than 14.7% NaOH. Higher temperatures tend to diminish the absorption, the most favorable steeping temperature being 20°. These results correspond closely to those employed in the viscose factory, where the average absorption is 0.18-0.23 gms. NaOH per gm. cellulose.

E. Hagglund and F. Klingstedt[2] obtained a 43% yield of alkalicellulose from pine wood, which was also found to contain 3.3% mannan, 5.3% pentosan, no galactan and only a trace of levulan. After mercerization with 17.5% NaOH an α-cellulose was obtained which still yielded 2.1% mannan and 1.5% pentosan. The total mannan present is determined by first converting the material completely to sugar, and then determining the mannose present. Lignin does not interfere with the determination of pentosan in the cellulose.

When cellulose in the form of cotton fiber is immersed in 18% NaOH solution at 20° in the presence of air[3], it absorbs an amount of NaOH equivalent to $C_6H_{10}O_5.7NaOH$ within one hr. The amount of caustic soda absorbed does not change within 8-12 hrs., after which it steadily decreases, becoming 5 mols. NaOH per mol. cellulose after 24 hrs., 2 mols. after 72 hrs., and 1 mol. after 120 hrs. That cellulose is oxidized by atmospheric oxygen is generally known when concentrated alkali solutions are present, and the oxidation is supposed to take place in the primary al-

1. Y. Kami and T. Yamashita, Cellulose Ind. (Tokyo), 1929, **5**, 178; abst. C. A. 1930, **24**, 2288; J. S. C. I. 1929, **48**, 713-B.
2. Cellulosechem. 1928, **9**, 77; abst. C. A. 1929, **23**, 5575.
3. K. Atsuki, K. Shimoyama and H. Matsumoto, J. S. C. I. (Japan), 1928, **31**, 204-B; abst. Pulp and Paper Mag. 1929, Jan. 3, 17.

cohol of cellulose. If the alcohol is combined with the alkali the combination is decomposed at first, and the alcoholic group oxidized to —CHO, =CO, or —COOH, the oxidation of the cellulose being proven by the decrease of cellulose regenerated after xanthation.

In a study of the solubility of regenerated cellulose in NaOH solutions, K. Atsuki and K. Shimoyama[1] immersed air-dried viscose rayon 4 hrs. in NaOH solutions of various concentrations, and, after filtration, the dissolved cellulose was determined by oxidation with potassium bichromate. Solubility increases with decreasing temperature, and under the conditions employed reaches a maximum at 0°. It is also highly dependent on the concentration of the NaOH solution, and is at a maximum at about 9 weight/per cent. Under these optimum conditions, a solubility of 92.9% was found[2].

In an investigation of the absorption of caustic soda solutions by cotton, H. Coward and L. Spencer[3] took 8.5 gm. samples of dry Egyptian sliver which had been treated 6 hrs. at 20 lb. pressure (125°) with 2% NaOH, washed with weak acid and then water until neutral and afterwards dried, and immersed them overnight in 100 cc. each of NaOH solutions of 0-48.8% strength, which were then centrifuged for 75 min. at 7000 r.p.m., and the weight of the centrifuged mass and the NaOH content determined. With increasing strength of NaOH solutions (0-14.8%) cotton absorbs rapidly increasing quantities of NaOH and of water. With stronger solutions, the NaOH absorption increases, but less rapidly, and absorption of water distinctly decreases, so that the absorption of caustic soda increases but slightly. These results, and those of R. Willows and A. Alexander[4] show that the swelling of cotton fibers

1. J. Cellulose Inst. Tokyo, 1930, **6**, 219; (Abstracts 1930, **6**, 39) abst. C. A. 1931, **25**, 3161; J. S. C. I. 1931, **50**, 107-B.
2. K. Atsuki and H. Sobue, J. S. C. I. (Japan), 1930, **33**, (Suppl. Binding) 511; abst. C. A. 1931, **25**, 4120.
3. J. Text. Inst. 1923, **14**, 32; abst. J. S. C. I. 1923, **42**, 221-A.
4. J. Text. Inst. 1922, **13**, 237; abst. J. S. C. I. 1923, **42**, 52.

when immersed in NaOH solutions is about equal to the volume of liquor absorbed, the cuticle of the fiber thus setting a limit to the swelling of the cellulose within. The ratio of absorbed NaOH to absorbed water is greater than the ratio of NaOH to water in the solution in which the cotton is immersed, and the amount of preferential absorption of NaOH is roughly proportional to the concentration of the alkali solution. Very marked hysteresis in the shrinkage of cotton fibers on replacement of mercerizing solutions by weaker solutions occurs.

The action of hot, dilute sodium hydroxide solutions on modified cellulose has been studied by D. Clibbens, A. Geake and P. Ridge[1], they finding that oxycelluloses suffer a considerable fall in viscosity in cuprammonium solution after boiling 6 hrs. with 1% NaOH solution, while hydrocellulose and normal bleached cotton is but slightly affected. The magnitude of this fall varies with the method of oxycellulose formation, but is very great for neutral hypochlorite oxycellulose—the most frequently occurring type of technically oxidized cotton. The percentage loss by weight of modified cottons after 4 hrs. treatment with boiling 1% NaOH under atmospheric pressure is about six times the copper number when the latter does not exceed 2.5, irrespective of the manner of modification[2].

According to I. Fukushima and Y. Takamatsu[3] the solubility of cellulose in NaOH solutions increases with decreasing temperature, and they have shown maxima for 10, 8, and 7-8 vol./% solutions respectively at 20°, 7° and —10°. Maximum solubility coincides with maximum swelling at 1° in an 8 vol./% solution. Maximum contraction of cellulose occurs with 10% and 12% solutions at 20° and 4° respectively, and contraction also increases with decreasing temperature. Contraction appears to be intimately as-

1. J. Text. Inst. 1927, **18**, 277; abst. J. S. C. I. 1927, **46**, 870-B.
2. C. Birtwell, D. Clibbens and A. Geake, J. Text. Inst. 1928, **19**, 349; abst. J. S. C. I. 1929, **48**, 90-B.
3. Cell. Ind. (Tokyo), 1929, **5**, 255; (English Abstract, 1929, 27); abst. C. A. 1930, **24**, 5151; J. S. C. I. 1930, **49**, 96-B.

sociated with solubility and swelling, and it appears that in mercerization, contraction and dissolution take place before swelling. The viscosity of solutions of regenerated cellulose in cuprammonia increases with increasing solubility of the cellulose during mercerization, i.e. with increasing removal of hemicellulose.

M. Chilikin[1] explains the phenomena of mercerization (swelling accompanied by a change in colloidal state) and absorption of NaOH by cellulose, by considering the cellulose to be a 2-phase system consisting of a crystalline network in an amorphous base. Adsorption from dilute NaOH solutions follows the law of adsorption, which holds also for adsorption by the mercerized cellulose. Mercerized cellulose absorbs more NaOH from aqueous-alcoholic solutions than does ordinary cellulose.

The swelling of cellulose in caustic soda, as G. Blanco[2] and G. Collins and A. Williams have pointed out[3], primarily depends upon the length and thickness of the fiber, increasing rapidly with increasing concentration, but falling off at the higher strengths. They are not in agreement with E. Heuser[4] that the ability of alkalis to induce swelling in cellulose is greater with increasing alkali conductivity. E. Heuser considers the law of hydration of ions as a means to explain decrease in swelling going from lithium hydroxide to caesium hydroxide[5] and also in concentrated alkali solution, a view concurred in by R. Lorenz[6].

It is generally conceded that swelling reaches its maximum when the electrolyte concentration is equivalent to the

1. J. Appl. Chem. (Russia), 1929, **2**, 739; abst. J. S. C. I. 1930, **49**, 610-B; Zhur. Prikladnoi Khimii, 1930, **3**, 221; abst. C. A. 1930, **24**, 3899.
2. Ind. Eng. Chem. 1928, **20**, 926; abst. C. A. 1929, **23**, 971; Pulp & Paper Mag. 1929, Jan. 3, 11.
3. J. Text. Inst. 1923, **14**, 287; abst. C. A. 1924, **18**, 474.
4. Cellulosechem. 1925, **6**, 19.
5. Zts. ang. Chem. 1924, **37**, 1010; abst. J. S. C. I. 1925, **44**, 94-B.
6. Papier Fabrikant. 1925, **23**, 129.

combining capacity of the cellulose[1], O. Faust[2] finding maximum swelling with 9.5-10% NaOH by weight, irrespective of the temperature. During swelling, it appears a contraction of the fiber along the long axis takes place, explainable on the assumption that the cellulose fiber crystallites which lie in rod shapes, are liquefied or softened and tend to assume a sphere[3]. Swelling ruptures the cellulose crystals and at least partially destroys the material which held them together in their natural state.

W. Bovard[4] favors the colloidal theory of hydration in which cellulose is assumed to possess a sponge-like structure comprising small particles united by surface tension or capillary forces, water being a continuous phase between the particles. If this is so, hydration is governed by the absorption of the hydroxyl ion by cellulose from caustic solutions. Metallic hydroxides[5], principally NaOH, exert on normal or unmodified cellulose, four possible influences: swelling and hydration, chemical combination of alkali hydroxide with cellulose, and degradation of the cellulose molecule. Undoubtedly under actual conditions two or more of these factors enter into the change. J. Mercer[6], J. Gladstone[7], E. Thiele[8], W. Vieweg[9], Lindemann[10], W. Norman[11], W. Traube[12], and K. Hess[13] believe in the formation of a chemical compound between cellulose and the alkali, in

1. R. Herzog, Kolloid. Zts. 1926, **39**, 98; abst. J. S. C. I. 1926, **45**A, 793.
2. Cellulosechem. 1926, **7**, 153; abst. J. S. C. I. 1926, **45**, 107-B.
3. W. Gordon, Kolloid Zts. 1926, **39**, 107; abst. J. S. C. I. 1926, **45**, 627-B.
4. Paper, 1918, **22**, 11; abst. C. A. 1918, **12**, 1251.
5. G. Payras, Rev. gen. Mat. Plas. 1926, **2**, 759; 1927, **3**, 3; abst. C. A. 1927, **21**, 1794.
6. Brit. Assoc. Reports, 1844, II, 32. E. P. 13296, 1850; abst. Dingl. Poly. 1850, **121**, 438; 1851, **122**, 318; Jahr. Chem. 1851, **4**, 747.
7. J. C. S. 1853, **5**, 17; abst. Phil. Mag. 1853, **5**, 313.
8. Chem. Ztg. 1901, **25**, 610; abst. J. S. C. I. 1901, **20**, 890.
9. Ber. 1907, **40**, 3876; abst. J. S. C. I. 1907, **26**, 1157.
10. Dissertation, Dresden, 1909.
11. Chem. Ztg. 1906, **30**, 584; abst. J. S. C. I. 1906, **25**, 652.
12. Ber. 1922, **55**, 1899; abst. J. S. C. I. 1922, **41**, 587-A.
13. Ann. 1923, **435**, 1; Zts. ang. Chem. 1925, **38**, 230.

contradistinction to the views of O. Miller[1], R. Joyner[2] and A. Leighton[3] who view alkalicellulose from a colloidal chemistry viewpoint as an adsorption phenomenon.

Since the property of hydration exhibited by cellulose is basically influenced by the condition or kind of cellulose[4], it becomes necessary to select a uniform product of high purity with low ash and low oxycellulose content. Much of the lack of corroboration in results published by earlier investigators appears to be due to a lack of appreciation of the importance of this preliminary step. This selection becomes particularly important when one remembers that in comparing the behavior of different celluloses, concentration of NaOH at which quantitative formation of alkalicellulose takes place, at which the X-ray diagram of cellulose disappears, and at which maximum swelling is obtained, varies with different celluloses.

In general, chemists concur that an alkalicellulose is formed, explanations and deductions having been made in the majority of instances on chemical means only, and neglecting the more intimate knowledge gained through X-ray spectrography, as evidenced by the contributions of R. Herzog and B. Londberg[5] and Clark[6]. The speed of NaOH absorption by cellulose is extremely rapid with caustic of mercerizing concentration, time of immersion beyond 10 min. appearing not to materially influence absorption, F. Dehnert[7], P. Karrer[8] and S. Liepatoff[9] showing that ad-

1. Ber. 1907, **40**, 4903. See also Ber. 1908, **41**, 4297; abst. C. A. 1909, **3**, 650.
2. J. C. S. 1922, **121**, 2395; abst. J. S. C. I. 1923, **42**, 90-A.
3. J. phys. Chem. 1916, **20**, 32; abst. C. A. 1916, **10**, 824; J. S. C. I. 1916, **35**, 249.
4. C. Beadle and H. Stevens, 8th Inter. Cong. Appl. Chem. 1912, **13**, 25; abst. J. S. C. I. 1912, **31**, 102.
5. Ber. 1924, **57**, 329; abst. J. S. C. I. 1924, **43**, 250-B.
6. Technical Assoc. Papers, Series X, 63.
7. Cellulosechem. 1924, **5**, 19. See also F. Dehnert and W. Koenig, Cellulosechem. 1924, **5**, 107; abst. C. A. 1924, **19**, 1050.
8. Cellulosechem. 1921, **2**, 216. See also Cellulosechem. 1921, **2**, 125; abst. J. S. C. I. 1922, **41**, 170-A.
9. (S. Lipatov), J. Russ. Phys. Chem. Soc. 1925, **57**, 48; abst. C. A. 1926, **20**, 2771. Kolloid Zts. 1925, **36**, 149.

sorption is completed in a comparatively few minutes—at least to the extent of above 95%.

Maxima for hydration and NaOH absorption takes place at greater concentration as the temperature rises, the extent to which the two curves differ from one another indicating change in composition due to absorption. Results obtained show that the mother-liquor concentration point of maximum hydration for any definite temperature corresponds roughly with the point at which there is osmotic equilibrium—i.e., the point at which no difference is discernible between the composition of the absorbed liquor and the surrounding solution. It has been demonstrated that difference in absorption in NaOH at different temperatures is not so great in cellulose of low caustic solubility[1].

The absorption of NaOH by cellulose is increased by the addition of sodium salts[2], sodium carbonate being most pronounced and sodium sulfate the least. The bicarbonate and phosphate also cause decrease in absorption. The degree of absorption is unaffected by sodium chloride or carbonate when using caustic concentrations below 12%, the salt concentration not being affected by the presence of cellulose. There is not unanimity of opinion as to the exact effect of salts as evidenced by the findings of J. Huebner[3], O. Miller[4], and R. Joyner[5]. The latter concludes KCl is more powerful than NaCl, owing probably to its slightly increasing the hydroxyl concentration, and also to a raising of the potential of the hydroxyl ions, or to specific action on the cellulose.

Sodium hydroxide absorption by cellulose at the same temperature is greater in ethyl alcohol solution than in water, and increases in direct proportion with increase in

1. C. Schwalbe and G. Robinoff, Zts. ang. Chem. 1911, **24**, 256; abst. C. A. 1911, **5**, 1838.
2. M. Numa, Cell. Ind. Tokyo, 1925, **1**, 87; abst. C. A. 1926, **20**, 2247.
3. J. S. C. I. 1909, **25**, 228; abst. C. A. 1910, **4**, 1241.
4. Ber. 1908, **41**, 4302; abst. C. A. 1909, **3**, 650.
5. J. C. S. 1922, **121**, 2395; abst. J. S. C. I. 1923, **42**, 90-A.

alcoholic content[1]. G. Kita[2] has indicated that the influence of alcohol on NaOH solution is negligible for lower alkali concentrations. J. Katz[3] in his work on the X-ray structure of mercerized cellulose used aqueous-alcoholic NaOH, because there is then complete proportionality between the amount of alkali taken up and the solution concentration. In determining the heat of reaction between cotton and NaOH of different concentration, T. Barratt and J. Lewis[4] found the curve shows a sharp rise with 10-15% NaOH, then climbs less and almost on a straight line to 30% NaOH, when it rounds off. Increased heat liberation during constant absorption is explainable by the fact that concentrations of 15-30% NaOH are accompanied by an enlargement of the cellulose grating, which indicates a breaking up of the molecular structure. The cause of heat development may be due to this intermolecular swelling.

It has been shown by X-ray measurements[5] that concentrations of NaOH lower than 8.5% would have no marked chemical action on cotton cellulose. F. Dehnert and W. Koenig[6] found no increase in caustic absorption by repeated mercerization, as would take place if depolymerization is brought about by mercerization. W. Vieweg[7] considers ageing of alkalicellulose as a colloidal modification of the cellulose. According to J. Huebner and E. Wootton[8], the maximum affinity of cotton for dyestuffs is apparent when mercerizing with 31-32% NaOH, and the greatest shrinkage with 19-20% NaOH, luster being explained as

1. J. D'Ans and A. Jaeger, Kunstseide, 1925, **7**, 252. J. Briggs, Chem. Ztg. 1910, **34**, 455; abst. J. S. C. I. 1910, **29**, 622.
2. G. Kita, T. Mazume, T. Nagashima and I. Sakrada, Cellulosechem. 1926, **7**, 125; abst. C. A. 1927, **21**, 1705. Kunst. 1926, **16**, 69; abst. C. A. 1926, **20**, 3079.
3. Zts. Elektrochem. 1926, **32**, 125; abst. C. A. 1926, **20**, 3565.
4. J. Text. Inst. 1922, **13**, 113; abst. J. C. S. 1922, **122**, i, 526.
5. J. Katz, Zts. Elektrochem. 1925, **31**, 157. See also Zts. Elektrochem. 1926, **32**, 269; abst. C. A. 1926, **20**, 3087.
6. Cellulosechem. 1924, **5**, 107; 1925, **6**, 1; abst. C. A. 1925, **19**, 1050; J. S. C. I. 1925, **44**, 200-B.
7. Zellstoff u. Papier. 1922, **2**, 18; abst. C. A. 1922, **16**, 2599.
8. J. Soc. Dyers Col. 1925, **41**, 10; abst. C. A. 1925, **19**, 1350; J. S. C. I. 1925, **44**, 167-B.

due to a combination of shrinkage, swelling, and untwisting of the cotton fibers during mercerization. This conforms to the work of J. Rumbold[1] who found the maximum effect in alkali absorption to be with 20% NaOH.

E. Percival, A. Cuthbertson and H. Hibbert[2] have studied the absorption of NaOH by cellulose over a wide range of concentrations at 25° by a carefully controlled method of washing, thus avoiding inaccuracies associated with the use of indicators. Evidence of chemical compound formation between 12.5-21.5% NaOH concentrations were found, the compound being regarded as resulting from the interaction of 1 mol. NaOH with each anhydroglucose unit of the cellulose. Maximum absorption of water during the action of alkali upon cellulose is shown to take place at an alkali concentration of 14% by weight at 25°, which corresponds with the concentration at which maximum swelling takes place.

T. Nakashima[3] has made extractions of cotton cellulose paper and sulfite paper with 10% NaOH solutions, the first extractions consisting of 2-3% hemicellulose, then the amount rapidly falls off to a small constant quantity, 0.03-0.06% for each successive extraction. He found that ageing in an atmosphere of hydrogen causes but little oxidation[4]. It is the opinion of S. Lipatov and N. Sokolova[5] that in alkaline solutions of cellulose, the molecules of the latter are covered by a unimolecular layer of water.

In a NaOH solution to which ethyl alcohol has been added, a maximum amount of combined alkali is attained with 10-20% NaOH, and remains constant with further increase in alkali concentration. The higher the alcohol

1. J. A. C. S. 1930, **52**, 1013; abst. C. A. 1930, **24**, 1971; J. S. C. I. 1930, **49**, 749-A.
2. J. A. C. S. 1930, **52**, 3257; abst. C. A. 1930, **24**, 4627; Cellulose 1930, **1**, 221.
3. J. S. C. I. Japan, 1930, **33**, 388. See also Cellulose Ind. (Tokyo) 1929, **5**, 199; abst. C. A. 1930, **24**, 2288.
4. T. Nakashima, J. S. C. I. (Japan), 1929, **32**, Suppl. Bind. 336; abst. C. A. 1930, **24**, 4930.
5. J. Russ. Phys. Chem. Soc. 1930, **62**, 1785; abst. C. A. 1931, **25**, 4120; J. S. C. I. 1931, **50**, 426-A.

percent, the lower is the alkali concentration at which the maximum is attained. A. Hall[1] believes that the action of NaOH on cellulose develops within it a greater reactive surface, with a consequent greater activity to moisture, acids and oxidizing agents. He has described mercerization experiments on mixed cellulose and viscose fabrics, i.e. upon normal and regenerated cellulose in the same alkaline bath[2].

An experimental method has been described[3] for the determination of the lattice constants of cellulose hydrate with greater accuracy than hitherto possible. The quantity of NaOH absorbed by cellulose at 20-22° increases with concentration up to 4-5*N*. For 5-8*N*, the quantity absorbed corresponds with the formula $C_{12}H_{20}O_{10}$.NaOH, and for 9-10*N* with $(C_6H_{10}O_5)_8$.5NaOH, the rate of reaction being maximal at 5*N*.[4]. D. van der Want[5] has developed a new method for the study of the system NaOH-cellulose-water, by introducing an inert material as sodium chloride or sod-

1. Cellulose, 1930, **1**, 144; abst. C. A. 1931, **25**, 3826.

2. A. Hall, Cellulose, 1930, **1**, 118, 252; abst. C. A. 1931, **25**, 4700. J. Soc. Dyers Col. 1929, **45**, 171. Dyer, Calico Printer, 1927, **57**, 30; abst. C. A. 1927, **21**, 1358.

3. A. Burgeni and O. Ktatky, Zts. Physikal. Chem. 1929, **B4**, 401; abst. C. A. 1930, **24**, 1500; J. S. C. I. 1929, **48**, 1132-A. Films of higher orienting power than usual were prepared by converting cellulose xanthate into cellulose hydrate. The *X*-ray analysis attempts to estimate the statistical symmetry of the crystalline aggregates, the crystalline arrangement, *i.e.*, the position of the translation lattice of the aggregates relative to the macroscopic form of the film, and the translation group of single crystals. It is assumed that as the statistical symmetry of the xanthate film is rhombic holohedral (anisotropic class 4), that of the hydrate film will be the same. This is proved by *X*-ray observations. As regards the crystalline arrangement, it may be described to a first approximation as a twin crystal with two mirror images, monoclinic in structure, one on each side of the plane of symmetry. The diagonal axis coincides with the direction of extension. The plane A_0 makes an angle of between 0° and 15° with the plane of symmetry. The exact determination of the crystalline arrangement is also attempted. To a first approximation the following conclusions are reached with regard to the translation lattice. A_0, A_3 and A_4 are probably unique planes in the lattice. The angle between A_3 and A_4 is between 20° and 45°. The angle between A_0 and A_3 and A_4 is larger than 45°. The translation lattice has rhombic or monoclinic symmetry.

4. F. Bogoyavlenski, J. Appl. Chem. Moscow, 1929, **2**, 167; abst. J. S. C. I. 1929, **48**, 976-B. See W. Schramek, C. Schubert and H. Velten, Cellulosechem. 1931, **12**, 126; abst. C. A. 1931, **25**, 5981.

5. Chem. Weekblad, 1931, **28**, 507; abst. C. A. 1932, **26**, 358.

ium iodide into the system. The results show that the quantity of combined NaOH increases, and the quantity of combined water decreases, with increasing NaOH concentration, the combination being solely one of absorption.

G. Champetier[1] determined the amount of sodium in samples of cotton left under constant conditions with NaOH solutions of varying concentrations, and by plotting the results against the NaOH concentration, four points were obtained corresponding to the following compounds: 2 (of cellulose) to 1 (of NaOH); 3 to 2; 4 to 3; and 1 to 1; indicative to him that the fixation of the NaOH by cellulose proceeds by a discontinuous series of definite molecular combinations. Interaction of sodium with cellulose in dry liquid ammonia at its boiling point yields rapidly the monosodio-derivative, Na $C_{10}H_6O_5$, the theoretical amount of hydrogen being evolved. Further reaction is then slow, but yields eventually the Na_3-derivative[2].

The cross-sectional area of regenerated cellulose fibers from viscose when immersed in water increases very rapidly, independent of the temperature, to a constant value after about 1 hr.[3]. When immersed in alkali solutions of various concentrations, the cross-sectional area rapidly increases with augmenting alkali concentration up to 9.7%, above which it decreases, the rate of decrease becoming less as the concentration of alkali increases[4]. G. Collins has given a summation of the literature on the swelling of cotton cellulose[5], with appended bibliography of 200 references.

Theory of Ageing of Alkalicellulose. In the viscose rayon industry, the theory and principles of alkali-

1. Compt. rend. 1931, **192**, 1593; abst. C. A. 1931, **25**, 4701; J. S. C. I. 1931, **50**, 941-A.
2. P. Scherer and R. Husser, J. A. C. S. 1931, **53**, 2344; abst. J. S. C. I. 1931, **50**, 1041-A; Ann. Rep. S. C. I. 1931, **29**, 104.
3. G. Saito, J. S. C. I. Japan, 1931, **34**, 437; abst. C. A. 1932, **26**, 2587; J. S. C. I. 1932, **51**, 140-B.
4. H. Gray, C. Staud and J. Fuess, Ind. Eng. Chem. 1930, **22**, 1018.
5. J. Soc. Dyers Col. 1923, **12**, 303, 669; J. Text. Inst. 1923, **14**, 264-T; abst. J. S. C. I. 1923, **124**, i, 1065.

cellulose maturation have long been recognized as a most important and delicate step. It appears in the cellulose ether art insufficient attention has been paid to this step, and it is only until comparatively recently that rigid control of the ageing of alkalized cellulose has been accorded the study and attention which its relative importance merits. Generalizations shown applicable in cellulose ester (viscose) formation, in the main, are equally applicable in cellulose ether production.

The period elapsing between formation of alkalicellulose and commencement of the etherification step has been variously termed "ageing," "maturing" and "ripening," although the latter time, in viscose manufacture, is more appropriately reserved for the period which elapses between cellulose xanthation and the spinning of the viscose solution. During this period when the alkalicellulose in a fluffy condition and fine state of division, technically called "crumbs" from a resemblance to bread crumbs, difficultly explainable changes take place which may be regarded as a degradation of cellulose in which oxygen plays little or no part, for the alkalicellulose is stored in tightly sealed metal cans. In general, the more thoroughly the alkalicellulose is freed from NaOH solution, the more rapidly does maturing progress. The higher the temperature during the ageing period, and the longer maturing is prolonged, the lower will be the viscosity of an etherified cellulose produced therefrom, and this generalization finds a parallel in the viscose industry as shown by the results of B. Rassow and M. Wadewitz[1], where the maturing was carried out at 20°, 56°, 0° and 10°, the length of time being 1, 1, 48, and 48 hrs., and the viscosity at the end of the period expressed in seconds was 202, 46, 93 and 59. The longer the ageing time of alkalicellulose at any given temperature, the smaller the amount of regenerated cellulose isolatable therefrom.

It is a fact that the time of ageing and the temperature during the ripening period exert little influence on the pro-

1. J. prakt. Chem. 1923, **106**, 266; abst. C. A. 1924, **18**, 1568.

portion of combined alkali in the alkalicellulose, but does materially lower the viscosity of the cellulose ether produced therefrom, and also diminishes the strength of the ether produced when dissolved and cast into film form or extruded into filaments.

The primary practical points in the ageing of alkalicellulose of import from the viewpoint of subsequent etherification are:

1. During the ageing of alkalicellulose, the soda solubles increase to a marked degree, and the increment of oxycellulose to only a slight degree.

2. Ratio of copper number to hemicellulose in reject soda (used mercerizing solution) is as the ratio between these two bodies in wood pulp, indicating that very little oxidation occurs in the steeping operation, primarily because the cellulose is *immersed* in NaOH solution during the mercerizing time.

3. The chief reaction during the ageing of alkalicellulose is one of hydrolysis secondarily accompanied by a negligible amount of oxidation, where the process is properly carried on.

4. If the ageing period is too short, viscosity of the dissolved cellulose ether is too high, the degree of solubility diminishes in a named solvent or solvent combination.

5. The length of time of alkalicellulose ageing is not materially influenced by the amount of solid NaOH added thereto as a portion of the etherification step.

6. Alkalicellulose prepared from cotton requires a longer ageing period than that prepared under comparable conditions from wood pulp.

7. Local overheating in the alkalicellulose storage cans must be guarded against during the ageing period, and this may be obviated by periodically rolling or otherwise agitating their contents. The process of ageing is accompanied by the development of heat, usually the rise is 2-3° during the earlier part of the ageing cycle, dropping to normal after the elapse of about 40 hrs.

It is claimed[1] that maturation of alkalicellulose may be retarded or arrested(?) by conducting the operation either in the presence of inert gases or in an atmosphere free from oxygen, or in a vacuum. Alternatively, the maturation may be accelerated by the employment of an atmosphere of oxygen or in one which is rich in this gas, but it is generally conceded that any material oxidation of the alkalicellulose results in the production of a cellulose ether or a viscose of reduced tensile strength. P. Waentig[2] considers ripening to be a chemical process.

Diffusion experiments made by D. Krueger[3] show that the ageing is accompanied by a decrease in size of the cellulose aggregates. An indication of the degree of ageing of a sample of alkalicellulose may be obtained by nitrating the product, dissolving the ester in acetone and determining the degree of diffusion against a standard sample, and the relative viscosity of the acetone solution obtained. Using a nitrating acid of 71.7% sulfuric acid, 18.7% nitric and 9.6% water, samples were withdrawn at intervals from cellulose undergoing the alkaline treatment with the following results: duration of immersion 1.5, 28, 76, 118 hrs.; copper number (Braidy method) 1.0, 0.8, 0.7, 0.8; relative viscosity of acetone solution of the corresponding nitrocellulose (1.5%) 20.8, 12.7, 8.4 and 6.4.

R. Tomahisa[4] matured alkalicellulose at 12°, 20° and 25° for varying periods up to 72 hrs., then xanthated, and the resulting viscose solutions after ripening for varying periods were spun into a normal setting bath. A study of the physical properties of the filaments obtained showed that (a) the longer the period of maturing of the alkalicellulose, particularly at the higher temperatures, the longer

1. Soie de Chatillon, E. P. 250617; abst. C. A. 1927, **21**, 1355.
2. Text. Forsch. 1921, **3**, 154; abst. C. A. 1922, **16**, 2988; Chem. Tech. Uebers, 1922, **46**, 97. Cellulosechem. 1929, **10**, 81.
3. Cellulosechem. 1927, **8**, 1; abst. C. A. 1928, **22**, 1235; J. S. C. I. 1927, **46**, 164-B; Caout. et Gutta. 1927, July 15, 13640; Rayon, 1928, Apr. 30, 24.
4. Cell. Ind. Tokyo, 1928, **4**, 113; abst. C. A. 1929, **23**, 3084; J. S. C. I. 1928, **47**, 743-B.

must the viscose solution be allowed to ripen to make it spinnable, and the thicker are the filaments; (b) at the lower temperatures, the time of maturing of alkalicellulose has no great influence on the maximum strength of the thread, but at higher temperatures, the more highly matured alkalicelluloses give a markedly weaker thread; (c) for production of strongest threads alkalicellulose should be matured for a moderate time at a not too high temperature; and (d) immature alkalicellulose gives viscose forming threads of increased elasticity but of diminished strength.

It has been shown[1] that maturing alkalicellulose in hydrogen instead of air gives a product showing higher viscosity, is more easily spun and gives threads of greater tensile strength. The use of hydrogen on a commercial scale is entirely too expensive. Maturing alkalicellulose in the pressed-out condition, it is reported, results in slightly higher viscosity of the viscose prepared therefrom, than when cellulose is steeped for a longer period, pressed out and used immediately, which is never done insofar as the author is aware[2].

It has been the observation of G. Kita and I. Sakurada[3] that during the ageing of pressed alkalicellulose, oxidation as determined by an increase in the copper number proceeds irrespective as to whether the air is excluded or has free access, or is replaced by hydrogen. This oxidation they claim is caused by oxygen absorbed during pressing, but remembering that alkalicellulose is surrounded by alkali solution during the major portion of the pressing period, we are of the opinion that it is caused (if at all) by oxygen absorbed during the disintegration of the alkalicellulose, an

1. G. Kita, R. Tomihisa and J. Onohara, Cell. Ind. Tokyo, 1928, **4**, 235; abst. C. A. 1929, **23**, 3084.
2. *Ibid.* Cell. Ind. Tokyo, 1928, **4**, 293; abst. C. A. 1929, **23**, 4064; J. S. C. I. 1929, **48**, 125-B. The effect of varying the periods of steeping and maturation of the alkali cellulose on the physical properties of the resulting viscose are examined.
3. Sci. Papers Inst. Phys. Chem. Research, Tokyo, 1929, **12**, 1; abst. C. A. 1930, **24**, 722.

operation which requires about 2 hrs. time, as against a normal pressing period of about 15 min. They report that viscose made from cellulose which was immersed in alkali for 25 hrs. had a slightly lower viscosity and formed a thread slightly bulkier, stronger in tension and greater in stretch. At low temperatures (12°) duration of ageing period exerted no great influence on the maximum tensile strength of the thread, while at 25° the influence was marked. With a longer immersion (mercerization) and shorter ageing period in air, the resulting thread strength was comparable with that from alkalicellulose aged in hydrogen.

A rather comprehensive study has been made of the preparation and ageing of alkalicellulose by B. Rassow and M. Wadewitz[1], and the relation to viscosity (of viscose). The preparation of alkalicellulose being impossible by purely chemical means, was studied in three ways, the preparative, analytical and direct. Two gms. cotton (ash 0.08%, α-cellulose 98.1%, pentosans 0.76%, copper number 0.06) were treated with 20 cc. 18% NaOH for 30 min., then pressed to 6 gms. The mass was then transferred to a 50 cc. separatory funnel and shaken with 25 cc. absolute alcohol. After 2 hrs. the alcohol was separated and titrated with 0.5 *N* acid. Repetition of this extraction process showed that the amount of NaOH extracted decreased gradually from 0.16 gm. to practically zero after 13-15 extractions. Water completely decomposed the alkalicellulose almost instantly. Assuming the complex, $C_6H_{10}O_5$.NaOH, 100 gms. cellulose should take up 24.7 gms. NaOH. The ratio of amount of NaOH actually combined to this value is termed the molecular ratio. With various concentrations of NaOH, the following molecular ratios were found: 10% NaOH, 0.17; 15%, 0.52; 20%, 0.68; 21%, 0.82; 25%, 0.89; 30%, 0.93; 35%, 0.99; 40%, 1.05, the values being determined after a 4 hr. ethyl alcohol extraction.

1. J. prakt. Chem. 1923, **106**, 266; abst. C. A. 1924, **18**, 1568.

It was found that time of mercerization has little influence on this value, the same results being obtained after 24 hrs. as after 5 min., which seems remarkable. The nature of the cotton exerts a marked influence, two samples under identical conditions giving values of 0.69 and 0.80. If the moist alkalicellulose from a 12-18% NaOH or a 25% KOH is distilled with toluene to remove the water, the same product results as with a 30% NaOH. Action of sodium ethylate upon cellulose does not give alkalicellulose, although this results by the action of water to the system. The most noticeable difference between unaged and aged alkalicellulose is the viscosity of its solutions, and of its reaction products (nitrocellulose). Nitrocellulose from unaged alkalicellulose showed a 324 seconds viscosity, that from the aged product, 157 seconds.

B. Rassow[1] has reported some very interesting results when air-dried purified cotton was treated with three different NaOH concentrations as follows: 9% (which has no mercerizing action), 18% (normal mercerizing lye), and 36% (to determine the action of excessively strong lye). The alkalicellulose was pressed out to 300% in all cases, aged in a thermostat at 20° in diffused daylight for various lengths of time, and then the alkali either washed out, or directly treated with reagents. The results pointed to a progressive degradation of the large molecule of cellulose as the intensity of the ageing increases, as already pointed out by W. Vieweg[2], C. Schwalbe[3] and E. Berl[4].

His generalizations are as follows:

1. When using lye of low concentration the cotton ca nscarcely be distinguished from untreated cellulose either with the naked eye or under the microscope. A peculiar smell only is present, like boiling soap.

2. With 18% lye the fibers show jagged broken edges

1. Zts. ang. Chem. 1929, **42**, 618. Textilber. 1929, **10**, 787; Melliand, 1930, **1**, 1712, 1828; abst. C. A. 1930, **24**, 3357.
2. Ber. 1907, **40**, 3876; abst. C. A. 1908, **2**, 178.
3. Chemie der Zellulose, I Ed., 1911, 186.
4. Zts. Schiess. Sprengs. 1909, **4**, 81; abst. C. A. 1909, **3**, 1926.

under the microscope; they have also untwisted due to the mercerizing action. With a longer period of ageing, the fiber continues to become more spread out and more brittle.

3. With 36% lye the fiber becomes crumbly like hydrocellulose, and large amounts go into solution as mucilage. These materials can be largely precipitated by alcohol or acids. Similar ageing effects can be obtained with quaternary organic bases as tetraethylammonium hydroxide, in sufficiently concentrated solution.

4. Practically no oxidation takes place operating under the conditions prevailing in the commercial manufacture of viscose.

5. The stronger the alkali concentration and the longer the time of ageing, the more the pentosans are dissolved out, but do not entirely disappear.

6. Hygroscopicity of the products increases greatly with ageing. The capacity of the cellulose molecule for taking up water increases, the same as its reactivity in general as it is opened up.

7. In a series of samples aged at —15°, it was found that mercerization with 9% NaOH and ageing at —15°, has the same effect as 18% NaOH aged at 20°, and 18% NaOH has the same effect as 36% NaOH aged at 20°, at —15° a distinct mercerizing effect being noticeable with 9% lye, which is lacking when working at room temperature.

8. By the nitration of various aged alkalicelluloses, it was determined that the original cellulose molecule splits up into quite distinctly different portions on ageing, some becoming soluble or oxidizable with consequent loss in yield of nitro product, and residual molecules, which on esterification take up the same number of nitric acid group as native cotton.

9. Upon acetating alkalicellulose, the color of the film formed on evaporating a 2% solution in ethyl acetate becomes darker as ageing increases, while its physical prop-

erties become correspondingly poorer, and at the end it can be pulverized in a mortar.

A composite statement of the more important results obtained is shown in Table I.

Table I. Ageing of Alkalicellulose.

Expt.	Time Hours	% NaOH in Lye	Regenerated Cellulose	Cellulose Present	Copper Number		Hydrolysis Number	
					Direct	After Rinsing	Direct	After Rinsing
0				...	.	(.06)	.	(6.25)
1a	48	9	99.5	99.4	.11	.20	6.57	9.06
b	96	9	99.5	99.2	.13	.24	6.65	9.41
c	144	9	99.5	99.5	.12	.25	6.72	9.29
2a	48	18	99.0	99.1	.15	.22	6.70	10.0
b	96	18	98.9	99.4	.17	.24	6.35	10.35
c	144	18	98.9	99.2	.16	.24	6.41	10.25
3a	48	36	98.0	99.0	.17	.16	6.35	11.60
b	96	36	89.3	98.0	.16	.28	6.46	11.32
c	144	36	77 6	98.9	.16	.42	6.75	11.67

	Pentosan Content		Hygroscopicity of Cotton		Mixed Acid A		Mixed Acid B	
	Cotton Cellulose Direct	Mercerized and Aged, After Rinsing	Mercerized and Aged at 20°	Mercerized and Aged at 15°	Percent Yield	Percent Nitrogen	Percent Yield	Percent Nitrogen
0		.78	10.35		156.3	10.3	165.8	12.6
1a	.79	.25	14.2	14.4	147.9	10.4	161.7	12.5
b	.77	.22	14.4	16.1	148.4	10.5	159.5	12.6
c	.78	.29	14.3	18.0	146.1	10.1	160.3	12.5
2a	.77	.10	14.5	14.5	142.8	10.2	155.6	12.6
b	.76	.09	16.3	17.1	139.9	10.3	150.5	12.6
c	.78	.09	18.3	20.2	132.2	10.3	146.2	12.6
3a	.74	.08	14.6		130.5	10.3	142.9	12.6
b	.75	.11	17.5		125.7	10.2	135.4	12.6
c	.75	.07	20.4		115.5	10.2	110.8	12.6

Mixed Acid A = H_2SO_4, 60.3%; HNO_3, 18.7%; water 20.0%. B = 63.6%, 19.8%, 16.8%.

G. Kita and I. Sakurada[1] have compared alkalicelluloses aged in the steeped and in the pressed-out condition, and have found that although both are oxidized by the action of air, the oxidation products in the steeped materials are dissolved by the NaOH and removed, whereas in the pressed-out material they remain in the mass. The effects

1. Cellulosechem. 1929, **10**, 113; abst. C. A. 1929, **23**, 5571; J. S. C. I. 1929, **48**, 749-B. See Sci. Papers Inst. Phys. Chem. Research. Tokyo, 1929, **12**, 1; abst. J. S. C. I. 1930, **49**, 279-B.

of ageing for varying lengths of time, of ageing in an atmosphere of air or of hydrogen, and of the time of steeping, on the copper number and spinning properties of the fibers after esterification (or etherification) have been determined. An increase of copper number results on ageing regardless of whether done in closed or open atmosphere of air or hydrogen. In general, however, there is little difference between the properties of viscoses prepared from pressed and from steeped alkalicellulose. In a closed atmosphere of air, the viscosity of the viscose decreases as the time of ageing or the temperature is increased, the fibers are thicker, and the ripening necessary to produce a spinnable product is increased. Under certain conditions, long steeping followed by a short ageing period, yields fibers as strong as those obtained by ageing in hydrogen, and good fibers can also result by ageing for a short time only in a closed atmosphere of air.

In a study of the mechanism of oxidation of alkalicellulose in ageing, K. Atsuki and H. Sobue[1] give four reactions to express the action of alkali on cellulose as follows:

1. $ROH + Na^+ + OH^- + H_2O = RONa + 2H_2O$
2. $ROH + NaH_2O^+ + OH^- = ROH.NaH_2O^+ + OH^-$
3. $ROH.NaH_2O^+ + OH^- = NaH_2O^+ + R(OH)_2^-$
4. $ROH.NaOH = R(OH)_2^- + Na^+ = RO^- + NaH_2O^+$

Essentially the cellulose acquires a negative charge and suffers oxidation. Reactions 1 and 2 take place with alkali concentrations equal to or less than those required for mercerizing; 3 and 4 occurring in more concentrated solutions.

At normal temperature[2], the curve expressing relation between time of ripening and the viscosity of viscose prepared therefrom is hyperbolic in shape, but the lower the temperature the less is its curvature, so that with decreasing temperature the curves approach nearer and nearer to a straight line parallel with the time axis.

1. J. S. C. I. Japan Suppl. Binding, 1930, **33**, 511; abst. C. A. 1931, **25**, 4120; J. S. C. I. 1931, **50**, 478-B.
2. Y. Kami, K. Kitazawa and T. Yamashita, Cell. Ind. Tokyo, 1930, **6**, 55; German Abstract, 1930, 12; abst. C. A. 1930, **24**, 5153.

X-Ray Data on Alkalicellulose. The older ideas of a very highly polymerized molecule for cellulose have within the past ten years been modified on the basis of the Roentgen spectrographic diagram which reveals particles or molecules in three-dimensional symmetry, leaving no room for more than four hexose residues[1]. When cellulose is swollen in a solution of alkali hydroxide the interference streaks in the Roentgen spectrum characteristic of cellulose gradually disappear as the concentration of alkali is increased and new equatorial bands appear with gradually increasing intensity. The concentration at which the most characteristic cellulose bands totally disappear and the new bands acquire their full development is the same, and coincides with the critical concentration indicated by the flat portion of W. Vieweg's absorption curve, at which chemical combination as alkalicellulose is complete. Moreover, these phenomena are identical with the various alkali hydroxides and appear in the case of lithium, sodium and potassium hydroxides at the concentrations at which equimolecular proportions of alkali are combined.

When the alkalicellulose is decomposed by washing with water the characteristic spectrum of the original cellulose is restored, but the size of the network is distinctly enlarged; at the same time the new band indicative of hydrated cellulose persists, its ultimate intensity depending on the strength of the alkali hydroxide solution and the time of its action. With such hydrated cellulose, when treated with NaOH solutions of increasing concentration, the point at which the intensity of the cellulose spectrum begins to diminish is at a considerably lower concentration than the corresponding point for the original cellulose; i.e., mercerized or hydrated cellulose is more easily attacked.

No appreciable alteration in the Roentgen spectrogram can be detected when cellulose (ramie fiber) is swollen with saline dehydrating agents or with sulfuric or hydroch-

1. J. Katz, Cellulosechem. 1925, **6**, 37; abst. C. A. 1925, **19**, 2273; J. S. C. I. 1925, **44**, 440-B.

loric acid[1], but the characteristic mercerization bands are produced by the alkali hydroxides, cuprammonium solution, and nitric acid, being the irreversible result of swelling by these particular agents. So far as can be detected, these new bands, however produced, have an identical position. The mercerization bands are present in artificial silks from viscose and cuprammonium solutions (both being a regenerated cellulose), and the parallelism of the crystallites in artificial silk is variable according to the conditions (tension) of spinning. In the process of mercerization and washing, cellulose fibers pass through a plastic stage, and if plastic cellulose be subjected to a stretching operation the phenomenon of hydration is partially reversed, in that the increased absorption capacity for water and dissolved substances is diminished; at the same time the parallel orientation of the crystallites is increased. Treatments which have the object of reversing or diminishing the degree of hydration as prolonged storing, heating under pressure or boiling with alcohol, may reduce the absorption capacity of hydrated cellulose, but have no effect on the characteristic mercerization bands of the Roentgen spectrum.

Since hydration may be produced without change in the spectrum of cellulose, and takes place without fading of the new bands, it appears probable these spectrum bands of mercerized fiber are not representative of the transition from cellulose to hydrated cellulose, being probably more indicative of a new chemical substance, possibility being that the cellulose undergoes isomeric modification by the action of the alkali with transposition of an oxygen bridge or opening up of a new hydroxyl.

J. Katz[2] believes the probable explanation of the appearance of new equatorial bands of X-ray photographs of

1. J. Katz and H. Mark, Zts. Elektrochem. 1925, **31**, 105; abst. C. A. 1925, **19**, 1773; J. S. C. I. 1925, **44**, 440-B. Zts. Physikal. Chem. 1925, **115**, 385; abst. J. S. C. I. 1925, **44**, 495-B.

2. Zts. physikal. Chem. 1926, **124**, 352; abst. C. A. 1927, **21**, 1929.

cellulose swollen in alkali solutions is shown in the swelling of cotton with 14% NaOH in which a new spectrogram results, comprising an "amorphous ring" due to the alkali solution itself, within which are two equatorial bands with the form of arcs of a circle. If the swollen fibers are dried, the amorphous ring disappears but the bands remain. Washing out the free alkali with alcohol does not effect the bands, but there also appears new circles and segments of circles, corresponding with an orderly arrangement of the crystallites in the fibers.

The curve representing the adsorption of NaOH from aqueous solution by cellulose[1] shows a flat portion which W. Vieweg[2] has attributed to the formation of a compound. Using aqueous alcoholic solutions of NaOH, the flat portion becomes absent, and a linear relationship appears, thought to indicate the formation of solid solutions of NaOH in cellulose[3]. This evidence favors the view that an alkalicellulose compound is formed also in aqueous-alcoholic alkali solutions, since the observed bands are similar to those found using aqueous solutions. The presence of alcohol exerts little influence on the limiting concentration at which the cellulose spectrum vanishes[4], but slightly hinders the formation of the compound—a fact difficult to reconcile with the observation that alcohol greatly assists the absorption of NaOH by cellulose.

R. Herzog[5] believes the difference between the X-ray diagram of natural and hydrated cellulose fibers may be due to a chemical or a physical change. By giving specimens of cotton the same chemical treatment (nitration and then denitration) but different physical treatment (formation of an artificial thread in the second case), he shows

1. Zts. Elektrochem. 1926, **32**, 125; abst. C. A. 1926, **20**, 3565; J. S. C. I. 1926, **45**, 468-A.
2. W. Vieweg, Ber. 1907, **40**, 3876; 1908, **41**, 3269; abst. J. C. S. 1907, **92**, i, 893; 1908, **94**, i, 857.
3. *Ibid.* Ber. 1924, **57B**, 1917; abst. J. C. S. 1925, **128**, i, 12.
4. J. Katz, Cellulosechem. 1925, **6**, 35; abst. J. C. S. 1925, **128**, i, 639.
5. Ber. 1927, **60B**, 600; abst. C. A. 1927, **21**, 2557.

that in the first instance the X-ray diagram of the natural fiber is obtained again, whereas the second specimen gives the hydrated cellulose pattern. Thus the *hydrated* differs from the *natural* fiber in possessing a physically distorted, though definite, structure. Although the swelling of cellulose during mercerization is reversible[1], this is not the case for the lattice changes which occur.

X-ray diffraction data have been given by O. Sponsler and W. Dore[2] for ramie cellulose which has been subjected to mercerization processes with various strengths of NaOH solution, the evidence showing that there is a critical concentration of the alkali at about 13%, above which the fibers are mercerized, but below which they remain unmercerized. From the diffraction patterns of mercerized ramie cellulose a space lattice has been developed. When compared with the unmercerized lattice, the *c* axis is seen to be unchanged while the *a* and *b* axes have been changed from $a = 5.40$ A units in the unmercerized, to $a = 4.53$ A in the mercerized, and from $b = 6.10$ to $b = 7.61$. The angle between axes *a* and *b* is changed from 90° to 83°. As a result of mercerization, the chains of glucose units are laterally shifted in the wall of the fiber and remain unbroken. Within the chain, the original glucose unit remained unchanged except for a shift of the hydroxyl of the sixth carbon atom. The X-ray diffraction patterns indicate that there is a partial rotation of some of the glucose units about the long axis of the chain. A comparative study of the structures of mercerized and unmercerized cellulose produces additional support to the view that the constituent units of cellulose are united in chains by primary valence linkages[3].

Variation of the X-ray diagrams of natural cellulose by treatment with aqueous, aqueous-alcoholic and alcoholic

1. R. Herzog, Zts. physikal. Chem. 1927, **127**, 108; abst. J. S. C. I. 1927, **46**, 724-A.
2. J. A. C. S. 1928, **50**, 1940; abst. C. A. 1928, **22**, 3291; Pulp & Paper Mag. 1929, Jan. 6, 16.
3. J. Katz, Cellulosechem. 1930, **11**, 17; abst. C. A. 1930, **24**, 6003.

NaOH solutions[1] have been recently investigated by K. Hess and C. Trogus, and, depending on the alkali concentration, two typical X-ray diagrams were observed, one due to alkalicellulose, and the other to alkalicellulose II. The fiber period of alkalicellulose I was 10.4 ± 0.2 A., and of alkalicellulose II (sodium cellulose II) 15.5 ± 0.2 A. Drying does not affect the diagram of II, but I goes over into a third form (alkalicellulose III), differing only in the combined water. This compound is considered identical with the water-free alkalicellulose of G. v. Susich and W. Wolff[2]. Alkalicellulose I is considered to be responsible for the swelling of the cellulose. Sharp fiber diagrams are obtained for potassium cellulose (fiber period 10.2 ± 0.2 A) formed by the action of 18.5% KOH solution on cellulose.

Swelling of Cellulose by Alkali. The intumescence of a solid in a fluid may be regarded as an extension into space while the system still retains rigidity, and may be measured by the ratio of total volume of swollen substance and the interpenetrating medium to the initial volume of the same. In the case of cotton or wood cellulose, there are two distinguishable effects, the true swelling as above outlined, and the change of shape arising from the release of relatively gross mechanical stresses in the cellulose or due to the anistropy associated with the existence of the lumen and of spiral fibrils[3].

Quantitative observations of the swelling of cotton cellulose with various reagents have been published by R. Willows, T. Barratt and F. Parker[4], and R. Willows and R. Alexander[5]; and on the changes in length and cross-section

1. K. Hess and C. Trogus, Zts. physikal. Chem. Abt. B. 1931, **11**, 381; abst. C. A. 1931, **25**, 2282.
2. Zts. physikal. Chem. Abt. B. 1930, **8**, 221; abst. C. A. 1930, **24**, 4399.
3. W. Balls and H. Hancock, Proc. Roy. Soc. 1922, **93B**, 426; abst. C. A. 1922, **16**, 3682.
4. J. Text. Inst. Trans. 1922, **13**, 229; abst. C. A. 1923, **17**, 1151.
5. J. Text. Inst. Trans., 1922, **13**, 237; abst. C. A. 1923, **17**, 1151.

of the hairs in NaOH by J. Mueller[1], E. Knecht and W. Harrison[2], P. Krais[3] and J. Huebner and W. Pope[4]. C. Beadle and H. Stevens[5] have outlined the mechanics of the hydration of cellulose solutions in NaOH, and R. Haller[6] on the microscopic measurement of the swelling of single cotton hairs.

The swelling action of caustic alkalis in the presence or absence of neutral salts on bleached and unbleached soda- and sulfite-cellulose has been determined by J. D'Ans and A. Jaeger[7], by observation of the increase in weight of the cellulose in the form of paper after immersion in the alkaline solutions and drainage from excess of liquor, correction being made for the liquor density. The maximum swelling effect was induced by solutions containing 11-12% NaOH and 15% (wt./vol.) KOH, the swellings being about 11% and 5.5% respectively. Swelling is considerably reduced by the presence of neutral salts and other substances, as sodium chloride, sodium carbonate, ammonia, alcohol, sugar, tannin and gelatin. For example, a 12% solution of NaOH containing 10% NaCl produces a swelling of but 4.9%. Swelling is also reduced by rise in temperature of the caustic liquor, but the effect is less obvious with highly concentrated alkaline solutions. Thus, a 10% NaOH solution produces swellings of 14.6% and 6.6% at 13-16° and 23-25° respectively, whereas under similar conditions the swelling produced by an 18% NaOH solution are 6.6% and 5.9% at these temperatures. Dry cellulose liberates 2.6 cal. per gm. when moistened with 6% water. Over a period of 20 hrs. alkalicellulose saturated with 17% NaOH liberates 0.417 cal. per hr. per gm., whereas under similar conditions during 24 hrs., dry alkalicellulose liberates 0.27

1. "La Turgometrie," Paris, 1917.
2. J. Soc. Dyers Col. 1912, **28**, 224; abst. C. A. 1913, **7**, 3030.
3. Zts. ang. Chem. 1912, **25**, 2649; abst. C. A. 1913, **7**, 894.
4. J. S. C. I. 1904, **23**, 404; abst. Meyer Jahr. Chem. 1904, **14**, 523.
5. 8th Int. Appl. Chem. 1912, **13**, 25; abst. C. A. 1912, **6**, 3013.
6. Kolloid Zts. 1917, **20**, 127; abst. C. A. 1917, **11**, 3441.
7. Kunstseide, 1925, **7**, 252; abst. J. S. C. I. 1926, **45**, 398-B.

cal. per hr. per gm., the rate of heat liberation not being affected by the presence of oxygen. Alkalicellulose heated to 60° and then cooled, liberates no heat on storing.

In the absorption of NaOH by cellulose[1], the influence of temperature is very considerable, and with certain types of cellulose as wood pulps, the solubility of the cellulose has to be taken into account. The absorption by sulfite pulp is somewhat higher than in the case of cotton, but the curves have the same characteristic form and both have horizontal portions between the concentrations above 36 gms. per 100 cc. The absorption curve at 2° has exactly the same shape as that at 23°, but the absolute values of the absorption at corresponding concentrations are considerably higher.

The addition of foreign salts as sodium chloride or carbonate has an influence on absorptions at concentrations up to 12 gms. NaOH per 100 cc., but above that the absorption is increased by the added salt, and rises with the concentration of salt. The concentration of salt or sodium carbonate is not changed in the lye by the presence of cellulose, the solubility of the cellulose in the caustic lye being dependent on the individual cellulose; at 23° it approaches a maximum value at a concentration of about 12 gms. per 100 cc., then sharply falls with increase in concentration. At concentration above 24 gms. per 100 cc. the soluble portion consists almost entirely of gamma-cellulose.

In studying the effect of concentration on the swelling of cotton cellulose in NaOH and KOH solutions, O. Faust[2] found that filter paper at 20° gives results comparable to those for sulfite pulp, the maximum in NaOH solutions being sharper with cotton, and in KOH solutions the maximum values are distinct. This is ascribed to the greater purity and higher α-cellulose content of cotton. In KOH solutions over 40% by weight, there is a sudden large increase in swelling, study of which is limited by the solu-

1. J. D'Ans and A. Jaeger, Cellulosechem. 1925, **6**, 137; abst. J. S. C. I. 1925, **44**, 984-B.
2. Cellulosechem. 1927, **8**, 155; abst. C. A. 1927, **21**, 821; Pulp & Paper Mag. 1927, **25**, #23, 743.

bility of KOH at 20°. Paper is greatly shrunk and thickened, while that swelled to the same extent in 10% NaOH thickens without shrinking. NaOH of above 28% by weight causes shrinkage, but less marked than with concentrated KOH.

The proportion of cellulose dissolved in alkali depends on the amount of cellulose taken[1], it being probable that both adsorption and peptization takes place. The degree of swelling of cellulose in water and alkali is similarly affected, the electrolyte content influencing the degree of swelling[2]. T. Nakashima[3] has taken samples of ground and finely sieved cotton which were treated in graduated tubes with NaOH solutions of varying concentration, and then subsequently centrifuged under standard conditions. The resulting volumes of the cellulose samples were taken as a measure of the swelling incident to treatment. Maximum swelling occurs in 10% solution followed by a decrease and then an increase in 18-35% solutions. The value for 35% strength is greater than that for 10%.

In a study of cellulose and its affinity relations with aqueous solutions, S. Neale[4] found that cotton cellulose swollen in *N*/2 NaOH solution absorbs nearly three times as much alkali as does the unswollen material.

Sodium Hydroxide for Alkalicellulose Formation. Electrolytic NaOH is preferable for alkalicellulose manufacture on account of its higher purity, solid caustic soda as produced for this purpose in the United States at the present time analyzing, NaOH 99.2%, sodium carbonate 0.45%, NaCl 0.18%, sodium sulfate 0.065%, silica 0.016%, ferric oxide 0.0014%, aluminum oxide 0.0028%, CaO

1. A. v. Buzagh, Kolloid Zts. 1927, **43**, 215; abst. C. A. 1928, **22**, 4310.
2. W. v. Neuenstein, Kolloid Zts. 1927, **43**, 241; abst. C. A. 1928, **22**, 4310.
3. J. Cell. Inst. Tokyo, 1929, **5**, 199; abst. Br. Plastics, 1929, **1**, #7, 283; J. S. C. I. 1929, **48**, 917-B.
4. J. Text. Inst. 1930, **21**, 225-T; abst. C. A. 1930, **24**, 6003. J. Text. Inst. 1931, **22**, 320-T. See also J. Text. Inst. 1929, **20**, 373-T; abst. C. A. 1930, **24**, 3110; Rayon Record, 1930, **4**, 98.

0.022% and MgO 0.0005%. It is usually purchased in solution in tank cars rather than in the solid form in drums.

M. Numa[1] is responsible for the statement that the dissolving power of NaOH for the modified cellulose contained in pulp is diminished by the presence of sodium carbonate, while small quantities of both sodium sulfate and chloride behave catalytically in assisting solution, but in large quantities their action is deleterious. The presence of sodium sulfate, even in small quantity, is said to produce a brittle film, but if so, this effect is not noticeable in producing cellulose ethers therefrom.

Caustic soda for mercerization purposes as purchased is seldom filtered. It is usually stored in large iron tanks, the relatively small amount of insoluble impurity therein subsiding and the clear, supernatant alkali liquid being periodically drawn off.

Commercial Production of Alkalicellulose. There is a marked lack of uniformity in the published methods and patented processes for alkalicellulose manufacture in connection with cellulose etherification, so much so, in fact, that in some processes it is difficult to perceive that a satisfactorily etherified cellulose is possible of attainment working with the proportions specified and under the conditions as set forth.

The general method is to treat wood or cotton cellulose with a solution of NaOH of stated composition at a definite temperature for a specified time, remove mechanically excess of alkali until the proportion of alkali to original cellulose has assumed a definite ratio, the alkalicellulose comminuted, perhaps aged, then etherified in this condition or additional alkali added in solid or liquid form, followed by the etherifying step. It should be remembered and allowed for in all etherifying operations, that a sufficient excess of

1. Cellulose Ind. (Tokyo), 1928, **4**, 82; abst. C. A. 1927, **21**, 3458; 1928, **22**, 2055; 1929, **23**, 3083.

free alkali must be present to neutralize the acid liberated from the reaction of the etherifying ester and still preserve an alkaline reaction.

The methods of alkalicellulose manufacture which have received patent recognition will be indicated herein under the headings (1) Lilienfeld, (2) Eastman Kodak, (3) Courtaulds, (4) I. G. Farbenindustrie, and (5) Others, followed by a step-by-step process for alkalicellulose factory production, especially applicable for large scale manufacture of the cellulose ethers.

(1) *Alkalicellulose Manufacture by L. Lilienfeld.* In a process applied for in 1919, 100 of cellulose are impregnated with 500-1000 NaOH solution 18%, and allowed to stand 1-3 days at room temperature. The mass is then freed from alkali solution until a weight of 180-300 is attained, finely divided under cooling, then 200-300 powdered NaOH added and thoroughly incorporated, advisedly with cooling. The final product is a fine, pulverulent, fibrous material suitable for immediate etherification[1]. In proceeding as herein indicated, it is imperative that the mass be cooled to 5° or lower during the incorporation of the solid NaOH with the alkalicellulose, and that the finished material be etherified without undue loss of time, else degradation rapidly occurs with the formation of cellulose ethers deficient in strength in film and filament form.

200 parts sulfite cellulose are impregnated with 1800 parts 9-18% NaOH solution at room temperature[2], allowed to stand 12-24 hrs., then pressed to 500-700 parts, and comminuted. After standing 2-3 days at room temperature, it is etherified under pressure with 25-90 parts ethyl chlo-

1. E. P. 149318; abst. C. A. 1921, **15**, 437; J. S. C. I. 1922, **41**, 10-A. Aust. P. 90080. Dan. P. 29846. Norw. P. 36611. Ital. P. 194922. See also E. P. 311697.

2. E. P. 177809; abst. C. A. 1922, **16**, 3545; J. S. C. I. 1924, **43**, 11-B; Chem. Zentr. 1922, IV, 682; Faserstoffe, 1924, **6**, 10; Caout. et Gutta. 1922, **19**, 11497. U. S. P. 1589607; abst. C. A. 1926, **20**, 3084; J. S. C. I. 1926, **45**, 661-B. D. R. P. 488446; abst. C. A. 1930, **24**, 2599. F. P. 549568; abst. Chim. et Ind. 1923, **10**, 1131. Can. P. 248232; abst. C. A. 1925, **19**, 3163; Aust. P. 83400.

ride for ethylcellulose manufacture. Experience has shown that it is not good practice to allow the cellulose to stand in the large bulk of alkali solution for 12-24 hrs., but that better results are obtained where a considerable shorter time of alkali immersion of cellulose is carried out, impregnation being made more uniform by circulating the NaOH solution during the mercerizing operation.

It has been proposed to dry the alkalicellulose upon formation, but this method, so far as aware, has never been used commercially on account of the cost and the absorption of carbon dioxide and possible oxidation of the alkalicellulose, unless the normal atmospheric air is replaced by an inert gas, which introduces inexcusable cost to the operation. The process recommended[1] comprises impregnating with 18% NaOH solution at below 10°, or treatment of the cellulose with a mixture of dissolved and dry NaOH, the water being preferably removed in a vacuum. The object of the drying treatment is to produce cellulose ethers so highly etherified that their sensitivity towards water is removed, and their solubility in organic solvents increased in range.

In a variation in the above method[2], 100 of sulfite cellulose are impregnated with 900-1000 of 15-18% NaOH solution, allowed to stand 24-72 hrs. (an unduly long period), pressed to 200-250 parts and distintegrated. The material may stand for 2-3 days or dried at once in vacuum or at room temperature to 120-150 parts, equivalent to a water content of 1-5%. Then 100-125 of powdered NaOH are slowly kneaded into the alkalicellulose with cooling, the kneading taking place in the presence of air during 4 hrs. of kneading, whereupon 40-60 parts of water are absorbed. A further 40-60 parts water are then kneaded in so that the total amount of water incorporated is 100 parts. This

1. U. S. P. 1683682; abst. C. A. 1928, **22**, 4246. E. P. 200816; abst. C. A. 1924, **18**, 328; J. S. C. I. 1925, **44**, 67-B; Chem. Zentr. 1923, IV, 808; Faserstoffe, 1924, **6**, 21. Aust. P. 111247.

2. U. S. P. 1683681; abst. C. A. 1928, **22**, 4246; J. S. C. I. 1928, **47**, 811-B. E. P. 200827; abst. C. A. 1924, **18**, 469; J. S. C. I. 1925, **44**, 67-B; Chem. Zentr. 1923, IV, 808.

is then etherified with 160-250 parts ethyl chloride for 6-24 hrs. at 90-130° with stirring, an ethylcellulose resulting soluble in benzene, alcohol, alcohol-benzene, chloroform, methyl acetate or glacial acetic acid.

The addition of alcohol has also been proposed in the production of alkalicellulose[1], an example being the treatment of 100 of cellulose with 600 NaOH dissolved in 635 parts of water, then adding 1000 of 96% ethyl alcohol, the mass being allowed to stand in a tightly closed vessel for 10-24 hrs., after which the mass is pressed to 850-900 and comminuted in a tightly closed shredder with cooling. The proportion of NaOH present in the mixture is about 30%.

Another method has been proposed for alkalicellulose formation, not used in the cellulose ether industry[2], in which the cellulose actually passes into a clear solution, mercerization being conducted at low temperatures, the amount of alkali required being much less than in the usual method of alkalicellulose formation. The details are shown in the following illustrative example: 10 parts cotton finely subdivided are mixed with 190-240 parts 8-10% NaOH solution at room temperature with stirring, until a homogeneous mass results. Either at once or after standing for some hours, stirring is continued and the temperature gradually reduced to —15° to —25°. When the temperature has fallen to —9° to —10° the mass is slightly frozen and resembles thin lard in consistency. Cooling is now interrupted and the temperature of the solution quickly raised. At about —5° to —3° the solution is usually free from NaOH crystals and therefore ready for use, being substantially transparent.

Realizing that the possibility of obtaining strong and elastic cellulose ether films and filaments depends "to an unexpected degree" upon the manner and thoroughness with which the alkali, water and cellulose are mixed prior to etherification, the components are drastically intermingled

1. U. S. P. 1682294; abst. J. S. C. I. 1928, **47**, 744-B.
2. U. S. P. 1658606; abst. J. S. C. I. 1928, **47**, 188-B. E. P. 212864; abst. C. A. 1924, **18**, 2249. D. R. P. 523271; abst. C. A. 1931, **25**, 3481.

as shown in the following example[1]: 100 gms. cellulose are impregnated with 500-1000 gms. 30% NaOH solution and allowed to stand 6-48 hrs. (some latitude). It is then pressed to 180-240 gms. (theoretically containing 24-58 gms. NaOH and 56-98 gms. water) and the pressed material finally subdivided, preferably under cooling, after which 200-300 gms. dry, powdered NaOH are added, and the mixture kneaded and torn in a machine having rotary tearing knives for 1-5 hrs., to give a homogeneous and uniform pulverulent and flocculent mass.

(2) *Eastman Kodak Alkalicellulose Processes.* The method of E. Farrow[2] is especially adapted for the formation of cellulose ethers, the principal object of the invention being the removal of water from the formed alkalicellulose that the etherifiant, especially when an alkyl halide is used, may be intimately intermingled to assure uniform ethylation. He soaks 100 parts cellulose for 1-3 days in 1800 parts of aqueous solution containing 720 parts NaOH, which is claimed to both produce alkalicellulose and properly ripen the same. The mass is then pressed to about 600 parts, then dried down to 400 parts, thus leaving approximately 100 parts water in intimate relation to the alkali and cellulose. It is recommended to dry at 160° F. by passing over air at a linear velocity of about 300 ft. per min. The material during drying is preferably agitated, as in a rotary drum.

The P. Seel method[3] of preparing pulverulent, intimately mixed alkalicellulose especially applicable for etherification purposes is indicated in Fig. 2, in which *1* is a diagrammatic sectional view of a ball mill in which the first step is carried out, *2* shows the condition of the material at the end of the first step, *3* is a diagrammatic sectional view illustrating another step in the process, and *4* shows

1. U. S. P. 1858017.
2. U. S. P. 1467107; abst. C. A. 1923, **17**, 3788; Chem. Met. Eng. 1923, **29**, 678.
3. U. S. P. 1469824; abst. C. A. 1923, **17**, 3919; J. S. C. I. 1923, **42**, 1172-A.

the final step in diagrammatic section. The cellulose fibers, alkali and water are introduced into *1* along with balls 3, a preferred charge being cellulose 100, NaOH 200 and water 250. The door 4 is closed and the mill rotated. The balls do not entirely grind up and mix the material, but clump or compact into a dense mass which lines the interior of the mill and some of the balls, as indicated in *2*, the compacted mass being shown at 11. The cover is then removed, the mass detached and broken up, and the process then repeated to insure a homogeneous mixing.

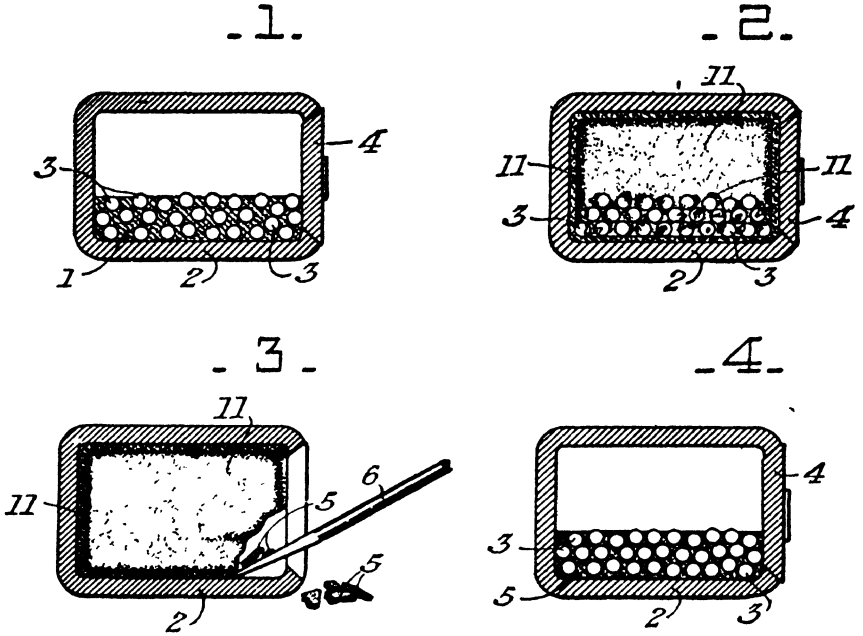


Fig. 2. Seel Apparatus for Alkalicellulose Manufacture.

(3) *Procedure of Courtaulds.* In order to hasten the production and ripening of alkalicellulose, it is proposed to conduct the mercerization step at about 65°, or to hasten ripening by oxidation as with a ferrous salt or sodium peroxide. E. van Weyenbergh[1] prepares alkalicellulose con-

1. U. S. P. 1569692; abst. J. S. C. I. 1926, **45**, 153-B. E. P. 237685; abst. C. A. 1926, **20**, 1904; J. S. C. I. 1925, **44**, 800-B.

taining a comparatively high percentage of caustic soda and a low percentage of water (at least 30% NaOH and not more than 35% water), and especially intended for cellulose etherification, by quickly immersing cotton in an excess of 60% NaOH solution for 5 min. at 65°, removing from the hot solution and quickly pressing to three times the original cellulose weight. The alkalicellulose obtained is said to have the approximate composition cellulose 32%, NaOH 45%, water 23%. Our experience is that it is extremely difficult to standardize the composition of alkalicellulose prepared at so high a temperature with but a five minute immersion. The high strength of alkali and elevated temperature cause the formation of an alkalized cellulose which upon etherification gives unduly low viscosities and deficient film and filament tensile strength.

W. Glover and L. Wilson[1] intentionally oxidize alkalicellulose in order to hasten the otherwise normal ageing period by the addition of an oxidizing agent as sodium peroxide, hydrogen dioxide, a hypochlorite or a current of oxygen or inert gases containing oxygen. As an example, 2 gms. sodium peroxide are dissolved in 200 cc. 17.5% NaOH solution and 5 gms. wood pulp in sheet form immersed therein at 18° for 4-5 hrs. The product is then removed and pressed to about 15 gms. after which it is ground and may be at once used, as for etherification purposes. Or ferrous sulfate or nickel sulfate may be employed as oxidants[2] as shown in the two following examples: 5 gms. cellulose are soaked in a 0.6% crystallized ferrous sulfate solution and then pressed to 8.5 gms., the cellulose then containing iron equivalent to 0.1% FeO. The cellulose thus treated is next steeped in 17.5% NaOH solution, pressed to about 16 gms., milled and then allowed to oxidize in

1. U. S. P. 1279328; abst. C. A. 1918, **12**, 2687. E. P. 13055, 1914; abst. C. A. 1915, **9**, 3130; J. S. C. I. 1915, **34**, 606-B; Chem. Ztg. 1915, **55**, 354. Swiss P. 70744. U. S. P. 1279329; abst. C. A. 1918, **12**, 2687. Swiss P. 71681.

2. L. Wilson, U. S. P. 1279200; abst. C. A. 1918, **12**, 2687. E. P. 14675, 1914; abst. J. S. C. I. 1915, **34**, 606.

closed containers for 15-24 hrs. or to a current of air at about 40° for about 1 hr. Instead of the amount of ferrous sulfate specified, 1.35% $NiSO_4$,7 aq. may be used. Cerium or vanadium oxides or hydroxides may be substituted as oxidants. We are unable to see how a cellulose ether of maximum desirable properties is obtainable by proceeding in this manner.

(4) *I. G. Farbenindustrie Alkalicellulose Manufacturing Processes.* In order to increase the receptivity of cellulose for alkali treatment, O. Leuchs[1] subjects the cellulose to preliminary acid treatment. When cellulose is treated energetically with inorganic or organic acids hydrocelluloses are obtained, structureless and friable, but it is proposed to so modify the action of the acid that hydrocellulose formation does not take place, the cellulose after the treatment retaining its exterior form "while its chemical composition remains unchanged." For example, one part of cotton is heated under reflux with 10-20 parts of 0.5-1% sulfuric acid for 4-6 hrs., or the cotton covered with 15-30% sulfuric acid at room temperature for 2-3 days. Boiling 3 hrs. with 75% acetic acid is also advocated. Acid treatment is continued until a test sample withdrawn indicates the commencement of complete solubililty in alkali. The action of acid is then interrupted, the cellulose filtered off, washed to neutrality and dried.

In alkalicellulose formation[2] it is recommended to drain and tilt the vats in which the cellulose sheets have been steeped until the sheets, which during the steeping hang vertically, lie in a substantially horizontal position. Gentle pressure is then applied to the sheets by means of partition walls which slide in grooves in the sides of the vat, thus expressing the major portion of the excess liquor, the remainder being subsequently removed in a press.

To form alkalicellulose free from water, M. Luther and

1. U. S. P. 1755657; abst. J. S. C. I. 1930, **49**, 1105-B. I. G. Farbenind. Holl. P. 21921.

2. I. G. Farbenind. D. R. P. 445728; abst. J. S. C. I. 1928, **47**, 228-B.

W. Becker[1] treat dry cellulose with alkali hydroxide dissolved in methyl alcohol.

(5) *Other Alkalicellulose Processes.* G. Richter[2] prepares the original pulp for more ready and uniform action of NaOH thereon by refining a kraft or soda pulp to high α-cellulose content by first treating with oxidizing agents as chlorine, and then with alkaline liquors, followed by a bleaching treatment. A. Liebster[3] proceeds by predigesting the cellulose with dilute alkali, washing with water and then drying, afterwards mercerizing with but a slight excess of concentrated alkali, the resulting unripened alkalicellulose being then directly etherified, as with ethyl chloride for ethylcellulose formation. C. Schwalbe[4] proceeds in a somewhat similar manner in that the cellulose is initially swollen by treatment with dilute caustic soda solution in the cold[5]. A. Thilmany[6] assures the absence of CO_2 to combine with the alkali to form the corresponding carbonate, by grinding cellulose in a vacuum at a raised temperature with NaOH solution of 15° B. (sp. gr. 1.116) until the alkali by evaporation of water therefrom has concentrated to the desired degree, when the alkalicellulose is pressed and comminuted in the usual manner[7].

More applicable to the mercerization of cotton in fabric form than in the sheet, is the procedure of Chemische Fabr. vorm. Sandoz[8] and the Imperial Chemical Industries[9]. The former facilitate penetration in and combination of cellulose by alkali by the addition of 1-2% of phenols (cresols) and hydrogenated aromatic compounds as tetrahydronaph-

1. D. R. P. 486493; abst. C. A. 1930, **24**, 1928.
2. U. S. P. 1839774.
3. E. P. 355563; abst. J. S. C. I. 1931, **50**, 1006-B.
4. D. R. P. 456929; abst. J. S. C. I. 1930, **49**, 184-B.
5. See also C. Stulemeyer, Aust. P. 86756 and Addn. 86757; abst. Chem. Zentr. 1922, II, 650, 960.
6. D. R. P. 328035; abst. J. S. C. I. 1921, **40**, 175-A.
7. Compare E. Gminder, D. R. P. 523600 Addn. to 516069; abst. Chem. Zentr. 1931, II, 1514, 3175.
8. E. P. 279784; abst. J. S. C. I. 1928, **47**, 228-B.
9. Imperial Chemical Industries, Ltd., F. P. 672808; abst. C. A. 1930, **24**, 2290.

thalene, *cyclo*hexanol, decahydro-*b*-naphthol; the latter prefer the use of a mixture of phenol containing about 10% benzyl alcohol[1].

A. Bernstein[2] places cellulose in an 18% NaOH solution for 2.3 hrs., squeezes to 3-4 times the weight of the cellulose and ages 2 days. H. Delahaye[3] dips cellulose in NaOH solution of 20-25° Be. strength at 0° Celsius for 1 hr., pressed to 2-3 times the weight of the cellulose originally used, and ripens for 2 days at 0° Cel. Afterwards the alkalicellulose is subjected to a slight "hydration" for 2-3 days in a chamber at 15°[4].

C. Huttinger[5] saturates wood pulp with NaOH solution of 1.17 sp. gr. (15%) for 1-5 hrs., presses to three times the cellulose used, the alkalicellulose formed assaying 13.5% NaOH, 27% cellulose, 59.5% water. According to another process[6], cellulose to be converted into alkalicellulose is treated one or more times with the waste lye from a previous mercerization, and finally with NaOH solution of mercerizing strength. It is claimed by proceeding in this manner that the hemicelluloses are completely removed. In practice, however, the usual procedure is to use a portion of waste lye, built up to the desired alkalinity by unused NaOH solution, the amount of fresh lye required being gauged by the hemicellulose content of the waste lye as well as its alkalinity. The process appears cumbersome for commercial use, due to the multiplicity of treatments of the same batch of cellulose.

1. See H. Hawlik and O. Sindl, Holl. P. 17163. Belg. P. 323797.
2. U. S. P. 1121605; abst. C. A. 1915, **9**, 377; J. S. C. I. 1915, **34**, 75. F. P. 462147; abst. C. A. 1914, **8**, 2947; J. S. C. I. 1914, **33**, 196. Belg. P. 259495.
3. U. S. P. 1470711; abst. C. A. 1924, **18**, 173. E. P. 195569; abst. C. A. 1923, **17**, 3612.
4. See DuPont Rayon Co., Holl. P. 22099.
5. U. S. P. 1425654, 1502101; abst. C. A. 1922, **16**, 3403; 1924, **18**, 2962.
6. H. Hawlik and O. Sindl, E. P. 229678; abst. C. A. 1925, **19**, 3163, 3165; J. S. C. I. 1925, **44**, 877-B. Neue Glanzstoff Werke, A. G., D. R. P. 476255; abst. C. A. 1929, **23**, 3807.

The Zellstofffabrik Waldhof[1] saturate cellulose with alkali, ripen the alkalicellulose formed, then wash the alkali from the material, 9% NaOH being used[2]. L. Jardin[3] directly transforms cellulose into defibered alkalicellulose, by tearing the cellulose to fine pieces in a suitable apparatus maintained at constant temperature, being at the same time sprayed with sufficient NaOH solution to convert it into alkalicellulose. Heberlein & Co. treat cotton with 16% alcoholic NaOH[4], while R. Schwarzkopf[5] agitates cellulose with caustic soda solution above 18° for about 20 min., then removes excess of alkali solution. Ripening is unnecessary[6].

In the H. Bassett method of alkalicellulose manufacture[7], cellulose is treated with caustic alkali solution of mercerizing strength for about 45 minutes, then introduced into a centrifugal machine and the excess of alkali removed. The partially alkalized cellulose is then aged 1-3 days, freed from additional amount of caustic soda by a dehydrating press until 25-35% actual cellulose content, then shredded in the usual manner, when the alkalicellulose is ready for etherification. By means of a special form of apparatus described in the patent[8], L. Jardin[9] treats sheets of wood pulp with a determined proportion of NaOH solution by spraying in such a manner that at the end of the operation the desired quantity of solution remains in the sheets so that they need not be subjected to pressing.

Continuous Manufacture of Alkalicellulose. Several methods for the continuous manufacture of alkalicellulose

1. Can. P. 293875. Zellstofffabrik Waldhof, O. Faust and V. Hottenroth, E. P. 317046 Addn. to E. P. 301088.
2. See A. Kampf, F. P. 529486; abst. Chem. Ztg. 1921, **45**, 1029.
3. E. P. 286619, 286620; abst. C. A. 1929, **23**, 512; J. S. C. I. 1928, **47**, 889-B.
4. E. P. 255453; abst. J. S. C. I. 1927, **46**, 473-B; Silk J. 1927, **3**, #34, 71; Chem. Zentr. 1927, I, 2360.
5. E. P. 165743; abst. C. A. 1922, **16**, 831.
6. See La Soie Artificielle Societe Anonyme Francaise, Ital. P. 148776, 165922. D. R. P. Anm. S. 36018; abst. Kunst. 1913, **3**, 439.
7. U. S. P. 1831647; abst. C. A. 1932, **26**, 843.
8. Cf. U. S. P. 1733393.
9. E. P. 286619; abst. C. A. 1929, **23**, 512. E. P. 286620; abst. C. A. 1929, **23**, 512; J. S. C. I. 1928, **47**, 889-B.

have been evolved, in one of which cellulose in the form of mill board is conducted through a vessel containing NaOH solution by means of an endless band conveyor, the speed of which, and the volume of the solution, are so adjusted that the cellulose is uniformly impregnated and the whole of the liquid absorbed. No pressing is employed, and hence hemicellulose is not removed. In another process[1], a band of cellulose is drawn through a drying chamber and an alkalizing bath, the product then pressed between rollers, the pressure being kept constant by automatically adjusting the gap between them according to the thickness of the cellulose band. A product of uniform composition is claimed to be thus obtained.

E. Schuelke[2] takes a 200 lb. roll of cellulose and propels it through a strong NaOH solution where it is engaged by pressure rollers adjusted so the finished roll has a predetermined weight per given area. J. Lamassiaude[3] has described an apparatus for the continuous manufacture of alkalicellulose in which wood pulp in rolls is passed through a NaOH bath circulating inversely to the travel of the sheet being mercerized.

Selecting and Blending the Cellulose. Wood pulp contains as made in the United States for etherification and esterification purposes, above 92% α-cellulose on a dry basis calculation, and cotton about 98% α-cellulose calculated on the same basis. In alkalicellulose formation and subsequent etherification these two sources of cellulose behave quite differently, in general wood cellulose being more reactive and furnishing cellulose ethers of lower viscosity and more ready solubility. Excellent results as to uniformity and maximum quality are obtainable from a mixture of 40 wood pulp, 60 cotton. As received at the plant, both are in sheet form, cut to the size required depending upon the type and size of mercerizing tank into which the sheets are to be

1. F. Melms, D. R. P. 513203; abst. C. A. 1931, **25**, 1378.
2. D. R. P. 335563; abst. Chem. Tech. Uebers. 1921, **45**, 215; Chem. Ztg. 1921, **45**, 233. F. P. 536649; Chem. Ztg. 1922, **46**, 507.
3. F. P. 643903; abst. C. A. 1929, **23**, 3343. See Ital. P. 240097.

placed. The usual steeping, rectangular, iron boxes are provided with 20 zinc septums with a number of eighth inch holes therein for free passage of alkali liquid therethrough. One method of blending the cellulose sheets is to have a number of bins corresponding to the number of septums or divisions in the steeping bath, the contents of an individual bale of wood or cotton sheets being distributed throughout the bins so that but one or two sheets from any single bin is contained within the individual septum of the steeping bath. Cotton and wood pulp sheets are uniformly mixed in the proportion they are to be used so that each septum contains the same proportion of each. As received at the plant the sheets contain from 4-8% moisture. They are stored in a temperature and moisture controlled for several weeks before use, that the moisture may attain a uniform level, which is about 5% when ready for steeping.

The sheets are placed in the mercerizing receptacle, septums inserted so that the softening effect of the alkali will not cause the sheets to crumple into a solid mass, and in this condition are ready for the introduction of the NaOH solution.

Wetting Agents. To increase the absorptive capacity of cellulose and its derivatives for liquids, wetting out agents have been advocated, the majority, however, being especially applicable to the treatment of cellulose in the woven or filament form. The Chemische Fabrik vorm. Sandoz[1] increase the wetting and penetrating power of alkalis by the addition of relatively small amounts of propyl, butyl, amyl and benzyl alcohols or diacetone alcohol. Mixtures of phenols and quaternary salts have also been put forward[2], as tri-(*b*-hydroxyethyl)amine, dimethylphenylammonium methosulfate or pyridine. *Cyclo*pentanone, *cyclo*hexanone, methyl*cyclo*pentanone, methyl*cyclo*hexanone, camphor and commercial acetone oil are efficient wetting out agents for

1. E. P. 350018 Addn. to E. P. 279784; abst. J. S. C. I. 1928, **47**, 228-B; 1931, **50**, 801-B.
2. Chem. Fabrik vorm. Sandoz, E. P. 364844; abst. J. S. C. I. 1932, **51**, 503-B.

use with mercerizing liquors[1]. An especially efficient formula is said to be crude cresol 90, butyl alcohol 5, methyl*cyclo*hexanol 5%[2]. Acetone glycerol, glyceryl phenyl ether, diethyleneglycol ethyl ether and diethyleneglycol monobutyl ether are also recommended.

The I. G. Farbenindustrie[3] recommend octodecyl lactate, *cyclo*hexanol lactate, benzyl lactate, octodecyl hexahydrosalicylate, either along or in the sulfonated form, as octodecyl lactylsulfonate. Cresol and pinacone[4], cresols and tetraethylhexane-1.6-diol (from adipic ester and ethyl magnesium bromide), xylenols, *p*-chlorphenol, and methyl*cyclo*hexanediol are further examples. Insofar as aware, no prior wetting out agents are used in alkalicellulose manufacture at the present time.

Mercerizing the Cellulose. The sheets are loosely stacked in the steeping vat, subdivided by metal perforated septums so that there are about ten sheets per septum, and immersed in clarified 18.5% NaOH solution, by introduction of the alkali from the bottom. The sheets begin almost immediately to contract in area, the ratio of alkali solution to cellulose being about 30 to 1. As soon as the sheets have been immersed to about 2 inches over the top of the sheet, it is advisable to separate each sheet by running a spatula between, thus liberating bubbles of air and facilitating uniform penetration of cellulose by alkali. As soon as the total amount of alkali has been run in at 18°, the steeping liquid is withdrawn from the bottom and pumped in the top, being distributed on top of the sheets at jets about two inches apart, the introduction of alkali solution being below the level of the mercerizing solution. The object of this is to remove alkali from a given zone which has dissolved hemicellulose and has been weakened by a combination of

1. Chem. Fabrik vorm. Sandoz, E. P. 365323; abst. J. S. C. I. 1932, **51**, 337-B.
2. *Ibid.* F. P. 38047, 38872, Addn. to 624174; abst. C. A. 1932, **26**, 320, 1780.
3. E. P. 348040; abst. J. S. C. I. 1931, **50**, 797-B.
4. Chem. Fabrik vorm. Sandoz, F. P. 38915, Addn. to 624174; abst. C. A. 1932, **26**, 1780.

a portion of the NaOH at that particular point, and replace it by new alkali. Mercerization period 2 hrs. The heat of reaction between alkali and cellulose is adjusted by pumping the mercerizing liquor being introduced after the sheets have been covered, by other lye which has passed through heating or cooling coils, depending upon the season of the year. Usually the alkali is pre-cooled one or two degrees upon first being brought into contact with the cellulose to allow for this normal rise in temperature. To insure maximum uniformity of combination between alkali and cellulose, the NaOH solution should be pumped through the mercerizing bath more vigorously at the commencement of the process than towards its close.

After the normal mercerization period of 2 hrs. has elapsed, the NaOH solution is drained off. That which runs off by gravity is clear and is used together with fresh NaOH solution for a subsequent mercerization. That which will not drain away by gravity, and has to be removed by means of the hydraulic end plunger is discarded. It is darker color than the first portion and turbid. Usually 15 minutes is required for the natural drainage of the alkali, and a further 15 min. for pressing to the point desired. With a 40 wood pulp to 60 cotton pulp, a total weight of 305-310 per 100 of bone dry cellulose is considered optimum. Great care should be exercised that the plunger squeezes out uniformly the alkali solution from the alkalicellulose.

Herminghaus & Co.[1] have described an apparatus for alkalicellulose manufacture in which the pulp sheets are arranged parallel to the longitudinal axis of the steeping tank while being mercerized, after which by turning the tank on its longitudinal axis it is brought into a more or less horizontal position before the sheets are removed from the tank. In operating with charges of 100-200 kilos cellulose, it is necessary to have a very powerful and rigid steeping apparatus to withstand the hydraulic plunger pres-

1. D. R. P. 398255; abst. Wag. Jahr. 1924, **70**, II, 22.

sure necessary to reduce the weight of alkalicellulose and alkali mixture to the minimum weight desired.

A process for steeping has been described[1] in which more rapid penetration of cellulose by caustic solution is obtained where the pulp is first subjected to a vacuum, the caustic solution then admitted, and finally an air pressure of 3-4 atms. applied to increase penetration. Where the alkalicellulose is to be used for viscose manufacture[2], the suggestion has been made to replace a portion of it by an organic sulfonium hydroxide as trimethylsulfonium hydroxide.

In order to increase surface area, the Du Pont Rayon Co.[3] propose to treat the pulp sheets so as to produce corrugations, thereby allowing more freedom for passage of alkali solution to all parts of the mass before complete swelling occurs. Plauson's, Ltd.[4], seek to increase uniformity in alkalicellulose production by rendering the cellulose colloidal by high speed mechanical disintegration, but cellulose treated with NaOH solution of mercerizing strength is exceedingly difficult to remove from such a mass when operating with large charges under factory conditions[5].

We are in accord with W. Dyes[6] that alkalicellulose should be carefully protected from CO_2 and hence from the atmosphere. During mercerization there is little opportunity for the absorption of CO_2 for the alkalicellulose is entirely immersed, but the time between removal of mercerizing solution and completion of comminution should be carefully guarded from the viewpoint of introduction of atmospheric air. There are good grounds for the statement that sodium carbonate in connection with alkalicellu-

1. C. Breda, E. P. 167201 Addn. to E. P. 167199; abst. C. A. 1922, **15**, 646; J. S. C. I. 1921, **40**, 609-A; Chim. et Ind. 1922, **8**, 880.
2. British Dyestuffs Corp., Ltd., and A. Hailwood, E. P. 281117.
3. E. P. 272475; abst. J. S. C. I. 1928, **47**, 853-B.
4. E. P. 184533; abst. C. A. 1923, **17**, 210; J. S. C. I. 1922, **41**, 693-A.
5. W. Marshall, E. P. 363883; abst. Text. Mfr. 1932, **58**, 248.
6. Chem. Ztg. 1929, **53**, 185; abst. C. A. 1929, **23**, 2569.

lose during the ageing operation is detrimental, in that observable weaknesses appear in both filaments and films obtained from cellulose ethers made therefrom.

Pressing the Alkalicellulose. Outside of laboratory demonstration, the centrifuge has not been a success in connection with alkalicellulose manufacture. The pressure required to bring the wet weight of alkalicellulose down to about 3:1 based on the cellulose is about 220-250 lbs. per sq. inch, and to obtain this equivalent would mean a per minute revolution not considered safe. In addition, with a centrifuge there is considerable handling and loss of material from impact against the holes in the basket. Furthermore, hydraulic pressure may be applied to the alkalicellulose while still in the mercerizing unit, a valuable point.

Immediately the alkalicellulose has been reduced in weight to the point desired, it is dropped in a trough leading to the disintegrating machines or Pfleiderers, jacketed, brine-cooled mixers with stirring arrangements, where comminution or shredding takes place for 2-2.5 hrs., and until a sample withdrawn shows individual particles of about 1 sq. mm. area. By means of a tipping arrangement, the contents of the shredder which is kept at 21° at the commencement of the operation but is allowed to rise naturally to the temperature of the ageing room which should be 23° is dumped into a series of iron cans with tightly fitting covers, each can being filled about ¾ths full and holding about 40 lb. of the disintegrated alkalicellulose or "crumbs." This is then quickly run into the ageing room. Due to internal heating in the cans during the ageing period, it is better to employ round cans rather than square or rectangular, that there may be air circulation around each can, to tend to equalize small rises in temperature in the interior of the can. It is useful to roll the cans with contents once or twice per 24 hrs. to guard against preheating in the interior.

W. Duetzmann[1], La Soie Artificielle Soc. Anon. Francaise[2], Ateliers de Construction Grosselin & Dehaitre[3], Maschinenfabrik M. Hauesser[4], H. Hanselmann[5], Siemens-Schuckertwerke A. G.[6] have described alkalicellulose presses. H. Wahlberg[7] has given a resume of the equations which have been proposed by various investigators to show the reactions involving cellulose, lignin and hemicellulose in the alkalicellulose pulping process, with graphs and illustrations of molecular structure, and Wolff & Co. and R. Weingand[8] a method of eliminating last traces of hemicellulose bodies from alkalicellulose.

Alkalicellulose suitable for etherification purposes may be obtained in the form of a downy mass[9] by subjecting cellulose moistened with NaOH solution to the action of high speed machines such as impact cross mills or spiked roller mills. The alkalicellulose formed may be transported through the plant by being drawn through a conduit by use of a fan[10].

The mixing apparatus of the British Celanese, Ltd.[11], comprises a vessel into which depend stationary vertical vanes between which vertical stirrers, mounted on a horizontal arm, rotate about a vertical shaft, means being provided to regulate the clearance between the bottom of the vessel and the stirrer. The A. Kampf[12] alkalicellulose disintegrator contains a trough and beaters provided with teeth and grooves closely engaging one with the other, and

1. U. S. P. 1690894, 1696474, 1863399. E. P. 344120; abst. C. A. 1932, **26**, 302. E. P. 341450.
2. D. R. P. 270618; abst. C. A. 1914, **8**, 2482; Chem. Zentr. 1914, I, 928. Belg. P. 244554; abst. Chem. Ztg. 1912, **36**, 846.
3. F. P. 710485; abst. C. A. 1932, **26**, 1781.
4. D. R. P. 521362; abst. C. A. 1931, **25**, 2847.
5. D. R. P. 513863; abst. C. A. 1931, **25**, 1993.
6. (H. Wilbert), D. R. P. 526481; abst. C. A. 1931, **25**, 4402.
7. Svensk Papers Tid. 1929, **32**, 44; abst. C. A. 1929, **23**, 3090.
8. E. P. 288997; abst. C. A. 1929, **23**, 703. F. P. 642176; abst. C. A. 1929, **23**, 1266.
9. Erste Boehmische Kunstseidefabrik, A. G., E. P. 258897; abst. C. A. 1927, **21**, 3128.
10. See Meneghini, Ital. P. 242516.
11. E. P. 331606.
12. E. P. 157982; abst. C. A. 1921, **15**, 1994. Can. P. 221282.

being arranged in such a manner that the material is subjected to a continuous cutting and pulverizing action as it is forced through and into the grooves.

Drying Alkalicellulose. P. Seel[1] prepares pulverulent, intimately mixed alkalicellulose suitable for etherification purposes, by compacting a mixture of cellulose, NaOH and water into a dense layer, breaking the layer up into fragments and grinding the fragments to powder. He controls the amount of moisture in alkalicellulose[2] and removes excess therefrom by passing in contact with the former a relatively dry gas, provided the gas be first made inert to the alkalicellulose, this especially applying to the removal of carbon dioxide on the supposition that when present they tend to break down the intimate union or mixtures of the alkalicellulose, so that upon etherification, unetherified fibers or particles remain in the product, articles made therefrom not being transparent but hazy or cloudy.

He circulates a stream of air successively through a station for removing the acid gases like CO_2, through a water-removing station, and then through a station containing the alkalicellulose carrying an excess of water. The apparatus for conducting the operation is shown in Fig. 3, in which a series of shelves *2* are arranged, either removable or readily accessible. At the top of the container is a pipe *3* connected with absorption chamber *7*. The latter has perforated shelves containing CaO or NaOH. The alkalicellulose containing excess of moisture is charged into shelves *2* and a current of inert gas forced through which picks up moisture from the alkalicellulose passing through pipe *3* to blower *5* which then forces the stream through the tower 7 where any CO_2 gas is absorbed.

L. Lilienfeld[3] dries alkalicellulose at a temperature

1. U. S. P. 1469824; abst. C. A. 1923, **17**, 3919.
2. U. S. P. 1635012; abst. C. A. 1927, **21**, 2985.
3. U. S. P. 1683682; abst. C. A. 1928, **22**, 4246. See E. P. 200816; abst. C. A. 1924, **18**, 328; J. S. C. I. 1925, **44**, 67-B; Chem. Zentr. 1923, IV, 808; Faserstoffe, 1924, **6**, 21. E. P. 200827; abst. C. A. 1924, **18**, 469; J. S. C. I. 1925, **44**, 67-B; Chem. Zentr. 1923, IV, 808.

below 10-15° by first impregnating cellulose 100 with 20% NaOH solution 1000, and after standing 24-72 hrs. is pressed to 600. The pressed residue is then disintegrated, and after standing for 1-3 days is placed in a vacuum shelf dryer as of the J. P. Devine type, and dried at a tempera-

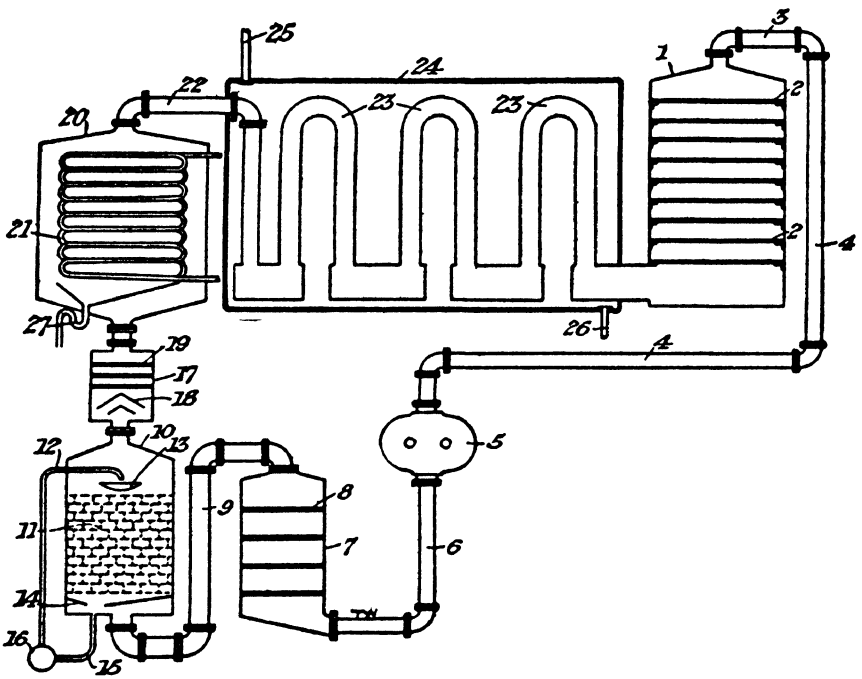


Fig. 3. Seel Apparatus for Drying Alkalicellulose.

ture below 15° and preferably below 10° until a test shows that the alkalicellulose contains 10-25% water. The dried sodacellulose is then placed in an autoclave which may be rotated and is provided with a stirring device and ethylated with ethyl chloride 200 for 10-24 hrs. at 90-100°. The resulting ethylcellulose is a powdery flocculent substance soluble in a number of organic solvents including alcohol-benzene.

Ageing of Alkalicellulose. With an alkalicellulose of initial cellulose composition previously stated, an ageing,

maturing or ripening period of 47-49 hrs. at 23° in a room with thermostatic temperature control, is considered best where the product is to be subsequently etherified. If the alkalicellulose is to be admixed with solid NaOH prior to the etherifying treatment, time should be deducted from the above period for the time consumed in adding the solid alkali, and the temperature of the mass during incorporation should be maintained as nearly as possible at 23°. An ideal method of ripening would be storage in a hermetically sealed container with temperature control and subjecting the alkalicellulose to a slow continuous agitation to obviate any possibility of local preheating.

A. Pinel[1] believes the ripening of alkalicellulose is more uniform, and certainly is more rapid, by heating the mass with agitation to 50-60° for 2-3 hrs. in an apparatus designed by him and having temperature control. Immediately at close of the ageing period, cold water is introduced through a worm in the apparatus to lower the temperature of the crumbs. After they have been aged the prescribed length of time, H. Bassett[2] boils with water to remove any soda solubles present and obtain an alkalicellulose of maximum purity.

A ripening chamber has been described by J. Lamassiaude[3], composed of a series of parallel isothermal tunnels, the dimensions of which are reduced to that necessary to allow the trucks containing the cans of crumbs to pass. The usual construction of the ageing chamber is cork board in 6 inch layers, iron grating being laid as flooring about 6 inches above the floor to maintain uniform and uninterrupted circulation of air. It is stated[4] that the maturation

1. E. P. 194693; abst. C. A. 1923, **17**, 3606; Aust. P. 99910. See E. Van Weyenbergh, U. S. P. 1569692; abst. C. A. 1926, **20**, 822.
2. U. S. P. 1733393; abst. C. A. 1930, **24**, 498.
3. F. P. 643902; abst. C. A. 1929, **23**, 3343.
4. Soie De Chatillon Soc. Anon., E. P. 250617; abst. C. A. 1927, **21**, 1355; J. S. C. I. 1927, **46**, 473-B. Swiss P. 119680. See E. P. 13055, 14675, 1914; 178152, 240717; abst. J. S. C. I. 1915, **34**, 606; 1922, **41**, 459-A; 1925, **44**, 986-B.

of alkalicellulose may be impeded or accelerated by removal or addition of oxygen thereto, and that in the absence of oxygen the material may be preserved indefinitely without substantial modification of the degree of maturation. To the last statement we do not concur for we have taken a ripened alkalicellulose, divided it in halves, xanthated one portion immediately after due ripening while the other half placed in a vacuum over an oxygen absorbent at 23° for 10 days and then xanthated gave a much inferior filament as compared with the first portion.

The Glanzfaeden A. G.[1] claim that little or no ripening of alkalicellulose is required for viscose filament formation, and H. Dreyfus avoids the necessity of ripening of soda cellulose intended for viscose manufacture[2] by mercerizing with high concentration NaOH solution in the proportion of 1 mol. NaOH per mol. cellulose. It is stated[3] that storage of alkalicellulose at 25° adversely affects the tenacity of the films made therefrom after esterification or etherification. Our experience is that alkalicellulose should be etherified as quickly as possible, once it has reached the optimum ageing period. H. Jentgen[4] has patented an apparatus for ripening alkalicellulose.

According to E. Paterno[5] the maturation of alkalicellulose is one of oxidation, *b*-(oxy)cellulose formed passing through into the final product. The action of oxygen on alkalicellulose[6] at 60-100° gives *b*-(oxy)cellulose, with a considerable increase of carbonate, being derived together with pentosans from the cellulose:

$$C_6H_{10}O_5+O_2=C_5H_8O_4+CO_2+H_2O.$$

1. E. P. 152350, 152351, 181330, 185718.
2. E. P. 183882; abst. J. S. C. I. 1922, **41**, 748-A.
3. G. Kita, R. Tomihisa, K. Sakurada and H. Kono, J. Cellulose Inst. Tokyo, 1927, **3**, 27; abst. Rayon, July 15, 1927, p. 24; J. S. C. I. 1927, **46**, 387-B.
4. D. R. P. 548368; abst. C. A. 1932, **26**, 3667.
5. Atti R. Accad. Lincei, 1932, vi, **15**, 113; abst. J. S. C. I. 1932, **51**, 638-B.
6. *Ibid.* p. 107; abst. J. S. C. I. 1932, **51**, 638-B.

Caustic Soda Recovery. The usual practice, in the United States at least, is to allow the NaOH solution to run off by gravity at the close of the steeping period and rejuvenate this clear liquid only, that obtained from pressure, being much darker and turbid, is discarded. In one method of rejuvenation[1] the alkaline liquid is heated under pressure with an oxidant as sodium chlorate or sodium nitrate in the presence of copper or iron oxide as catalyst, to destroy the organic substances (hemicelluloses) present, oxygen being introduced to facilitate the reaction, the alkali metal carbonate formed being recovered by causticizing. The I. G. Farbenindustrie[2] heat under pressure with air or oxygen above 100°, the sodium carbonate formed being causticized into alkaline earth hydroxide by lime. M. Freiberger treats with lime and sufficient bleaching powder to yellow the solution without augmenting the oxidizing power[3], sodium bisulfite being then added until the yellow color disappears. The precipitate formed is filtered off and the filtrate concentrated. U. Orlandi[4] re-utilizes the used caustic liquor by a process depending upon electrolysis with mercury electrode, while C. Sundstrum and C. Lykes[5] concentrate the crude liquor by evaporation with strong agitation and with introduction of air, then remove the separated impurities while a suitable temperature is maintained for their effective separation from the clear, purified solution.

In the R. Winternitz process[6], the hexosan and pentosan dissolved in the waste lye are precipitated by the addition of methyl or ethyl alcohols, a small quantity of lead acetate or other lead salt being added to remove the

1. J. D'Ans and Chemische Werke vorm. Auerges. Kommanditges, E. P. 217685; abst. C. A. 1925, **19**, 382.
2. E. P. 309237; abst. J. S. C. I. 1929, **48**, 432.
3. Textilber. 1921, **2**, 345; abst. J. Soc. Dyers Col. 1922, 25; C. A. 1922, **16**, 2412.
4. Giorn. chim. Ind. Applicata, 1926, **8**, 35; abst. C. A. 1927, **21**, 4063; Rayon 1927, July 30, p. 20.
5. Can. P. 268951; abst. C. A. 1927, **21**, 2362.
6. E. P. 303482; abst. C. A. 1929, **23**, 4572. D. R. P. 536914; abst. C. A. 1932, **26**, 1121.

color. The solution is then filtered, distilled to remove the alcohol, and treated with CaO to regenerate NaOH. The organic material may be removed by heating with sodium hydrogen sulfate as in the process of L. Bradley and E. McKeefe[1], and then causticizing with a larger proportion of calcium hydroxide than is chemically equivalent to the sodium carbonate present[2]. Or[3], the hemicellulose may be precipitated by the introduction of CO_2, or by the addition of acid sodium carbonate[4].

L. Barbisan[5] employs two vats, one containing the lye and the other the purifying reagent, the two being allowed to flow together into another receptacle, then passing to a quartz filter[6]. G. Van Barnevald Kooij[7] claims dialysis is the only feasible method of recovery of the press lye from alkalicellulose manufacture, and like F. Kuttner[8], passes the lye through a series of vegetable parchment partitions as a dialyzer. G. Donagemma[9] has described a suitable diaphragm made of natural stone of a micro-granular structure, the water used in the dialyzer containing 1-2% NaOH intentionally added thereto to prevent crust formation on the diaphragms[10].

Where comparatively little organic matter is present, the lye after filtration may be recausticized with lime and concentrated, but is not effectual in the removal of hemicellulose. Treatment with CO_2 obtained from flue gases from steam-generator installations for the precipitation of organic matter has been patented[11], copper hydroxide being

1. U. S. P. 1754207; abst. C. A. 1930, **24**, 2601.
2. L. Bradley and E. McKeefe, U. S. P. 1754208; abst. C. A. 1930, **24**, 2601.
3. E. Rinman, F. P. 401856; abst. J. S. C. I. 1909, **28**, 1163.
4. *Ibid.* D. R. P. 231254 Addn. to 222302; abst. J. S. C. I. 1911, **30**, 485; Chem. Zentr. 1911, I, 700. See also E. P. 8175, 1909; abst. J. S. C. I. 1910, **29**, 18.
5. F. P. 700709; abst. C. A. 1931, **25**, 3835.
6. D. Mastro, Ital. P. 269344.
7. Rayon Record, 1929, **3**, 463; abst. C. A. 1930, **24**, 1215.
8. D. R. P. 287092; abst. Chem. Zentr. 1915, II, 774.
9. F. P. 641886; abst. C. A. 1929, **23**, 1269.
10. F. P. 641901; abst. C. A. 1929, **23**, 1269.
11. E. Chambers and T. Hammond, E. P. 3063, 1913; abst. J. S. C. I. 1914, **33**, 418.

added if desired to facilitate precipitation of cellulosic matter[1]. The addition of lime[2], or a mixture of lime and clay[3] is said to flocculate the cellulosic matter so that it may readily be removed by sand filtration.

The Ashi Rayon Co. of Japan has perfected a dialyzer for the recovery of NaOH from waste steeping liquor[4], which looks like a plate filter press and consists of 121 sheets of mild steel welded screens, each 1561 mm. long and 520 mm. wide, parchment paper tightened up against the screens, being used as diaphragms. The E. Czapek and R. Weingand device for dissolving NaOH[5] claims speed, efficiency and cheapness in operation. C. Wagner[6] has published a summation of patent literature covering the past 60 years for alkali recovery from mercerizing liquor.

1. La Soie Artificielle Soc. Anon. Francaise, E. P. 1573, 1912. Hung. P. Appl. S-6079; abst. Chem. Ztg. 1913, **37**, 92.
2. O. Venter, E. P. 993, 1908; abst. J. S. C. I. 1908, **27**, 1017. F. P. 387621; abst. J. S. C. I. 1908, **27**, 852.
3. M. Petzold, E. P. 17626, 1911; abst. J. S. C. I. 1912, **31**, 184.
4. Rayon and Synthetic Yarn J. 1931, **12**, #12, 23. See Text. Mfr. 1931, **57**, 684.
5. U. S. P. 1574561; abst. C. A. 1926, **20**, 3084. D. R. P. 414852.
6. Paper Trade J. 1932, **94**; T. A. P. P. I. Sect. 187; abst. J. S. C. I. 1932, **51**, 677-B.

CHAPTER V

CARBOHYDRATE ETHERIFYING AGENTS

One of the most frequent operations in synthetic organic chemical research is that of alkylation, aralkylation or arylation, it being often necessary to produce an ether from a phenol or alcohol, a secondary or tertiary amine from a primary, an ester from a carboxylic acid or replace hydroxyl by alkyl. Until comparatively recently the chief reagents for this purpose of introducing an alkyl or aryl group into a molecule were the corresponding halides, which in many respects are inapplicable, the chlorides being deficient in reactivity and the bromides and iodides unduly expensive, especially in view of the fact that a small weight of alkyl group is introduced as compared with the weight of the halogen. However, due primarily to the boiling points and evaporative speed of the various alkylating agents, cost considerations are of minor importance in carbohydrate etherification when special properties are desired in the finished product.

The combination of etherification and esterification, i.e., the etherification of a partially esterified cellulose or carbohydrate body, whether the ester has attached to the cellulose an inorganic or organic acid radical or both, and the formation of mixed ethers by a selection of different alkylating agents in order to obtain specific effects in the mixed ester or ether produced, have led to an intensive study of the applicability of various etherifying agents when confronted with unattacked or partially esterified celluloses. The well known solubility and swelling tendency in water of the lower etherified members, and the fact that these undesirable properties may be mitigated or overcome by the judicious selection of etherifying agents for normal cellulose or cellulose which has been partially esterified or otherwise modified in composition and chemical deportment,

especially in conjunction with a modification of the etherification process so that a predetermined ratio or alkyl, aryl or aralkyl is introduced into the cellulose aggregate, has resulted in a meticulous investigation of the influence of etherifying bodies in connection with cellulose of varying degrees of hydrolysis or degradation, and it would appear that the outcome of these manifold investigations—as judged by the results already attained—is the conservation of the most desirable properties of both cellulose ethers and ester-ethers, which normally—price considerations being not taken into consideration—have properties desirable in many of the arts far above the cellulose esters, both of inorganic and organic acid radical origin.

By "alkyl" is to be understood the univalent radical, group or residue, of an aliphatic hydrocarbon, a term first applied by J. Wislicenus, and by "alkylation" the introduction of one or more similar or dissimilar groups into cellulose or other carbohydrate body, by substitution of alkyl for the hydrogen of a replaceable hydroxyl. Although the number of replaceable groups is very large, the technical development of the cellulose ethers has been primarily built up on the use of methyl, ethyl, allyl and benzyl rests.

Methyl bromide, and to a lesser degree methyl iodide, were formerly used to prepare alkylcellulose to a greater extent than at the present time on account of higher expense per unit weight of reacting alkyl, combined with the necessity of employing higher temperatures with its concomitant adverse effect upon the carbohydrate. In many of the reactions of the alkyl sulfates, an inert solvent as benzene, toluene or naphtha is used, to better control the progress of the reaction.

As a generality the alkyl sulfates possess several advantages over the corresponding alkyl halides, in that they are less expensive, the action of the first alkyl group is quite rapid, a lower temperature of alkylation is usually possible, the yields are uniformly better, their higher boiling points permit operation in open containers, and there is no after-

recovery of subsidiary products, as is advisable where a bromine or iodine compound is used.

The use of alkyl sulfates is practically limited to the methyl and ethyl compounds for the reason that the higher homologues are either difficult of preparation or are obtainable in but poor yields. In recent years where the higher alcohols have become available in large quantities, especially through the cracking of petroleum products, research in this direction has been greatly stimulated and there is much cumulative evidence to support the premise that the higher alkylcelluloses may be prepared with properties highly desirable and at a not prohibitive cost. Where the higher alkyl sulfates are contraindicated, the corresponding alkyl sulfites may be employed, and have recently been described in an article by W. Voss and E. Blanke[1]. They have demonstrated that many organic compounds with higher alkyl groups may be successfully synthesized from the alkyl sulfites, the one drawback being that they cannot be used in aqueous alkaline solution on account of too ready hydrolysis. In this case, sodium derivatives of the compound to be alkylated (alkalicellulose for example) may be employed with the sulfites to avoid the aqueous alkali used with the sulfates.

The *p*-toluenesulfonic esters have been used for some time, and apparently with increasing satisfaction, especially in the matter of yields. In conjunction with nitrogenous bodies, some unexpectedly satisfactory technical results have been obtained. The alkyl *p*-toluene sulfonates are possibilities for the introduction of higher alkyl groups that apparently are just becoming appreciated. K. Slotta and W. Franke[2] have shown that the higher alkyl, in addition to the methyl and ethyl esters may be used for alkylating purposes, and undoubtedly their scope of application will be considerably widened.

1. Ann. 1931, **485**, 250; abst. C. A. 1931, **25**, 1797. See W. Voss, Metallborse, 1930, **20**, 1854; abst. C. A. 1931, **25**, 69.
2. Ber. 1930, **63B**, 678; abst. C. A. 1930, **24**, 3498.

Methyl Chloride, CH_3Cl. (Chlormethane.) May be prepared from methyl alcohol, sodium chloride and sulfuric acid[1]; from methane and chlorine[2]; by heating basic chlorine compounds of cacodyl[3]; by heating methane with carbonyl chloride at high temperatures[4]; by heating methyl sulfate with stannic chloride[5]; or by dropping methyl sulfate into HCl, sp. gr. 1.112 at about 50°[6]. The direct chlorination of methane of E. Szarvasy[7] and J. Pfeifer and E. Szarvasy[8] is said to give too low yields, and the process of Holzverkohlungs-Industrie[9] to be difficult of control. In one method[10], methyl alcohol vapor is passed over HCl gas in the presence of silica gel at 250-300° which may be conducted as a continuous process, while E. Sper[11] uses graphite as the catalytically acting body.

Methyl chloride has been manufactured on the large scale by the dry distillation of vinasses from beets, the methylamine contained therein being saturated with HCl, heated to 260-300°, the methyl chloride, mono- and trimethylamine formed being separated by fractionation[12]. When gases containing the lower olefines are treated with HCl in the presence of a catalyst[13] as ferric oxide or chloride, methyl chloride is formed. A larger and more uniform yield is said to result when proceeding according to

1. J. Dumas and E. Peligot, Ann. 1835, **15**, 17; J. de Pharm. 1835, **21**, 377; Pogg. Ann. 1935, **36**, 88; Ann. de Chim. 1835, **58**, 5.
2. M. Berthelot, Ann. Chim. 1858, **52**, 97; J. pr. chem. 1858, **73**, 461; J. de Pharm. 1858, **33**, 461; Ann. 1858, **105**, 241.
3. R. Bunsen, Ann. 1843, **46**, 44.
4. A. Hochstetter, D. R. P. 292089; abst. J. S. C. I. 1916, **35**, 867.
5. C. Boulin and L. Simon, Compt. rend. 1919, **169**, 618.
6. *Ibid.* Compt. rend. 1920, **170**, 595.
7. Aust. P. 91240. D. R. P. 336205; abst. Chem. Tech. Uebers, 1921, **45**, 135.
8. D. R. P. 242570.
9. Aust. P. 96825, 106241. D. R. P. 378137, 393550, 437450, 477494.
10. I. G. Farbenind., D. R. P. 444799, 503716; abst. C. A. 1930, **24**, 5768.
11. E. Sper, U. S. P. 1721873; abst. C. A. 1929, **23**, 4482.
12. C. Vincent and B. Delachanal, Bull. Soc. Chim. 1879, (2), **31**, 11. See Jahr. Chem. 1878, **31**, 1135.
13. T. Goldschmidt A. G., E. P. 235547; abst. C. A. 1926, **20**, 918.

the directions of G. Curme[1], in which the chlorination of the hydrocarbon takes place in the gaseous phase and under anhydrous conditions. B. Lacy claims that in the chlorination of methane for the purpose of obtaining methyl chloride[2], the use of a large excess of methane over the theoretical causes the reaction to proceed slowly, without separation of carbon and free from explosive danger. Where 1 volume of chlorine and 6 volumes of methane are conducted in rapid current through appropriate reaction chambers, and a small amount of water introduced, no separation of carbon results, and the percentage yield of methyl chloride is above 80% of theory[3]. M. Douane[4] has devised an apparatus for carrying a similar process into effect. The C. Carter and A. Coxe method[5], in addition to the production of methyl chloride, carries the step to the stage of ester formation[6].

Properties of Methyl Chloride. Colorless gas of ethereal odor, burning with a white flame with green border, 35 volumes being soluble in one volume ethyl alcohol, 4 volumes in water, and 40 volumes in acetic acid. Decomposes in sunlight to methylene chloride, chloroform and carbon tetrachloride. Sp. gr. 0.99145 at —23°, 0.95231 at 0°[7]; boiling at —21°[8], or —23.7°[9].

1. G. Curme, U. S. P. 1422838.
2. U. S. P. 1111842 and Re-14105. Aust. P. 88549. Norw. P. 27040.
3. R. Leiser and F. Ziffer, U. S. P. 1459777. D. R. P. 222919, 438372. Aust. P. 89298.
4. U. S. P. 777406; abst. J. S. C. I. 1905, **24**, 455; Mon. Sci. 1905, **63**, 119.
5. U. S. P. 1459971; abst. J. S. C. I. 1923, **42**, 952-A. D. R. P. 472421; abst. C. A. 1929, **23**, 2448. E. P. 245991; abst. C. A. 1927, **21**, 415. S. Karpen & Bro., Belg. P. 325963.
6. For manufacture of methyl chloride, see U. S. P. 1421733, 1422838, 1455508, 1459777. Apparatus for producing methyl chloride is described in U. S. P. 1245553, 1263906, 1286353, 1365740, 1455508; catalysts for effectuating the reaction, U. S. P. 1262769, 1520506; chlorine for methylating, U. S. P. 1190659, 1216174, 1242208, 1317648, 1520506.
7. C. Vincent and B. Delachanal, Bull. Soc. Chim. 1879, (2), **31**, 11.
8. M. Berthelot, Ann. Chim. Phys. 1858, (3), **52**, 97.
9. V. Regnault, Ann. Chim. Pharm. 1840, **33**, 328; J. pr. Chem. 1840, **19**, 193, 264.

In addition to use in alkylation of carbohydrates (see pp. 24, 100, 118, 150, 238, 239, 278, 286, 287, 288, 301), methyl chloride has been patented for condensation with allylene and vinyl halides[1]; preparation of anisol[2]; as a bactericide[3]; solvent for caffeol[4], carbonyl chloride[5], chlorine, iodine, sulfur and methyl acetate[6]; and for the manufacture of 3.6-diamino-2.7.10-trimethylacridine[7], dimethyl ether[8], mellitic acid[9], refrigeration purposes[10], and vanillin[11].

When methyl chloride mixed with steam is passed at 350-375° over calcium hydroxide as hydrolyzing agent, methyl alcohol results[12], amyl alcohol being similarly formed from amyl chloride. G. Jones[13] has reported upon the inflammability of methyl chloride and other refrigerants, and S. Pickering[14] a summation of the critical constants of this gas.

Toxicity of Methyl Chloride. According to Thorpe, "Dictionary of Applied Chemistry," 1922, **4**, 311, "its (methyl chloride) vapour is non-poisonous," but there are a number of well authenticated instances on record of the poisonous nature of this ester. The U. S. Government authorized statement ERW:HA V-7 on the "number of deaths which occurred in Chicago, Ill.," as the result of leakage of methyl chloride from refrigerating systems, was issued by the Bureau of Standards, Washington, D. C., under date of July 31, 1929, and is available for free distri-

1. H. Plauson, U. S. P. 1425130.
2. L. Redman, U. S. P. 1209333.
3. P. Huessy and M. Hartmann, U. S. P. 1259517.
4. C. Trigg, U. S. P. 1367724.
5. H. Weber, U. S. P. 1454873.
6. C. Carter and A. Coxe, U. S. P. 1459971.
7. P. Huessy and M. Hartmann, U. S. P. 1227624, 1228926.
8. C. Carter and A. Coxe, U. S. P. 1459177.
9. E. Kressel, U. S. P. 1134956.
10. A. Henning, U. S. P. 1356765, 1386497. H. Edwards, U. S. P. 1498021.
11. F. Bidaud, U. S. P. 1418904.
12. R. McKee, U. S. P. 1688726; abst. C. A. 1929, **23**, 156.
13. J. I. E. C. 1928, **20**, 367; abst. C. A. 1928, **22**, 1687.
14. U. S. Bur. Stand. Sci. Papers No. 541, 1926, page 620.

bution. J. Mueller[1], and especially H. Baker[2] have exhaustively studied this subject. Commercial methyl chloride is absorbed by the respiratory tract in amounts sufficient to intoxicate workmen, unless special precautions are taken to guard against this danger.

It is very slowly expelled from the body and therefore becomes cumulative in its action. It may be detected in the urine as ammonium formate before symptoms of intoxication develop. Baker reports upon a series of 21 cases of poisoning. G. Morpurgo[3] has given the requirements and precautions for transportation of methyl chloride.

Methyl Bromide. CH_3Br. Brom-methane. May be produced by the general methods indicated under *Methyl Chloride,* by the action of bromine and phosphorus on methyl alcohol[4], or by the use of phosphorous tribromide[5]; by the interaction of aluminum bromide on methyl chloride[6], or of HBr on methyl alcohol in the presence of calcium bromide[7]; or by the distillation of a mixture of methyl alcohol, water, and a mixture of 1 mol. sulfuric acid and 2 mol. HBr into which SO_2 is run[8]. If a cooled mixture of 600 gm. concentrated sulfuric acid and 450 gm. methyl alcohol is mixed with 230 gm. water and 300 gm. powdered potassium bromide and heated, and the gas evolved led through water and sulfuric acid and finally dried over calcium chloride, methyl bromide of 83-84% of theory is obtained[9].

This ester is a colorless, neutral, strongly smelling liquid, of sp. gr. 1.7331 at 0°/0°, 1.7235 at 2.2°/2.2°, and

1. Arch. exptl. Path. Pharmakol. 1925, **109**, 276; abst. C. A. 1926, **20**, 455.
2. J. Amer. Med. Assoc. 1927, **88**, 1137; abst. C. A. 1927, **21**, 2342. Amer. J. Pub. Health, 1930, **20**, 291; abst. C. A. 1930, **24**, 2214.
3. Notiz. Chim. Ind. 1927, **2**, 697; abst. C. A. 1928, **22**, 833.
4. J. Pierre, Ann. 1845, **56**, 146; Ann. Chim. Phys. 1845 (3), **15**, 325; abst. Jahr. Chem. 1847-1848, **1**, 60.
5. J. Walker and F. Johnson, J. C. S. 1905, **87**, 1592.
6. C. Pouret, Compt. rend. 1900, **130**, 1192; abst. Bull. Soc. Chim. 1901, (3), **25**, 193.
7. Akt. ges f. Anilin Fabrik. D. R. P. 280740; abst. Chem. Zentr. 1915, I, 104.
8. F. Bodroux, Compt. rend. 1915, **160**, 205.
9. A. Bygden, J. prakt. Chem. 1911, (2), **83**, 422; abst. J. C. S. 1911, **100**, 413.

b. pt. 4°. It has a pleasant smell somewhat resembling chloroform, and burns with a greenish-brown, smoky flame. Miscible with alcohol, ether, chloroform and carbon disulfide. Poured into cold water a white, ice-like mass forms.

Methyl bromide is used to a limited extent as a methylating agent for cellulose and the carbohydrates primarily on account of cost of production (see p. 294, n. 1). Methylcellulose and methyldextrin have been made with methyl bromide as alkylating agent (p. 100, n. 3)[1].

Methyl Iodide. CH_3I. Iodomethane. Results from the action of iodine and yellow, or better red, phosphorus on methyl alcohol[2], yield 94-95% of theoretical; by adding methyl alcohol saturated with HCl to potassium iodide[3]; by dropping dimethyl sulfate on potassium iodide and warming[4]; or, methyl or ethyl iodides may be prepared by acting upon dimethyl or diethyl sulfate with alkaline earth iodide in aqueous solution. Methyl or ethyl iodide may also be prepared in 84.5% and 66.6% yields respectively from potassium iodide and methyl or ethyl *p*-toluenesulfonates[5], or methyl, ethyl, propyl, butyl and amyl iodides in 90-100% yields by the use of yellow or red phosphorus[6] in a special apparatus[7].

Methyl iodide is a colorless liquid of sp. gr. 2.2852 at 25°/25°[8], boils at 42.8°[9], and burns with difficulty. On ac-

1. For other uses of methyl bromide see U. S. P. 1253055, 1261067, 1336709, 1386497, 1393124, 1421733, 1440918, 1459971, 1473550, 1475522, 1497251, 1497252, 1497253, 1504178, 1518689.
2. W. Ipatiew, J. prakt. Chem. 1896, (2), **53**, 275; abst. Chem. Zentr. 1896, I, 1222.
3. J. de Vrij, J. pharm. 1857, (3), **31**, 169; abst. Jahr. Chem. 1857, **10**, 441.
4. R. Weinland and K. Schmid, D. R. P. 175209; abst. Ber. 1905, **38**, 2327; Chem. Zentr. 1906, II, 1589; C. A. 1907, **1**, 1086.
5. D. Peacock and B. Menon, Quart. J. Indian Chem. Soc. 1925, **2**, 240; abst. C. A. 1926, **20**, 1784.
6. J. Walker, J. C. S. 1892, **61**, 717.
7. R. Adams and V. Voorhees, J. A. C. S. 1919, **41**, 789; abst. C. A. 1919, **13**, 2032.
8. W. Perkin, J. C. S. 1884, **45**, 459.
9. P. Dobriner, Ann. 1888, **243**, 23; abst. J. C. S. 1888, **54**, 334. See also A. Castanares, Anales inst. med. nacional (Mexico), **11**, 75; abst. C. A. 1911, **5**, 3187.

count of the cost and preponderance in weight of the iodine, methyl iodide is used as a carbohydrate alkylating agent only in special instances (see pp. 91, 123, 161, 205). It has been recommended for the methylation of cellulose, flax, jute and hemp (p. 294, n. 1), as a cellulose acetate solvent (p. 549, n. 8), and in general organic synthesis[1]. The relative inflammability of ethyl bromide and methyl and ethyl iodides has been determined[2].

Methyl Sulfate, *Dimethyl Sulfate,* $(CH_3)_2SO_4$, is a favored alkylating agent for the methylation of cellulose and other carbohydrate bodies, being an extremely active substance, one of its two methyl groups ordinarily reacting at room temperatures. In order that the second methyl group may be available for alkylating purposes heating is required. Where cost is of minor consideration as in non-commercial processes, methylation may be conducted at lower temperatures, utilizing only one of the methyl groups. Such a procedure is especially applicable in the methylation of carbohydrates for the reason that, as compared with methyl bromide or iodide, lower etherification temperatures may be used, and hence diminished liability of attacking the cellulose molecule with the formation of inferior degradation products due to change in configuration incident to applying a higher degree of heat.

Manufacture of Methyl Sulfate. This neutral methyl ester of sulfuric acid was first prepared by J. Dumas and E. Peligot[3] by distilling 1 part methyl alcohol with 9 parts of concentrated sulfuric acid; and by P. Claesson and C. Lundvall[4] by distilling anhydrous methyl hydrogen sulfate

1. For other uses for methyl iodide, see U. S. P. 892900, 1253252, 1336709, 1392768, 1408405, 1413494, 1429714, 1434306, 1437802, 1459971, 1471213, 1475522, 1479293, 1497252. See also E. P. 5533, 1913; 207499. F. P. 361539, 518553. D. R. P. 178299.

2. Y. Nagai, Proc. Imp. Acad. 1926, **2**, 284; abst. C. A. 1927, **21**, 1186.

3. Ann. Chim. Phys. 1836, (3), **61**, 193; abst. J. prakt. Chem. 1836, **8**, 58; J. de pharm. 1836, **22**, 316.

4. J. prakt. Chem. 1879, (2), **19**, 244; abst. Ber. 1880, **13**, 1699.

in a vacuum. V. Regnault[1] submitted dry methyl alcohol vapor to the action of anhydrous sulfuric acid. S. Weidmann and E. Schweitzer[2] distilled 1 part wood alcohol with 1 part concentrated sulfuric acid and obtained a mixture of dimethyl sulfate and methyl sulfuric acid ($(CH_3)HSO_4$) which they termed Methol.

M. Müller[3], by the action of fuming sulfuric acid on methyl alcohol at high temperatures obtained oxymethane sulfonic acid, but the Actien Ges. fur Anilin Fabrikation found[4] that if the reaction be conducted at low temperatures, a good yield of methyl sulfate is obtained, the process claimed being for the action of fuming sulfuric acid on methyl alcohol at 30°-40°C., and distillation of the product *in vacuo*. In the patented process of E. Merck[5] for methyl- and ethyl-sulfate manufacture, methyl alcohol and sulfur trioxide are admixed at 0° C. and after standing,

1. Ann. Chim. Phys. 1837, **66**, 107; abst. Berz. Jahr. 1839, **18**, 455; Ann. Pharm. 1837, **27**, 11; J. prakt. Chem. 1838, **13**, 429.

2. Pogg. Ann. 1838, **43**, 593; abst. Berz. Jahr. 1840, **19**, 577.

3. Bonn. Sitz. Ber. Niederrhein. Ges. 1873, **30**, 178; abst. Ber. 1873, **6**, 1031. Compare C. Graebe, Ann. 1905, **340**, 244; P. Ray and P. Neogi, J. C. S. 1906, **89**, 1900.

4. D. R. P. 113239, 1900; abst. Chem. Zentr. 1900, II, 614; Chem. Ind. 1900, **23**, 450; Chem. Ztg. 1900, **24**, 722; Jahr. Chem. 1900, **53**, 615; 1903, **56**, 789; Friedlander, July, 1907, **5**, 930; Mon. Sci. 1900, **56**, 72; Meyer Jahr. Chem. 1900, **10**, 406; Tech. Chem. Jahr. 1900-1901, **23**, 420; Wag. Jahr. 1900, **46**, II, 2; Zts. ang. Chem. 1900, **13**, 819. E. P. 7020, 1899; abst. J. Soc. Dyers, 1900, **16**, 62; J. S. C. I. 1900, **19**, 273. F. P. 287572, 1899; abst. Mon. Sci. 1900, **56**, 24; Chem. Ztg. 1900, **24**, 270; Rev. de Chim. Ind. 1899, **10**, 266. F. P. 287572. See also E. Merck, D. R. P. 102634, 1898; abst. Wag. Jahr. 1899, **45**, 570; Chem. Zentr. 1899, II, 408; Chem. Ztg. 1899, **23**, 441; Zts. ang. Chem. 1899, **12**, 404; Jahr. Chem. 1899, **52**, 2159; Chem. Ind. 1899, **22**, 204; Bied. Tech. Chem. Jahr. 1899-1900, **22**, 235; Friedlander, 1901, **5**, 807; Mon. Sci. 1899, **54**, 128. F. Ullmann, 1900, **33**, 2476.

5. D. R. P. 133542, 1901; abst. Mon. Sci. 1903, **59**, 74; Chem. Zentr. 1902, II, 314; Chem. Ind. 1902, **25**, 452; Chem. Ztg. 1902, **26**, 681; Jahr. Chem. 1902, **55**, 807; Wag. Jahr. 1902, **48**, II, 5; Zts. ang. Chem. 1902, **15**, 739. See also A. Villiers, Bull. Soc. Chim. 1880, (2), **34**, 26. See also Beilstein Hdb. d. org. Chem. 1893, I, 330. J. Dumas, L'Inst. 1834, II, 106, 112; Ann. 1835, **16**, 164; Pogg. Ann. 1834, **31**, 650. M. Berthelot, Bull. Soc. Chim. 1873, **19**, 295. E. Merck, D. R. P. 77278, 1893; abst. Wag. Jahr. 1894, **40**, 570; Chem. Zentr. 1895, I, 192; Zts. ang. Chem. 1894, **7**, 626; Ber. 1895, **28**, 31; Friedlander, 1899, **4**, 17; Bied. Tech. Chem. Jahr. 1894-1895, **17**, 445; Jahr. Organ. Chem. 1894, **2**, 33.

the water, sulfuric acid and methyl-sulfuric acid formed are removed from the dimethyl sulfate by distillation in a vacuum. By dissolving chlorsulfonic acid with sulfur trioxide in the presence of carbon tetrachloride and methyl alcohol, the Soc. Anon. des Prod. de Fontaines[1] obtain a high yield of methyl sulfate, the products of reaction being removed by distillation under reduced pressure, local superheating being avoided by operating with a diluent as CCl_4. An enamelled vessel, equipped with reflux condenser, is charged with 6.4 kilos of 99% methyl alcohol and 20 kilos carbon tetrachloride, and under stirring, 24 kilos chlorsulfonic acid slowly introduced. Then the solvent is distilled off on the water bath for re-use, and the operation repeated. The acid may be replaced by sulfur trioxide (sulfuric anhydride).

The process of W. Haworth and J. Irvine[2] consists in the union of dimethyl ether with sulfur trioxide by direct means, and under selected conditions, they having discovered that combination of the two reagents takes place with readiness in the presence of a solvent or diluent, methyl sulfate resulting. They place 50 grms. pre-formed methyl sulfate in a vessel in which are arranged two leading tubes dipping below the surface of the liquid, through one of which a stream of dimethyl ether gas is admitted, and through the other a current of sulfur trioxide vapor, which latter vapor may be mixed with air as an aid to its transmission. During the passage of the gases, the liquid medium is agitated, the rate of admission being so regulated that no escape of dimethyl ether or sulfur trioxide takes place, approximately equimolecular quantities being admitted. Immediate combination of the two reagents takes

1. D. R. P. 193830, 1906; abst. C. A. 1908, **2**, 1861; Mon. Sci. 1910, **73**, 149; Chem. Zentr. 1907, I, 1112; Chem. Ind. 1908, **31**, 101; Chem. Ztg. 1907, **31**, 1298; Chem. Ztg. Rep. 1908, **32**, 32; Chem. Zts. 1908, **7**, 670; Jahr. Chem. 1905-1908, II, 304; Wag. Jahr. 1908, **43**, II, 5; Zts. ang. Chem. 1908, **21**, 1089.

2. U. S. P. 1401693; abst. C. A. 1922, **16**, 935; J. S. C. I. 1922, **41**, 119-A; Mon. Sci. 1922, (5), **12**, 66; Chem. Ztg. 1922, **46**, 190. E. P. 122498; abst. J. S. C. I. 1919, **38**, 233-A; C. A. 1919, **13**, 1716; Kunst. 1920, **10**, 34.

place. The crude product is treated with a reducing agent such as iron filings, pure methyl sulfate being obtained by rectification under diminished pressure.

When methyl or ethyl alcohols are treated with sulfuryl chloride (1 mol. part) or with a corresponding amount of sulfur dioxide and chloride[1], there is formed alkyl chloride, alkyl hydrogen sulfate and alkyl sulfate. The methyl or ethyl chlorides may be allowed to escape and separately collect, or may be returned into the reaction mixture to assist in the formation of alkyl sulfate. When ethyl alcohol is used, the ethyl hydrogen sulfate is separated from the ethyl sulfate, converted into its sodium salt, and the latter distilled *in vacuo* to produce more sulfate[2].

The E. Kuh process[3] comprises distilling *in vacuo* an alkyl sulfuric acid to which has been added a quantity of sodium sulfate or of a sodium alkyl sulfate sufficient to combine with all the resulting sulfuric acid to form sodium hydrogen sulfate. The process is quantitatively carried out by placing 252 parts of ethyl sulfuric acid and 150 parts dehydrated sodium sulfate in a vessel provided with a stirrer, the product being distilled under an absolute pressure of 10-15 mm. Hg. The ester acid is preferably added gradually to the heated sodium sulfate, the contents of the vessel throughout the distillation being kept in a dry pulverulent condition. Where ethylsulfuric acid is used, the ethyl sulfate formed begins to distil over between 90-100° C., and at 160-170° is complete, the yield being about 85% of the theoretical. Where 20 parts anhydrous sodium sulfate, 111 parts dry sodium ethylsulfate are heated together and 126 parts free ethyl sulfuric acid gradually added, the yield of ethyl sulfate is said to be about 85-90% of theory.

1. J. Irvine and W. Haworth, E. P. 117824; abst. C. A. 1918, **12**, 2573.

2. L. Lilienfeld, E. P. 13882, 1913; abst. C. A. 1914, **8**, 3840. U. S. P. 1074633; abst. C. A. 1913, **7**, 4046. D. R. P. 272339; F. P. 459282; abst. C. A. 1914, **8**, 3100.

3. U. S. P. 1411215; abst. C. A. 1922, **16**, 1781; J. S. C. I. 1922, **41**, 348-A.

The T. Durrans process[1] is based upon the treatment of 2 mols. of methyl alcohol with approximately 1 mol. each of sulfur dioxide and chlorine, the latter being preferably in slight excess. The gases may be passed either simultaneously or successively, in the former case the necessary excess of SO_2 being added at the start. Methyl chloride is a gaseous product of the reaction, being subsequently transformed into methyl sulfate, which is isolated and purified by distillation under reduced pressure[2]. It is said that yields of well over 50% by weight of methyl sulfate are obtained, which in conjunction with methyl chloride also produced, "represents a yield approaching that possible theoretically"[3].

J. Guyot and L. Simon[4] add methyl alcohol to sulfuric acid sp. gr. 1.84, and into this mixture is distilled the calculated quantity of sulfur trioxide, or alternatively the methyl alcohol-sulfuric acid mixture is added to the calculated quantity of 60% oleum. In either case the mixture is subsequently distilled under diminished pressure to remove the products of reaction and recover the methyl sulfate in a pure state. A more direct method is to add 4 parts of 60% oleum to 1 part of methyl alcohol cooled to —18° C., and subsequently distil the mixture under reduced pressure, the yield being over 90% of theory. In a subse-

1. U. S. P. 1317648; abst. C. A. 1919, **13**, 70; J. C. S. 1920, **118**, i, 213; J. S. C. I. 1919, **38**, 926-A; J. Soc. Dyers. Col. 1920, **36**, 297; Chem. Ind. 1921, **5**, 70. E. P. 119250.

2. P. Behrend, J. prakt. Chem. 1877, (2), **15**, 23; abst. J. C. S. 1877, **32**, 287; Jahr. Chem. 1877, **30**, 516; Jahr. reinen Chem. 1877, **5**, 148.

3. The methyl chloride may be isolated from the other gaseous products of the reactions by passing them through sodium hydroxide solution, or through a tower filled with slaked lime, the alkali absorbing the sulfur dioxide and the hydrogen chloride while the methyl chloride passes on. The methyl chloride may be used in its gaseous state or may be condensed to a liquid, by means of cold or pressure or a combination of these.

4. Compt. rend. 1919, **169**, 435; abst. J. C. S. 1919, **116**, i, 465; J. S. C. I. 1919, **38**, 792-A; C. A. 1920, **14**, 1303.

quent communication[1] it is recommended to pass the vapor of methyl ether into 60% oleum until the whole of the sulfur trioxide which it contains is converted into methyl sulfate, and *then* distil the mixture[2].

Chlorsulfonic acid is employed in the F. Ullmann process[3], 100 grms. being combined gradually with 27 grms. anhydrous methyl alcohol at —5°-10° C., the methyl sulfate formed being distilled off at 20 mm. pressure. Methyl sulfate also results, according to M. Blackler[4], by distilling a mixture of dimethyl ether in concentrated sulfuric acid to 160° C., or by heating dimethyl ether with lithium salts or alkaline earth metal salts with methyl sulfuric acid to 200°.

In the W. Bader process[5], the distillation of alkyl hydrogen sulfate is effected under reduced pressure in such a manner that at any given moment only a small portion of the liquid which is actually undergoing distillation is under the influence of the heat. In this manner the side reactions which result in the formation of such bodies as ethylene, ethyl ether, ethionic acid, isoethionic acid and methionic acid are avoided. The yield is about 110% of the theoretical yield calculated on the alkyl hydrogen sulfate originally present.

In another process[6] there is introduced into a receptacle 66° Be. sulfuric acid 160, methanol 200, which is

1. J. Guyot and L. Simon, Compt. rend. 1919, **169**, 795; abst. J. C. S. 1919, **116**, i, 566; J. S. C. I. 1919, **38**, 924-A; Chem. Zentr. 1919, III, 981; C. A. 1920, **13**, 539. See also Chem. Ztg. 1920, **44**, 507; abst. Chem. Tech. Uebers. 1921, **45**, 333.

2. Actien ges. fur Anilin Fabrikation, F. P. 287572, 1899; abst. Mon. Sci. 1900, **56**, 24; Chem. Ztg. 1900, **24**, 270; Rev. Chim. Ind. 1899, **10**, 266.

3. Ann. 1903, **327**, 106; abst. J. S. C. I. 1903, **22**, 412; J. C. S. 1903, **84**, i, 394; Chem. Zentr. 1903, I, 1213; Jahr. Chem. 1903, **56**, 788.

4. Chem. News, 1901, **83**, 303; abst. Jahr. Chem. 1901, **54**, 654.

5. U. S. P. 1484249; abst. C. A. 1924, **18**, 1129.

6. Etablissements Lambiotte Freres, E. P. 336681; abst. C. A. 1931, **25**, 1841. F. P. 702272; abst. C. A. 1931, **25**, 4012. Belg. P. 368156. See E. P. 122498. In the process of N. V. de Bataafsche Petroleum Maatschappij (F. P. 718943; abst. C. A. 1932, **26**, 3261) dialkyl sulfates are prepared by bringing olefins in excess in contact with concentrated sulfuric acid, preferably at least 2 mols. olefin per

added in full before heating, or in portions during the heating of the product between 100-160°. The ether formed is conveyed to absorption towers containing 60% oleum 417, kept at 30°. When all the ether is absorbed the mixture is distilled. Yield, methyl sulfate 374.

The R. Taveau[1] and F. Apgar[2] processes use the gases from pyrogenetic decomposition of hydrocarbon oils containing ethylene, propylene and butylene, which in the former process are treated in three successive stages with sulfuric acid of progressively increasing concentration, the butylenes and more readily polymerized substances being absorbed with a relatively weak acid at a temperature not exceeding 30°, the gases being thereafter treated with stronger acid for the absorption of propylene, to separately produce corresponding acid alkyl sulfates. Apgar has devised an apparatus for carrying out the process.

K. Fuchs and E. Katscher[3] have given details for the commercial production of dimethyl sulfate, methylene sulfate, chlormethyl sulfate, *s*-dichlordimethyl sulfate, chlormethyl sulfate chloride, dichlormethyl ether and methylene chloride, of minor importance in cellulose etherifying operations.

Properties of Methyl Sulfate. Colorless, heavy, toxic liquid, b. pt. (corr.) 188.3-188.6°[4] or 186°[5], density 15°/15°, 1.33344, 25°/25°, 1.32386. Readily soluble in turpentine oil, ionized by water[6] and readily saponified by water or

mol. 90-100% acid concentration. In the W. Engs and R. Moravec method (U. S. P. 1854581; abst. C. A. 1932, **26**, 3265), dibutyl sulfate is produced by treating the corresponding olefin with concentrated sulfuric acid, in the molecular proportions of 2:1. According to Chem. & Met. Eng. 1932, **39**, 465, a plant for the manufacture of methyl sulfate is under erection at Belle, W. Va., by the Ammonia Department, E. I. du Pont de Nemours Co.

1. U. S. P. 1810192; abst. C. A. 1931, **25**, 4557.
2. U. S. P. 1846666. See W. Webb and Carbide & Carbon Chemicals Corp., U. S. P. 1560625. Belg. P. 318416.
3. E. P. 299064; abst. C. A. 1929, **23**, 2990.
4. W. Perkin, J. C. S. 1886, **49**, 785.
5. M. Dubroca, J. Chim. Phys. 1907, **5**, 463; abst. Chem. Zentr. 1908, I, 641.
6. P. Walden, Zts. physik. Chem. 1906, **54**, 174.

acids[1], the aqueous solutions reacting with alkali and alkali earth iodides to produce methyl iodide[2]. As a valuable methylating agent, it may be substituted in all cases for the relatively more costly methyl iodide. When a substance which contains hydroxyl, amido or imido groups is treated with dimethyl sulfate and an aqueous solution of alkali hydroxide, the H atoms of these groups are displaced by methyl groups. It has been proposed for the estimation of tar oils in mixture with resin oils and mineral oils[3], and as a catalyst in the acetylation of cellulose, as in the processes of A. Corti[4], L. Lederer[5], and Knoll & Co.[6] esterify cellulose in the presence of methylamine sulfate. S. Peachey[7] has reported on the property of methyl sulfate as an indigo solvent.

Uses of Methyl Sulfate. In addition to the etherification of cellulose and carbohydrate bodies (see pp. 4, 24, 25, 28, 29, 32, 35, 36, 39, 56, 57, 58, 73, 74, 76, 78, 79, 123, 124, 145, 161, 170, 209, 279, 293), methyl sulfate has been employed for the methylation of vanillin[8], hydroxyazo com-

1. R. Kremann, Monats. 1907, **28**, 13.

2. R. Weinland and K. Schmid, D. R. P. 175209; abst. Chem. Zentr. 1906, II, 1589; Wag. Jahr. 1906, II, 7.

3. P. Behrend, J. pr. Chem. 1877, (2), **15**, 32; abst. J. C. S. 1877, **32**, ii, 287.

4. A. Corti and Fabrique de Produits Flora Societe Anonyme, U. S. P. 826229; abst. J. S. C. I. 1906, **25**, 825; Mon. Sci. 1907, (4), **66**, 35; E. P. 9998, 1905; abst. J. S. C. I. 1905, **24**, 855. F. P. 345764; abst. J. S. C. I. 1905, **24**, 40; Mat. Color. 1905, **9**, 53; Mon Sci. 1906, (4), **64**, 12. D. R. Appl. C.-12963, 1903. Belg. P. 183877. Ital. P. Appl. dated April 17, 1905.

5. Methyl sulfate is an oily liquid of sp. gr. 1.33 at 15° and boiling with partial decomposition at 188°. Ethyl sulfate (L. Lilienfeld, E. P. 13882, 1913; F. P. 459282. U. S. P. 1074633; abst. C. A. 1913, **7**, 4046; J. S. C. I. 1913, **32**, 1030, 1130) may be prepared by distilling sodium ethyl sulfate in a vacuum, with or without the addition of a suitable diluent. See L. Lilienfeld, E. P. 6387, 1913; abst. Kunst. 1914, **4**, 256.

6. Knoll & Co., E. P. 2491, 4353, 16905, 1913.

7. J. Soc. Dyers Col. 1914, **30**, 84; abst. C. A. 1914, **8**, 1673.

8. H. Decker and O. Koch, Ber. 1907, **40**, 4794; abst. C. A. 1908, **2**, 822.

pounds[1], hydroxy-4-benzeneazobenzoic acid[2], thiophenyl ethers[3], carbamides[4], phenols[5], glucose[6], phenylmethylamine[7], sinomenine[8], quercetin[9] and salicylic acid and methyl salicylate[10]. It has been used in the preparation of benzene-, toluene-, and xylene-dialkylsulfonamides[11], dimethyltoluenesulfonamide[12], film manufacture[13] and in the treatment of hydrocellulose[14]. Other proposed uses are in the methylation of aminoanthraquinone[15], benzaldehyde[16], celluloid substitute manufacture, dyestuff production[17], guaiacol preparation[18], thioureas formation[19], plastic manufacture[20] and fumaric acid condensation[21]. It is to be remembered that, as ordinarily used, but one-half of the methyl groups of methyl sulfate go into the methylation, the other half forming methyl hydrogen sulfate or its salts, or dimethyl ether. In consideration of this fact, it is of

1. A. Colombano, Att. accad. Lincei, **16**, (II), 457; abst. C. A. 1908, **2**, 1719.
2. *Ibid.* Att. accad. Lincei, **16**, (II), 547; abst. C. A. 1908, **2**, 1720.
3. K. Auwers and F. Arndt, Ber. 1909, **42**, 2173; abst. C. A. 1909, **3**, 2577.
4. E. Werner, J. C. S. 1914, **105**, 923; Proc. Chem. Soc. **30**, 26; abst. C. A. 1914, **8**, 2342.
5. L. Simon and M. Fréjacques, Compt. rend. 1923, **176**, 900; abst. C. A. 1923, **17**, 2110; J. S. C. I. 1923, **42**, 1098-A.
6. L. Maquenne, Bull. Soc. Chim. 1905, (3), **33**, 469; abst. J. C. S. 1905, **88**, 415.
7. T. Johnson and H. Guest, J. A. C. S. 1910, **32**, 761; abst. C. A. 1910, **4**, 2266.
8. K. Goto and K. Takubo, Bull. Chem. Soc. Japan, 1931, **6**, 126; abst. C. A. 1931, **25**, 4551.
9. A. Gomm and M. Nierenstein, J. A. C. S. 1931, **53**, 4408.
10. L. Simon and M. Fréjacques, Compt. rend. 1923, **176**, 533; abst. J. S. C. I. 1923, **42**, 1098-A; C. A. 1924, **18**, 240.
11. H. Dreyfus, U. S. P. 1454959, 1454960, 1454961.
12. *Ibid.* U. S. P. 1508928.
13. *Ibid.* U. S. P. 1501206.
14. *Ibid.* U. S. P. 1451330.
15. W. Haworth, U. S. P. 1426380.
16. A. Lapworth, U. S. P. 1431470.
17. M. Kardos and P. Nawiasky, U. S. P. 1200848, 1253252. F. Singer and A. Holl, U. S. P. 1329435. P. Nawiasky, U. S. P. 1505912.
18. E. Zollinger, U. S. P. 1281662.
19. P. Thomaschewski, U. S. P. 1218655.
20. Diamond State Fibre Co., E. P. 221553.
21. W. Ponndorf, D. R. P. 362752; Addn. to D. R. P. 338737.

paramount importance that the conditions involved in the particular process employed be critically studied, especially if on large scale production[1].

Toxicity of Methyl Sulfate. There appears to be a divergence of opinion as to the relative toxicity of this chemical, but well authenticated cases are on record as to poisoning. Danger lies in the harmless appearance of the compound. Moreover, the danger is increased by the fact that it has a considerable vapor pressure in spite of its high boiling point, and that its action upon the skin and mucous membrane is not immediate. The vapors attack the delicate membranes of the eyes and respiratory organs, while the liquid is readily absorbed by the skin, and then acts internally. The poisonous action appears to be due to its hydrolysis to methyl sulfuric acid and methyl alcohol, and the following precautions in its handling should be observed. All containers should be stored out of doors, in a cool, dry place, small bottles for laboratory use being kept in a separate room with other dangerous chemicals. Plant storage tanks should be installed in sheds outside the methylation building, the reaction tank being tightly covered with ventilating pipe leading through the roof, equipped with a steam ejector so that a slight vacuum is formed in the pipe and any escaping methyl sulfate vapor destroyed. All transference of methyl sulfate from one tank to another should be by vacuum. When dropped on the floor, cover with sodium carbonate or soda lime and wash away with water. Eyes attacked with the vapors should be washed with car-

1. For complete methylation by means of methyl sulfate, see J. Tambor, Ber. 1910, **43**, 1882; action on alkali polysulfides, W. Strecker, Ber. 1908, **41**, 1105; hydrolysis with sodium methoxide or ethoxide, J. Pollak and A. Baar, Monats. f. Chem. 1918, **38**, 501; action of chlorsulfonic acid on, R. Levaillant and L. Simon, Compt. rend. 1919, **169**, 140; hydrolysis with aqueous alkali, A. Klemenc and E. Edhofer, Monats. f. Chem. 1918, **38**, 553; and action of heat on the methyl sulfates of the alkalis and alkaline earths, J. Guyot and L. Simon, Compt. rend. 1919, **168**, 1054. H. Lewis, O. Mason and R. Morgan (Jour. Ind. Eng. Chem. 1924, **16**, 811) have exhaustively studied the hydrolysis of methyl sulfate at 95°.

ron oil[1]. Apparently there has been an exaggerated conception of the danger of this product[2]. The toxicity rapidly diminishes with its hydrolysis[3].

P. Erdmann[4] has described a case of inflammation of the eyes caused by methyl sulfate. It appears[5] that edema of the lungs and increased phosphates in the urine normally result in poisoning. A. Hamilton[6] has made a study of factory conditions where methyl sulfate and other poisonous products were employed in dyestuff and intermediates manufacture, and laid down detailed preventative methods. The local action[7] represents closely that of sulfuric acid[8]. It is a centrally attacking nerve poison, the mechanism of the effect being, first of all, absorption as an undecomposed molecule which gradually hydrolyzes in the tissues to sul-

1. M. Mueller, Chem. Met. Eng. 1920, **23**, 833; abst. C. A. 1921, **15**, 509.

2. In this connection see Ullmann Ency. der Tech. Chemie, 1904, **1**, 262. Weyl, vol. 2, 604. H. Decker and O. Koch, Ber. 1907, **40**, 4794. E. Werner, J. C. S. 1914, **105**, 2762; abst. C. A. 1915, **9**, 607. N. Shepard, J. A. C. S. 1916, **38**, 2507; abst. C. A. 1917, **11**, 51. F. Ullmann and P. Wenner, Ber. 1900, **33**, 2477; abst. Jahr. Chem. 1900, **53**, 616. Ann 1903, **327**, 104. H. Decker, Ber. 1905, **38**, 1147. C. Graebe, Ann. 1905, **340**, 205. E. Grandmougin, Chem. Ztg. 1913, **37**, 812. F. Ullmann, Ann. 1903, **327**, 106; abst. Jahr. Chem. 1903, **56**, 788. S. Weber, Arch. f. exp. Path. u Pharm. **47**, 113; abst. Chem. Zentr. 1902, I, 364; Jahr. Chem. 1902, **55**, 807. Agfa. Chem. Ind. 1900, **23**, 549.

3. J. Michels, Arch. intern. pharmacodyn, **21**, 467; abst. C. A. 1912, **6**, 1932.

4. Arch. Augenheilk, **62**, Nos. 2, 3; abst. Biochem. Centr. **8**, 650; C. A. 1909, **3**, 2834.

5. F. Mohlau, J. Ind. Hyg. 1920, **2**, 239; abst. C. A. 1921, **15**, 395. See also Zts. f. expt. Path. u Ther. 1920, **21**, 1. T. Sommerfeld and R. Fischer, Ohio State Board of Health, 1914, 19. G. Kober and E. Hayhurst, "Industrial Health," 1924, 642-662; abst. C. A. 1924, **17**, 872. Mock, "Industrial Medicine and Surgery" (1919).

6. Textile Colorist, 1920, **42**, 325, 399, 400, 471, 475; abst. C. A. 1920, **14**, 2989.

7. J. Bodenstein, Wiener. Klin. Wochschr. 1921, **34**, 226; abst. C. A. 1922, **16**, 2925.

8. H. Strothmann, Klin. Wohnschr. 1929, **8**, 493. See also Chem. Ind. 1900, **23**, 559. J. Auer, Proc. Soc. Exper. Biol. and Med. 1918, **15**, 104. See also "The Occupational Diseases," Thompson, 1914, 330-331. "Industrial Poisoning," J. Rambousek, 1913. Translated by T. Legge, 1913, 22-23. The Local Effects of Dimethyl Sulfate, Wein. Klin. Wochauschr., May 12, 1921. Flury-Zernik, "Schädliche Gase," 1931, 368-370. K. Lehmann, "Arbeits und Gewerbehygiene," 1919, 241.

furic acid and methyl alcohol and probably also to formaldehyde, typical irritations being developed in the eyes and the entire respiratory tract, with corrosion of the mucous membranes down to the deepest ramifications of the bronchi. A reabsorptive effect takes place only after the reception of of considerable quantities of poison; then occur centrally conditioned spasms, lowering of the blood pressure, spasms and coma.

Ethyl Chloride. *Kelene.* C_2H_5Cl. Ethyl chloride may be formed by the direct union of chlorine and ethane[1]; by the interaction of phosphorous trichloride upon ethyl alcohol[2], which may be made a quantitative process[3] by heating diethylbenzamid with phosphorous pentachloride[4]; from ethyl alcohol and HCl (19° Be.) in the presence of calcium chloride[5]; or from benzoyl chloride and ether by the action of methylzinc iodide[6].

Ethyl chloride at the present time is produced commercially by one of the following five general processes:

I. *Reaction of Hydrochloric Acid on Ethylene.* In the process of J. Wibaut[7], gaseous olefine as ethylene in admixture with halogen halide is passed over catalytic material at a temperature below 250°. Compounds of metals of the fifth periodic group are employed as catalysts, e.g., oxides, hydroxides, chlorides and oxychlorides of bismuth, antimony or vanadium, bismuth nitrate, or the chlorides of nickel and tantalum. Lighting gas, coke-oven gas, oil gas or gas mixtures may be used, obtained by cracking petroleum products, the reaction gases being first washed with water to remove excess of HCl, the alkyl halide being then

1. M. Schorlemmer, Ann. 1864, **131**, 76; **132**, 234. W. Darling, Ann. 1869, **150**, 216.
2. W. Wurtz, Compt. Rend. 1845, **21**, 357.
3. J. Walker and F. Johnson, J. C. S. 1905, **87**, 1592.
4. E. Merck, D. R. P. 168728; abst. Chem. Zentr. 1906, I, 1469.
5. Akt. Ges. f. Anilin. Fabr., D. R. P. 280740; abst. Chem. Zentr. 1915, I, 104.
6. E. Blaise, Bull. Soc. Chim. 1911, (4), **9**, 5.
7. E. P. 209722; abst. C. A. 1924, **18**, 1673; J. S. C. I. 1924, **43**, 731-B; C. Zent. 1925, I, 895. F. P. 574800. D. R. P. 361041, 369702. Belg. P. 314537.

separated by cooling, by washing with a solvent, or by absorption on activated charcoal.

In the H. Suida processes[1], ethyl chloride is formed from ethylene and HCl under about 30 atms. pressure and at temperatures of 10-50° in the presence of anhydrous chlorides of aluminum, antimony, chromium, iron, cobalt, manganese, magnesium, nickel, titanium, zinc or tin, in their highest state of oxidation, or double compounds of these chlorides with ethylene. As a specific example of carrying the process into effect, equal volumes of dry ethylene and hydrogen chloride are pumped into a steel autoclave containing ferric chloride and some glass balls until the pressure attains 30 atms. The reaction begins at 10°, and is maintained by forcing in more reacting gases. The process may be discontinued at intervals for the withdrawal of the formed ethyl chloride, or the operation may be made continuous by the provision of an outlet to the bottom of the autoclave through which the product may be withdrawn. In another process somewhat similar[2], chlorinated hydrocarbons obtained from the chlorination of paraffin oil, road oil, shale oil, asphalts, natural waxes or coal are employed with a catalyst.

The Farbwerke vorm. Meister, Lucius & Bruening process employs sulfur dioxide in addition to hydrochloric

1. U. S. P. 1637972; abst. C. A. 1927, **21**, 3057. E. P. 229298; abst. C. A. 1925, **19**, 3092; J. S. C. I. 1925, **44**, 652-B; C. Zentr. 1925, II, 2090. E. P. 253521; abst. C. A. 1926, **20**, 918; J. S. C. I. 1925, **44**, 737-B; C. Zentr. 1926, I, 2240. F. P. 591753; abst. C. Zentr. 1925, II, 2090. D. R. P. 361041, 369702; abst. Ber. 1924, **57**, 95. D. R. P. 417170, Addn. to D. R. P. 369702; abst. J. S. C. I. 1923, **42**, 578-A; Chem. Tech. Uebers, 1923, **47**, 87; C. Zentr. 1923, II, 906. K. Dachlauer and E. Eggert, D. R. P. 441747. H. Suida, D. R. P. 420441; abst. J. S. C. I. 1926, **45**, 464-B; C. Zentr. 1926, I, 2241. D. R. P. 478082; abst. C. A. 1929, **23**, 4231. D. R. P. 485434; abst. C. A. 1930, **24**, 866. Aust. P. 103496, 103497. Aust. P. 106039, Addn. to Aust. P. 103497. I. G. Farbind., Aust. P. 119959. H. Suida, Swiss P. 113348. D. R. P. 413447. See G. Gustavson, J. pr. Chem. 1886, **34**, 161.

2. E. Payne and S. Montgomery, U. S. P. 1520506.

acid[1], the chloride of ethylsulfurous acid being formed as an intermediate product. Ordinary or activated charcoal, bauxite, burnt pyrites or terra cotta are used as catalysts, the reaction being carried out under pressures.

J. Garner and H. Clayton[2] have found that by the use of charcoal as a catalyzer, the operations proceed smoothly and regularly, the reaction chamber being filled with the charcoal of suitable size to permit free penetration of the mixture of gases throughout the mass. If HCl in a dry state with olefine as ethylene is passed over aluminum chloride at about 150°, a high yield of ethyl chloride is obtained[3]. When working under strictly anhydrous conditions as in the process of G. Curme[4], excellent yields of ethyl chloride, and especially propyl chloride, may be obtained by submitting ethylene or propylene at 15 atms. pressure for propyl, or 35 atms. for ethyl, no special form of apparatus being required. Aluminum chloride is the preferred catalyst.

If a mixture of ethylene free from benzene, and HCl is heated to 200-300° in the presence of heat carriers as pieces of alumina, porcelain, pumice stone, diatomite or wood charcoal, with or without the addition of heavy metal oxides as catalysts[5], a high yield of ethyl chloride is said to result with practically no side reaction products. Instead of aluminum, the metal may be activated or mixed or alloyed with other metals as zinc[6], to produce nearly theoretical yields of ethyl chloride from ethylene and HCl.

1. E. P. 216368; abst. C. A. 1925, **19**, 78; J. S. C. I. 1924, **43**, 654-B; Ann. Rep. S. C. I. 1924, **9**, 104; C. Zentr. 1925, I, 1240. F. P. 566041; abst. C. Zentr. 1925, I, 1240. Swiss P. 104789; abst. C. Zentr. 1925, I, 1240.
2. U. S. P. 1262769. See U. S. P. 1484289.
3. W. Webb, U. S. P. 1560625; J. S. C. I. 1924, **45**, 77-B; Ann. Rep. S. C. I. 1926, **11**, 90; C. Zentr. 1926, I, 1713.
4. U. S. P. 1518182; abst. C. A. 1925, **19**, 523; J. S. C. I. 1925, **44**, 150-B; C. Zentr. 1925, I, 1129.
5. H. Liebmann, D. R. P. 361041; abst. C. Zentr. 1923, II, 475; J. S. C. I. 1923, **42**, 520-A; Chem. Tech. Uebers, 1923, **47**, 4.
6. A. Mittasch and M. Mueller-Cunradi, D. R. P. 403507; abst. J. S. C. I. 1925, **44**, 378-B; Ann. Rep. S. C. I. 1924, **9**, 104; C. Zentr. 1925, I, 1370.

II. *Reaction of Ethyl Alcohol and Hydrochloric Acid.* Ethyl chloride is obtained by passing a mixture of alcohol and HCl over or through liquid phosphoric acids at a temperature of about 200°[1]; or a mixture of ethyl alcohol, water and ferric chloride in the proportions of about 16:11:73 at about 80° or slightly higher[2]. Ethyl chloride may also be made at normal pressure and under augmented atmospheric pressure by employing anhydrous alcohol and HCl gas[3], esterification being conducted in a system which has a large surface of contact, the operation being in a closed cycle. The temperature used varies between 13° and 16°. Where gaseous HCl and alcohol are allowed to react in the presence of a fused catalyst as zinc chloride[4] maintained at a sufficiently high temperature to drive off the water formed in the reaction, and the product then fractionated, a yield of 80-85% of theory is obtainable, temperature of 110-150° being recommended[5]. If ethyl alcohol vapor and HCl are passed over a phosphoric acid-active carbon catalyst at 280-300°, the yield is 95-97%[6].

In the reaction between ethyl alcohol and HCl, by decreasing the water content, the velocity of formation of ethyl chloride increases, but the speed of its hydrolysis decreases, the latter reaction not being catalytically influenced by acids, whereas in the formation of ethyl chloride, the catalytic action of HCl is ascribed to the formation of a

1. A. Wacker Ges., fuer Elektrochemische Ind., F. P. 687855; abst. C. A. 1931, **25**, 709. D. R. P. 541566.

2. E. Harding, U. S. P. 1816845; abst. C. A. 1931, **25**, 5433. See T. Callan, Chem. Age (London), 1920, **3**, 557; A. Henning, J. S. C. I. 1920, **39**, 1-T.

3. M. Douane and A. Vila, F. P. 529558; abst. Chim. et Ind. 1922, **8**, 621.

4. A. Backhaus, U. S. P. 1509463; abst. C. A. 1925, **19**, 78; C. Zentr. 1925, I, 573.

5. J. Frei, U. S. P. 1784423; abst. C. A. 1931, **25**, 303. E. I. DuPont de Nemours & Co., F. P. 692790; abst. C. A. 1931, **25**, 1537.

6. K. Dachlauer and E. Eggert, D. R. P. 441747; abst. J. S. C. I. 1928, **47**, 35-B; C. Zentr. 1927, I, 2945.

complex, $C_2H_5OH.HCl$, which is easily decomposed by water[1].

III. *Decomposition of Chlorsulfonic Ethyl Ester with Water.* According to M. Mueller[2], this decomposition takes place with formation of alcohol, sulfuric acid and HCl, the ethyl chloride being produced as a by-product, which has been shown by F. Bushong[3], in approximately 16% of the theoretical quantity possible. Mueller found that considerable quantities of ethyl chloride are also formed if a concentrated caustic potash solution, or zinc powder and water is allowed to act upon the chlorsulfonic ethyl ester (ethyl chlorsulfonate). J. Claessen has pointed out[4] that where the latter is mixed with alcohol, considerable quantities of ethyl chloride are produced in addition to ethyl ether and HCl, and eventually ethyl sulfate; and J. Nef[5] has shown that the ethyl chlorsulfonate prepared by the action of phosphorous pentachloride on ethyl sulfuric acid is identical with the product obtained from ethyl alcohol and sulfuryl chloride of P. Behrend[6].

The patented process of W. Traube[7] depends primarily upon the observation that HCl decomposes ethyl chlorsulfonate in such a manner that ethyl chloride is produced in much more satisfactory yield than with the process just above mentioned. If concentrated HCl be employed the output of ethyl chloride is nearly theoretical, sulfuric acid being simultaneously formed. In this manner it is possible to produce without alcohol, ethyl chloride of high degree of purity. As an illustrative example, 1.5 parts strong HCl are slowly admixed while stirring with 1 part ethyl chlorsul-

1. S. Kilpi, Ann. Accad. Sci. Fennicae, 1920, **16**-A, #3, 27; abst. C. A. 1923, **17**, 2810. Ann. Univ. Fennicae Aboensis Serie, 1923, A, **1**, 3011; abst. Chem. Zentr. 1924, I, 1021; abst. C. A. 1924, **18**, 3306.
2. M. Müller, Ber. 1873, **6**, 229; abst. J. C. S. 1873, **26**, 841.
3. Amer. Chem. J. 1903, **30**, 212; abst. J. C. S. 1903, **84**, i, 732.
4. J. pr. Chem. 1879, (2) **19**, 231.
5. Ann. 1901, **318**, 1; abst. J. C. S. 1901, **80**, i, 626.
6. J. pr. Chem. 1877, (2), **15**, 23; abst. J. C. S. 1877, **32**, ii, 287.
7. U. S. P. 1470656; abst. C. Zentr. 1924, II, 2821. D. R. P. 362741; abst. J. S. C. I. 1923, **42**, 628-A; Chem. Tech. Uebers, 1922, **46**, 383; C. Zentr. 1923, II, 741.

fonate in a vessel with a stirring device and connected with a descending condenser, the temperature being gradually increased to 100° and the reaction liquid maintained at this temperature for 1-2 hrs., during which the ethyl chloride produced distils off uniformly and is condensed by the descending condenser which is preferably filled with a freezing mixture. The yield is stated to be approximately theoretical.

IV. *Photochemical Reactions.* W. Snelling[1] has devised a method and patented an apparatus for the production of ethyl chloride and other haloid substituted hydrocarbons, involving exposing mixtures of the reagents to actinic rays for the purpose of inducing their interaction, his apparatus comprising a liquid-sealed, transparent container provided with a fluid inlet and fluid outlet. The container may be in spaced series of transparent reaction vessels[2], those composing each series being connected by inlet and outlet conduits, and a series of light sources disposed between, each of the light sources being opposite to one of the reaction vessels of each adjacent series.

V. *Ethyl Chloride from Ethane.* In the B. Lacy process[3], a mixture of 8 vols. ethane which may contain the usual moisture carried by gases stored over water, and 1 vol. chlorine gas are passed into a heated reaction vessel composed of or lined with a material as silica, earthenware or brick, which neither is appreciably attacked by chlorine nor causes separation of carbon from the hydrocarbon, the reaction vessel being maintained at a temperature in the neighborhood of 300-550°. The reaction velocity increases considerably with rise of temperature. From the reaction vessel the off-gas, consisting substantially of HCl, ethyl chloride and excess ethane, is passed through a water absorption system arranged on the counter-current principle.

1. U. S. P. 1365740. 2. W. Snelling, U. S. P. 1339675.
3. U. S. P. 1242208. See M. Schorlemmer, Compt. rend. 1864, **58**, 703. W. Darling, Ann. 1869, **150**, 216; Lit. Phil. Soc. Proc. 1868, **7**, 173; **8**, 59; Chem. Soc. J. 1868, **7**, 496. U. S. P. 1263906. See U. S. P. 1111842, 1190659. Norw. P. 26837.

A strong solution of HCl leaves the system at the bottom, while the off-gas consists of ethyl chloride and excess of ethane.

Somewhat analogous is the procedure of W. Snelling[1], who brings ethane into contact with gaseous chlorine under the influence of actinic rays or equivalent agent capable of promoting combination between the hydrocarbon and halogen hydride, but there is a tendency to substitution of more than one halogen atom in each hydrocarbon molecule. The amount of polyhalogen hydrocarbon produced may be materially reduced, however, by using a considerable excess of hydrocarbon as compared with the halogen present, in which case polyhalogen compounds are reduced to a negligible quantity.

Applications of Ethyl Chloride. (See pp. 87, 150, 161, 170, 190, 233, 238, 239, 247, 278, 287, 288, 289, 290, 293, 294, 297, 301.) Ethyl chloride has been used as a cellulose acetate solvent (p. 484, n. 4), for the etherification of cellulose (p. 9; 100, n. 3; 870, n. 3); for plastic formation with tar oil or cresol (p. 561, n. 1); as a cellulose ether solvent[2], for the etherification of pentaerythrite[3], the production of *p*-toluenediethyl sulfonamide[4], and for general alkylating purposes[5]. A. Henning[6] claims ethyl chloride is equal to the sulfate as an ethylating agent.

Ethyl chloride has also been recommended for use in the preparation of dry batteries[7], for bottle closures[8], as a solvent for caffeol[9], carbonyl chloride[10], cellulose nitrate[11], and chloric ether[12]; for disinfectant manufacture[13], and for the preparation of emulsions[14]. Ethyl chloride also enters into the manufacture of ethylamine[15], motion picture films[16],

1. U. S. P. 1421733. See also U. S. P. 1271790, 1285823, 1325214.
2. F. P. 483316.
3. U. S. P. 1774500.
4. U. S. P. 1454959, 1454960, 1454961.
5. E. P. 184825.
6. J. S. C. I. 1919, **38**, 452-R.
7. U. S. P. 1357160.
8. U. S. P. 1414169.
9. U. S. P. 1367724.
10. U. S. P. 1454873.
11. U. S. P. 1439293.
12. U. S. P. 1510759.
13. U. S. P. 1302905.
14. U. S. P. 1229681.
15. U. S. P. 1471213.
16. U. S. P. 1471592.

imitation gold leaf[1], and for refrigeration purposes[2]. Ethyl chloride has also been advocated as an extractive[3], and in combination with collodion as an adhesive[4]. As an ethylating agent, ethyl chloride contains a much larger proportion of ethyl than does ethyl sulfate, the ratios being 290/645 ethyl in the chloride, to 58/154 ethyl in the sulfate, or 45% and 37.6% respectively.

Properties of Ethyl Chloride. Ethyl chloride has m. pt. —142.50°[5], boils at 12.5°[6], critical temperature 187.2°[7], sp. gr. 0.9214 at 0°, 0.9176 at 8° and 0.9295 at 2°[8]. It is a colorless, pungent, ethereal smelling, mobile liquid with sweetish taste, is inflammable, burning with a green-edged flame evolving HCl, and soluble in about 3000 parts of water, although readily miscible with alcohol and ether. A solvent of phosphorus, sulfur, fats, oils and many natural and synthetic resins. The flash point of the liquid is below —18°[9].

Ethyl chloride when heated to 625°, either alone or in contact with pumice, is completely decomposed into ethylene and HCl, but when passed over soda-lime at 350°, yields hydrogen, ethane, water and ethyl alcohol, but very little ethylene. The calculated heat of formation from ethylene and HCl is 20.7 calories[10]. When heated under pressure with water or KOH, it is decomposed into ethyl alcohol and HCl. Ethyl chloride is known commercially as Kelene,

1. U. S. P. 1201758.
2. U. S. P. 1498021. For general methods of production of ethyl chloride, U. S. P. 1242208, 1262769, 1263906, 1339675, 1470656, 1518182.
3. The Solvent Extraction Refrigeration Co., Ltd., F. P. 563443; abst. Chem. Zentr. 1924, II, 2214.
4. H. Helbing, U. S. P. 628463. E. P. 25779, 1896.
5. B. v. Schneider, Zts. physik. Chem. 1897, **22**, 233.
6. V. Regnault, Jahr. Chem. 1863, **16**, 67.
7. A. Berthoud, J. Chim. Phys. 1917, **15**, 3; abst. Bull. Soc. Chim. 1918, (4), **23**, 105.
8. W. Perkin, J. pr. Chem. 1885, (2), **31**, 491.
9. E. Deiss, Zts. Elektrochem. 1923, **29**, 586; abst. C. A. 1924, **18**, 924; Chem. Zentr. 1924, I, 1020. See also T. Price, J. C. S. 1924, **125**, 115; abst. C. A. 1924, **18**, 977; Chem. Zentr. 1924, II, 2777.
10. E. Berl and J. Bitter, Ber. 1924, **57B**, 95; abst. C. A. 1924, **18**, 2126; Chem. Zentr. 1924, I, 749. For general data on ethyl chloride, see C. Baskerville, J. I. E. C. 1913, **5**, 828.

Chelene and Antidolorin; when admixed with methyl chloride as Anaesthesin or Anaestol; and when combined with ethyl bromide as Comnoform, Ethyloform or Narcoform.

Ethyl Bromide. Hydrobromic or Bromhydric Ether. Ethyl bromide may be made by the action of phosphorus and bromine upon alcohol[1], by heating absolute alcohol with bromine and distilling[2], by distilling potassium bromide[3] or sodium bromide[4] sulfuric acid and alcohol, or by treating ethylene with HBr in the presence of aluminum chloride at 0°[5]. It may be purified by shaking with dilute alkali and distilling with 10% of sweet almond oil[6].

Ethyl bromide is a colorless liquid of sweet taste, slightly soluble in water, and burns in the air with a green flame, evolving HBr. M. pt. —116°[7] to —125°[8], b. pt. 38.22°[9]. Sp. gr. 1.4189 at 15°. Ethyl bromide has been patented for the alkylation of cellulose (p. 20), and for the ethylation of flax, hemp, jute and linen (p. 294, n. 1). It has been advocated for the manufacture of allocain S[10], cephaline ethyl ether[11], 3-chlormethyl-3-octanol[12], diethylaniline[13], N.N-diethylmydriatin[14], vulcanization accelerator[15], transparent coatings[16], triethylacetamide[17] and as a wax solvent. The increased cost of bromine over chlorine, limits the use of ethyl bromide over ethyl chloride for carbohydrate alkylation.

1. G. Serullas, Ann. Chim. Phys. 1827, (2), **34**, 99; J. de pharm. 1827, **12**, 361; Pogg. Ann. 1827, **9**, 338; Quart. J. Sci. 1827, I, 476.
2. C. Loewig, Ann. 1832, **3**, 288.
3. J. de Vrij, J. pharm. 1857, (3), **31**, 169; abst. Jahr. Chem. 1857, **10**, 441. F. Taboury, Bull. Soc. Chim. 1911, (4), **9**, 124.
4. F. Weston, J. C. S. 1915, **107**, 1489.
5. G. Gustavson, J. Russ. Phys. Chem. Soc. 1884, **16**, 95; Ber. 1884, **17**, 163; 1885, **18**, 208; abst. Jahr. Chem. 1884, **37**, 515; 1885, **38**, 207. See also U. S. P. 1421733, 1429714.
6. A. Adrian, Mon. Sci. 1894 (4), **8**, 835; abst. Chem. Zentr. 1895, **66**, i, 20; J. C. S. 1895, **68**, i, 485.
7. A. Ladenburg and C. Krügel, Ber. 1899, **32**, 1818.
8. B. v. Schneider, Zts. phys. Chem. 1897, **22**, 233.
9. T. Thorpe and J. Rodger, Phil. Trans. 1894, A, **11**, 472.
10. U. S. P. 1399312.
11. U. S. P. 1219572.
12. U. S. P. 1150251.
13. U. S. P. 1429714.
14. U. S. P. 1399312.
15. U. S. P. 1471213.
16. U. S. P. 1277904.
17. U. S. P. 1482343.

Ethyl Iodide. Hydriodic Ether, Monoiodoethane. May be prepared from ethyl alcohol and HI[1]; from alcohol, iodine and phosphorus[2]; by dissolving iodine in liquid paraffin, adding yellow phosphorus and alcohol[3]; by adding ethyl sulfate slowly to a warm, aqueous solution of potassium iodide[4]; from potassium iodide and ethyl *p*-toluenesulfonate in 66.6% yield[5]; by using 80% alcohol[6], or absolute alcohol[7] with red phosphorus; or from alcohol 700, yellow phosphorus 50 and iodine 1000, when a yield of 96-98% of the theoretical is obtained[8].

Ethyl iodide is a colorless, pleasant smelling liquid, miscible with alcohol or ether, boiling at 72.42°[9] or 71°[10]. Soluble at 30° in water to the extent of 0.404%. J. Timmermanns and F. Martin[11] have given the following physical constants:

	B. pt.	M. pt.	D_{15}	D_{30}	Viscosity 15°	Viscosity 30°
Ethyl iodide	72.30°	−111.1°	1.94707	1.91326	617	540
*iso*Propyl chloride	34.8°	−117.0°	0.86797	0.84910	335	286
*iso*Propyl bromide	59.35°	−89.0°	1.32223	1.29720	536	437
*sec*Butyl chloride	68.25°	−131.3°	0.87880	0.86210	439	363
*iso*Butyl bromide	91.40°		1.27197	1.24980	679	567

The water solubility, in mols. per liter is as follows: Methyl iodide, 22°, 0.0959; ethyl iodide, 22.5°, 0.0251;

1. L. Gay-Lussac, Ann. Chim. Phys. 1814, (1), **91**, 89; Gilbert, Ann. 1814, **48**, 364; 1815, **49**, 1, 211; Paris, Mem. de l'Inst. 1812, (pte. 2), 59; Paris, Soc. Philom. Bull. 1814, 112; Thomson, Ann. Phil. 1815, **5**, 101, 207, 296, 401; **6**, 124, 183.
2. G. Serullas, Ann. Chim. Phys. 1824, (2), **25**, 323; 1829, (2), **42**, 119; J. de Pharm. 1829, **15**, 444; Pogg. Ann. 1829, **17**, 388.
3. L. Crismer, Ber. 1884, **17**, 649.
4. R. Weinland and K. Schmid, D. R. P. 175209; abst. C. A. 1907, **1**, 1086; Wag. Jahr. 1906, **52**, II, 7.
5. D. Peacock and B. Menon, Quart. J. Indian Chem. Soc. 1925, **2**, 240; abst. C. A. 1926, **20**, 1784.
6. B. Hunt, J. C. S. 1920, **177**, 1592; abst. C. A. 1921, **15**, 1019.
7. F. Beilstein and R. Rieth, Ann. 1863, **126**, 250.
8. J. Walker, J. C. S. 1892, **61**, 717.
9. P. Gross and J. Saylor, J. A. C. S. 1931, **53**, 1744; abst. C. A. 1931, **25**, 3544.
10. J. Timmermanns, J. Chim. Phys. 1928, **25**, 418.
11. J. Chim. Phys. 1928, **25**, 411; abst. C. A. 1908, **22**, 4024.

propyl iodide, 20°, 0.0051; butyl iodide, 17.5°, 0.0011; ethyl chloride, —, 0.0890; propyl chloride, 12.5°, 0.0297; butyl chloride, 12.5°, 0.0072; ethyl bromide, 17.5°, 0.0881; propyl bromide, 19.5°, 0.0185[1]. Ethyl iodide has been brought forward as a cellulose ether solvent (p. 51, n. 1), as an ethylating agent (pp. 124, 293), and as a plastic with cresol and formaldehyde (p. 561). As an ethylating agent, ethyl iodide is too expensive for general use with the carbohydrates, there being but 19% alkyl available for etherification purposes.

Ethylsulfuric Acid. *Sulfovinic Acid.* $(C_2H_5)HSO_4$, is of interest in this connection as being the intermediate body in the conversion of ethyl alcohol to ethyl sulfate. Of the three important reactions between ethyl alcohol and sulfuric acid, leading, respectively, to ethyl ether, ethylene and ethylsulfuric acid, the latter reaction is the one of importance in cellulose alkylation. Since the manufacture of the dialkyl sulfates requires a pure alkylsulfuric acid as a starting material, the production of ethylsulfuric acid assumes a prime importance in the cellulose ether art. The reaction of treatment of alcohols with concentrated sulfuric acid is never complete, since the reaction is reversible. Where absolute ethyl alcohol and pure sulfuric acid monohydrate (100% H_2SO_4) are mixed in stoichiometrical amounts, there results 57% of ethylsulfuric acid.

Manufacture of Ethylsulfuric Acid. This acid may be formed by the absorption of ethylene in sulfuric acid[2]; by warming diethyl ether with sulfuric acid[3]; by action of sul-

1. H. Fuehner, Ber. 1924, **57B**, 510; abst. C. A. 1924, **18**, 2493.
2. H. Hennell, Phil. Trans. 1828, 365; Ann. Chim. Phys. 1829, **42**, 77; Phil. Mag. 1829, **6**, 342; Pogg. Ann. 1828, **14**, 273; Trommsdorff, N. Jour. d. Pharm. 1830, **21**, 224; Schweigger J. 1829, **56**, 116. M. Berthelot, Compt. rend. 1855, **40**, 102; Ann. chim. Phys. 1855, **43**, 385; J. prakt. Chem. 1855, **65**, 274; J. de Pharm. 1855, **27**, 329; Ann. 1855, **94**, 78. See also J. Behrens, D. R. P. 275049; abst. C. A. 1914, **8**, 3359; Wag. Jahr. 1914, II, 26.
3. G. Magnus, Pogg. Ann. 1833, **27**, 367; Ann. Chim. Phys. 1833, **52**, 139; J. d. Pharm. 1833, **19**, 557; Ann. 1833, **6**, 152.

furyl chloride on alcohol[1]; or from alcohol and chlorsulfonic acid with cooling[2].

In the C. Ellis method[3] still gases from the cracking of petroleum products are utilized, especially the unsaturated hydrocarbons ethylene, propylene and butylene. The hydrogen sulfide is first removed by treatment with NaOH or iron hydroxide, the gases being passed through sulfuric acid of 1.8 sp. gr., then contacted with more concentrated sulfuric acid to combine with the ethylene at a temperature above 60°. The process of Farben. vorm. F. Bayer & Co. is similar[4], except silver sulfate or other catalyst[5] is used.

The preparation of alkylsulfuric acids by treatment of alcohols with sulfur trioxide in presence of sulfuric acid may be unfavorable as the result of sulfonating side reactions of the sulfuric anhydride[6], but if the latter is allowed to act in the cold upon the alcohol or the alcohol diluted with alkylsulfuric acids, then a complete conversion ensues, and decomposition and formation of sulfurous acid is practically excluded, the alkylsulfuric acids produced being practically free from sulfuric acid and of high purity. The essence of the process depends upon the observation that gaseous SO_3 when led into alcohol under cooling and stirring, using the ratio of absolute alcohol 92, ethylsulfuric acid 200-300, and sulfur trioxide 160, when slowly introduced so that the reaction temperature remains below 0°, a yield of 80-85% on theory is obtained. A solution of gaseous SO_3 in chlorsul-

1. W. Heusser, Ann. 1869, **151**, 249.
2. J. Claessen, J. prakt. Chem. 1879, (2), **19**, 245.
3. C. Ellis, U. S. P. 1464153; abst. C. A. 1923, **17**, 3248. See P. Evans and J. Albertson, J. A. C. S. 1917, **39**, 456.
4. R. Engelhardt, W. Lommel and A. Ossenbeck, U. S. P. 1458646; abst. C. Zentr. 1924, I, 1867. Farben. vorm. Friedr. Bayer & Co., E. P. 185757; abst. C. Zentr. 1923, IV, 657. F. P. 555769; abst. C. Zentr. 1924, I, 1101. W. Lommel, A. Ossenbeck and R. Engelhardt, D. R. P. 390621; abst. C. Zentr. 1924, I, 1867. W. Lommel and R. Engelhardt, D. R. P. 397685; abst. C. Zentr. 1924, II, 1399.
5. S. Hunt, E. P. 146957; abst. C. A. 1920, **14**, 3674. E. P. 173538, C. A. 1922, **16**, 1435. D. R. P. 417411.
6. L. Lilienfeld, Aust. P. 83399. See also D. R. P. 77278; abst. Jahr. Org. Chem. 1894, II, 33. D. R. P. 133542; C. Zentr. 1902, II, 314. D. R. P. 193830; C. Zentr. 1908, I, 1112.

fonic acid is said to result in a more uniform reaction[1], the proportions being 318 parts of a solution of 61.4% SO_3 in chlorsulfonic acid, which is dropped into 147 pts. of 96% alcohol under stirring, and at a temperature between 0-10°. Time of dropping 6 hrs. The ethylsulfuric acid produced is wine-yellow and contains about 5% HCl after 1 hr. treatment with compressed air.

The G. Adamson process claims to be more controllable[2] and erratic fluctuations in temperature avoided, where the alcohol is first introduced with the SO_3 into a container containing alkylsulfuric acid, then withdrawing periodically or continuously the alkylsulfuric formed, still leaving the original proportion of alkylsulfuric acid introduced into the reacting chamber. The Compagnie de Bethune[3] have described a continuous process in which the ethylene is circulated in a closed circuit through columns containing sulfuric acid and comminuted materials for increasing contact. A complete saturation of the acid, increased economies in heating and manipulation are said to result.

In the R. Taveau invention[4], ethylene or butylene gases are passed in succession through absorbing chambers containing respectively sulfuric acid of 65% and then of 85% concentration, maintaining the chambers below 30°, whereby there is a separation of ethylsulfuric and propylsulfuric acids which are then separately purified. If copper sulfate or sulfate of other heavy metal which is practically insoluble in sulfuric acid is used as catalyst[5], a higher and much more uniform yield of alkylsulfuric acid is said to be obtained.

In the esterification of sulfuric acid to the ethylsulfuric acid and ethyl sulfate stages, the law of mass action has

1. L. Lilienfeld, Aust. P. 87694. See also D. R. P. 83399.
2. G. Adamson, U. S. P. 1399238.
3. E. P. 199007; abst. C. A. 1924, **18**, 274. E. P. 221512, C. A. 1925, **19**, 832. D. R. P. 474502; abst. C. Zentr. 1929, II, 468. D. R. P. 504325, C. Zentr. 1930, II, 2304. Belg. P. 320282.
4. U. S. P. 1845007.
5. A. Damiens, M. de Loisy and O. Piette, U. S. P. 1589372; abst. C. A. 1926, **20**, 3015.

been shown to hold when the molecular proportions of ethyl alcohol to sulfuric acid vary between 4:1 (80% H_2SO_4) and 0.5:1 (35% H_2SO_4)[1], the degree of completeness of the reaction being determinable by titration with methyl orange as indicator[2]. From determinations at 0° of the velocity coefficients of the reaction[3], in which the concentration of the H_2SO_4 is 60-75%, it appears that the reaction is of the first order[4]. The hydrolysis of ethylsulfuric acid[5], and the kinetics of ethyl ether formation from alcohol and ethylsulfuric acid[6] have been detailed.

Methyl-, propyl-, *iso*propyl-, *n*-butyl- and *iso*-amyl-ethyl sulfates have been prepared by the action of ethylchlorsulfonic acid on the corresponding sodium alkoxide[7].

Ethyl Sulfate. *Diethyl Sulfate.* $(C_2H_5)_2SO_4$. The major number of patented processes for the ethylation of cellulose and other carbohydrate bodies, specify the use of ethyl sulfate (see pp. 17, 20, 21, 24, 30, 38, 39, 44, 83, 91, 124, 171, 223, 224, 293; also topic *Ethylcellulose*).

Ethyl sulfate is a colorless, inflammable liquid, smelling rather like peppermint, melts at —24.5°[8], b. pt. 96° at 15 mm., 120.5° at 45 mm., and at 208° with decomposition at atmospheric pressure[9]. Density 25°/4° vac., 1.1723[10], 1.210 at 0°/4°[11]. It begins to decompose slowly at 140°.

1. H. Dunncliff and G. Butler, J. C. S. 1921, **119**, 1384; abst. C. A. 1922, **16**, 53.
2. P. Evans and J. Albertson, J. Am. Chem. Soc., 1917, **39**, 456; abst. C. A. 1914, **8**, 665; C. A. 1917, **11**, 1427.
3. M. Hamid, K. Singh and H. Dunncliff, J. C. S. 1926, **129**, 1098; abst. C. A. 1926, **20**, 2656; Cf. C. A. 1922, **16**, 53.
4. R. Kremann, Monat. f. Chem. **31**, 275; abst. C. A. 1910, **4**, 2404.
5. W. Penniman, W. Randall, C. Miller and L. Enslow, J. Ind. Eng. Chem., 1916, **8**, 904; abst. C. A. 1916, **10**, 2963.
6. R. Kremann, Monat. f. Chem. **31**, 671; abst. C. A. 1911, **5**, 19.
7. L. Bert, Compt. rend. 1924, **178**, 1182; abst. J. C. S. 1924, **126**, i, 605; C. A. 1924, **18**, 1980.
8. J. Nef, Ann. 1901, **318**, 43; abst. J. C. S. 1901, **80**, i, 626.
9. A. Villiers, Compt. rend. 1880, **90**, 1291. Bull. Soc. Chim. 1880, (2), **34**, 26.
10. P. Walden, Zts. physik. Chem. 1906, **55**, 224.
11. S. Sugden, J. Reed and H. Wilkins, J. C. S. 1925, **127**, 1525; abst. C. A. 1925, **19**, 2926.

The success of ethyl sulfate as an etherifying agent depends primarily upon the fact that it readily ethylates both hydroxyl and amido groups, and having a low volatility, the use of an autoclave is usually unnecessary[1]. In most cases the reaction is rapid at 100-125°, but any desired rate of reaction may be maintained by controlling the temperature and rate of addition of the reagent. In some cases, the use of an inert organic solvent gives excellent results, in which case fibrous cellulose ethers are obtained, i.e., the cellulose does not pass into solution in changing to the ethyl ether. The first ethyl group substituted is usually quantitative, depending, however, upon the degree of degradation of the cellulose being operated upon, the second ethyl group gives a high yield, although, generally speaking, it is better to stop the reaction when the first ethyl group has been substituted or a little beyond, and submit the cellulose to a new series of ethylations. Where the cellulose has not been appreciably degraded, an ethylcellulose of 2.1-2.4 ethyl groups has been found to possess the most desirable technical properties, a cellulose ester of ethoxy equivalent to the introduction of 3 ethyl groups being usually deficient in tensile strength and tenuity in filament and film formation, due to drastic treatment incident to introduction of the maximum of ethyl into the cellulose aggregate.

Ethyl sulfate is insoluble in cold water, hot water decomposing it to ethyl alcohol and ethylsulfuric acid. Alcoholic potash at 70-80° gives diethyl ether and potassium ethylsulfate. At 220° it decomposes into ethylidene (2 mols.) and sulfuric acid (1 mol.). Di-*n*-propyl sulfate and di-*iso*-amyl sulfate decompose in a similar manner. On account of the fact that ethyl sulfate is more difficult to obtain than the lower homologues, it is therefore relatively more expensive to produce[2].

1. G. Curme, Chem. Met. Eng. 1921, **25**, 907, 957; abst. C. A. 1922, **16**, 553.
2. Summary U. S. Tariff Information Report, 1921, 102.

Preparation. Ethyl sulfate may be prepared by introducing sulfur trioxide into absolute alcohol[1]; by the vacuum distillation of ethylsulfuric acid[2]; by the gradual addition of alcohol to ethyl chlorsulfonic acid[3]; by the interaction of ethyl iodide and silver sulfate[4]; or by mixing absolute alcohol with Nordhausen sulfuric acid, separating by chloroform, and distilling *in vacuo*[5].

Manufacture. In the methods of L. Lilienfeld, one process[6] comprises distilling sodium ethyl sulfate *in vacuo*, being first admixed with anhydrous sodium sulfate, the ethyl sulfate distilling over being collected in any suitable receiver. For example, anhydrous sodium ethyl sulfate 4000, is distilled *in vacuo*, the distillate mixed with cold water and extracted with chloroform, dried by calcium chloride, and the chloroform removed by distillation. The residue of pure ethyl sulfate is 1720-1870 parts, equivalent to 83-90% of theory.

When chlorsulfonic acid is allowed to act upon ethyl alcohol[7], and the ethylsulfuric acid formed is not distilled but only heated up to the formation of ethyl sulfate, the latter being then precipitated with water, the mother liquid consists chiefly of sulfuric acid and ethylsulfuric acid. Heating but for a few minutes to 90-100° is said to be sufficient to convert a considerable proportion of the ethylsulfuric

1. C. Wetherill, Ann. 1848, **66**, 117.
2. J. Claessen, J. pr. Chem. 1879, (2), **19**, 257.
3. A. Strecker, Ann. 1856, **100**, 199.
4. N. Stempnewsky, Ber. 1878, **11**, 514.
5. P. Claesson and C. Lundvall, Ber. 1880, **13**, 1699.
6. U. S. P. 1074633; abst. C. A. 1913, **7**, 4046; J. S. C. I. 1913, **32**, 1030; Mon. Sci. 1914, **81**, 28; Chem. Ztg. Rept. 1914, **38**, 347. E. P. 13882, 1913; abst. C. A. 1914, **8**, 3840; J. S. C. I. 1913, 32, 1130; Chem. Ztg. 1913, **37**, 922; 1476. D. R. P. 272339; abst. C. A. 1914, **8**, 3100; Chem. Zentr. 1914, I, 1385; Chem. Ztg. 1914, **38**, 377; Chem. Ztg. Rept. 1914, **38**, 347; Wag. Jahr. 1914, **60**, II, 9; Zts. ang. Chem. 1914, **27**, 278; Friedlaender, 1912, 14, **11**, 38. F. P. 459282; abst. J. S. C. I. 1913, **32**, 1130; Mon. Sci. 1914, **80**, 73; Chem. Ztg. Rept. 1914, **38**, 347. Aust. P. 69323, 1914; abst. Kunst. 1915, **5**, 213. Aust. P. 63526; abst. J. C. S. 1915, **106**, i, 919; Chem. Ztg. 1914, **38**, 142. Aust. P. 67843, 67844. See D. R. P. 133542.
7. L. Lilienfeld, Aust. P. 92317. D. R. P. 360527; abst. J. S. C. I. 1923, **42**, 331-A; Chem. Tech. Ueber. 1922, **46**, 366; Chem. Ztg. 1922, **46**, 754.

acid into ethyl sulfate. The proportions recommended are 46 of absolute alcohol previously cooled, which is slowly introduced into 116.6 of chlorsulfonic acid with stirring, the HCl resulting being led off and absorbed in water. The reaction mixture is then heated on the water bath for about 2 hours and the ester separated by pouring into cold water or onto ice.

Lilienfeld has found that it is possible to obtain dialkyl sulfates from two molecules of alcohol and one molecule sulfuric anhydride[1] with the splitting off of one molecule of water. This may be commercially carried out by diluting 92 of absolute ethyl alcohol with 400 of carbon tetrachloride, 48 of phosphorous pentoxide being added while cooling the mixture. Then, while agitating, 59 of SO_3 is introduced and further quantity of 26 of P_2O_5 added. Excess alcohol is then distilled off, 88 of ethyl sulfate being the yield, or 75% of theory.

J. Compton[2] treats ethylene with concentrated sulfuric acid under conditions favorable for absorption, the rate of which is quite slow at first, but increases as the ethylene is absorbed and reaches a maximum when 60-80 mols. of ethylene have been absorbed for each 100 mols. sulfuric acid, that is, when the ethylene which has been absorbed is 60-80% of that required to convert all the acid to ethylsulfuric acid, or 30-40% of that theoretically necessary to transform all the acid to ethyl sulfate. A somewhat similar process has been described[3], in which the combination is accelerated by raising the temperature of the acid to enhance speed of reaction, increasing the pressure to intensify

1. L. Lilienfeld, U. S. P. 1427215; abst. C. A. 1922, **16**, 3665; J. S. C. I. 1922, **41**, 838-A. E. P. 143260; abst. J. S. C. I. 1921, **40**, 322-A; J. C. S. 1921, **120**, i, 299. F. P. 520070; abst. Mon. Sci. 1922, (5), **12**, 62. D. R. P. 404173, 1924. Aust. P. 92318 Addn. to Aust. P. 92317. See also W. Haworth and J. Irvine, E. P. 122498.

2. U. S. P. 1598560. Carbide and Chemicals Corp., Belg. P. 319049.

3. A. Damiens, M. de Loisy and O. Piette, U. S. P. 1574796; abst. C. A. 1926, **20**, 1415. A. Damiens, Compt. rend. 1922, **175**, 585; abst. C. A. 1923, **17**, 259. Bull. Soc. Chim. 1923, **33**, 71; abst. C. A. 1923, **17**, 1208.

the fixation of ethylene, and employing a catalyzer as vanadium oxide, uranyl sulfate, or tungstic or molybdic acids. During the reaction of sulfuric acid on ethylene in presence of the catalyst, the temperature must be maintained between 15-50°, at the end of the operation ethylsulfuric acid and ethyl sulfate (both soluble in concentrated sulfuric acid) being obtained. The ethyl sulfate separates by coming to the surface of the liquid when the acid is diluted, any rise in temperature being avoided. As catalyst a ferrous or cuprous compound, as ferrous sulfate or cuprous oxide[1] has been found to give maximum yields.

In the H. Curme process[2], ethylene, substantially free from diluting gases, is brought into intimate contact with 93% sulfuric acid, the former being in large excess, there being produced in addition to ethylsulfuric acid, a proportion of ethyl sulfate. The latter forms before the sulfuric acid has been completely transformed into ethylsulfuric acid, and may be produced and removed as such, while there still remains sulfuric acid in the uncombined state. As ethyl sulfate has a higher vapor tension at the reacting temperature than either ethylsulfuric acid or sulfuric acids, by suitable control of temperature and volume of introduced ethylene passing through the liquid, ethyl sulfate may be periodically or continuously vaporized, being recovered in a state of satisfactory purity by a suitable condenser.

W. Bader[3] distils ethylsulfuric acid (ethyl hydrogen sulfate) or mixtures containing it, under reduced pressure in such a way that at any given moment only a small portion of the liquid which is actually undergoing distillation is under the influence of the heat. The still is a vertical tube electrically heated, the liquid to be heated flowing in at the top through a small revolving orifice which deposits it uniformly all round on the inner surface of the tube.

1. A. Damiens, M. Elysee and O. Piette, U. S. P. 1599119.
2. U. S. P. 1339947; abst. C. A. 1920, **14**, 2001. Can. P. 208018. G. and H. Curme, Chem. and Met. Eng. 1921, **25**, 957.
3. U. S. P. 1484249. British Cellulose and Chemical Mfg. Co., Ltd., and W. Bader, E. P. 175077; abst. C. A. 1922, **16**, 2149; J. S. C. I. 1922, **41**, 309-A; Chem. Tech. Uebers, 1922, **46**, 295.

A high vacuum is maintained, which has connection with an ice-cooled condensing system. The temperature maintained depends upon the vacuum obtainable, varying for ethyl hydrogen sulfate between 100-150°. The mixture, consisting of 40 of fuming sulfuric acid of 70% sulfur trioxide content and 60 of ethyl alcohol is drawn into the still by the vacuum, which is kept at 110° under 5 mm. pressure. Sulfuric acid and some tarry matter collects at the bottom of the still, while the distillate consists principally of sulfate, some ethyl sulfuric acid, free alcohol and a little water. The yield of ethyl sulfate is 110% or more of the theoretical yield calculated on the ethylsulfuric acid originally present.

The H. Dreyfus process employs alkali metal chlorsulfonates or pyrosulfates for the production of ethyl sulfate by reaction with ethyl alcohol or ethyl ether, and distilling under reduced pressure[1]. In carrying out the process sodium pyrosulfate and ethyl alcohol are mixed at ordinary temperature for some hours, then heated until combination takes place, and finally distilled *in vacuo*. Or the alcohol may be passed in the form of vapor over the pyrosulfate at a temperature suitable to cause a combination to take place, the ethyl sulfate being then removed by vacuum distillation.

Neutral ethyl esters of sulfuric acid are formed, according to E. Kuh[2], by distilling ethylsulfuric acid under vacuum, if care is taken that the sulfuric acid generated during the splitting of the ester acid is combined as a salt during the reaction itself. As cathion carrier, any compound may be introduced into the still which neither in itself nor after the substitution of hydrogen for the metal, exerts a saponifying action on the ester acids. Such a salt, for instance, is ethyl sodium sulfate, the reaction being quantitatively carried out by one mol. ethylsulfuric acid with one mol. ethyl sodium sulfate, yielding ethyl sulfate and sodium

1. U. S. P. 1506228; abst. C. A. 1925, **19**, 78. E. P. 177189; abst. C. A. 1922, **16**, 3094; J. S. C. I. 1922, **41**, 438-A; Chem. Tech. Uebers, 1922, **46**, 295.

2. U. S. P. 1411215; abst. C. A. 1922, **16**, 1781; J. S. C. I. 1922, **41**, 348-A. E. P. 149688; abst. C. A. 1921, **15**, 374. D. R. P. 342969, 1921.

acid sulfate. The process may be carried out by introducing into a vessel with stirring arrangement, 266 of ethylsulfuric acid and 150 of anhydrous sodium sulfate, and distilling under 10-15 mm. pressure, the contents of the vessel during the distillation being kept in a dry, pulverulent condition. The ethyl sulfate formed begins to distil at 90-100° and is complete at 160-170. Yield about 85%.

If one molecule of chlormethylmethyl ether (CH_2C10-CH_3) is cooled to 5°, and treated with stirring and no rise in temperature with 1 molecule sulfuric acid chlorhydrin[1], then warmed under reflux condenser until cessation of HCl evolution, the ester, which is the same as previously prepared by J. Houben[2], is isolated in the usual manner. If methylpropyl ether is treated with sulfuric acid chlorhydrin in an analogous manner, methylpropyl sulfate, b. pt. 125° at 7 mm. pressure, is formed in good yield.

Ethyl sulfate results in nearly theoretical amount where anhydrous sodium sulfate 90 is heated under vacuum to 155-165°, and a mixture of ethyl alcohol 50, and concentrated sulfuric acid 104.5 allowed to drop in gradually, the distillation requiring 1-1.5 hrs., and the yield, 32.6[3]. The C. Leproux process[4] involves collecting in a reservoir, acetylene and nascent hydrogen, which is then converted into ethylene, led into a mixing vessel charged with sulfuric acid, the unacted-upon gas being returned to the heater, and the ethyl sulfate removed by liquefaction in a brine cooled condenser.

Yields of 80% or more of the amount of ethyl sulfate theoretically obtainable[5], are claimed to result when a large

1. Chemische Fabrik Dr. v. Kereszty Dr. Wolf & Co., A. G., (G. v. Kereszty and E. Wolf), Aust. P. 67843, 1914. Aust. P. 67844; Addn. to 67843.
2. Ber. 1908, **41**, 3708; abst. C. A. 1909, **3**, 322.
3. E. Lynn and H. Shoemaker, J. A. C. S. 1924, **46**, 999; abst. C. A. 1924, **18**, 1980; J. C. S. 1924, **126**, i, 605; J. S. C. I. 1924, **43**, 536-B.
4. F. P. 421628; abst. C. A. 1912, **6**, 1981.
5. Ledoga Soc. Anon. and C. Maimeri, E. P. 215000; abst. C. A. 1924, **18**, 2901. Belg. P. 317135. C. Maimeri, Atti. congr. naz. chim. ind. 1924, 269; abst. C. A. 1925, **19**, 1402.

excess of ethylene gas of at least 90% purity is treated with sulfuric acid of at least 100% strength at 15 atms. pressure, at about 65-75°, without the aid of a catalyst. It is claimed that at a lower temperature, ethylsulfuric acid is formed, while if a high temperature be employed, decomposition of ethyl sulfate ensues. The process may be carried out by introducing a dry current of ethylene gas into 10 parts monohydrated sulfuric acid with energetic stirring, keeping the pressure at 15 atms. and cooling when the temperature rises above 75°. Absorption continues until about the theoretical amount of ethylene (about 5-7 parts) has been absorbed. Through the formation of the reaction products, the volume of sulfuric acid nearly doubles. The reaction mass is poured onto ice forming two layers, the upper one containing a small amount of ethylsulfuric acid, and the lower, nearly pure ethyl sulfate. This is dried and then distilled at 105-110° at 15 mm. pressure. Somewhat analogous is the method of N. Sidgwick and S. Plant[1], who pass ethylene through 80-100% sulfuric acid at 75°, using considerable excess of ethylene, the yield being considerably augmented by replacing a portion of the sulfuric acid by ethylsulfuric acid. A. Wohl[2] emphasizes the necessity of conducting the operation under as nearly absolute vacuum as possible.

In the method of R. Levaillant[3], alkyl sulfates are prepared by the action of alkyl nitrites on alkyl chlorsulfonates. Thus, ethyl chlorsulfonate and ethyl nitrite at 80-145° give ethyl sulfate in 55% yield.

Uses of Ethyl Sulfate. In addition to employment as an alkylating agent in the ethylation of cellulose and starch,

1. N. Sidgwick, S. Plant and A. Boake, Roberts & Co., Ltd., E. P. 157578; abst. J. S. C. I. 1921, **40**, 195-A; C. A. 1921, **15**, 1905; Chim. et Ind. 1922, **7**, 330.

2. A. Wohl, D. R. P. 350808; abst. Chem. Ztg. 1922, **46**, 190; Chem. Tech. Uebers, 1922, **46**, 145. See D. R. P. 113239, 133542.

3. Compt. rend. 1928, **187**, 234, 730; abst. C. A. 1926, **22**, 3880; J. S. C. I. 1928, **47**, 990-A, 1354-A. See also U. S. P. 1074633. E. P. 13882, 1913. F. P. 459282. D. R. P. 272339, 339947, 360651. Ital. P. 126805. Swed. P. 38392. Aust. P. 56250, 63524, 65288. Hung. P. 51653.

ethyl sulfate has been proposed as a cellulose nitrate solvent[1], in the separation of oxidized fatty acids and resin acids[2], in the examination of hydrocarbon oils[3], and differentiation of paraffins and naphthenes from aromatic and unsaturated hydrocarbons[4]. It has also been patented for use in the manufacture of paracoumarone[5], and as a condensate with phenol-aldehyde[6].

According to the experience of A. Cade[7], and G. and H. Curme[8], ethyl sulfate is no more dangerous to handle than such organic liquids as benzene or aniline. It is but necessary to use the general precautions in respect to the inhalation of fumes, and contact with the skin, because ethyl sulfate is absorbed cutaneously. It appears that the toxicity of methyl sulfate is much greater than the corresponding ethyl ester. As with methyl sulfate, close attention should be given to the purity of the product, free acid being detrimental in any ethylation operations.

The advantages of ethyl sulfate as an alkylating agent in cellulose technology is that it permits rapid and complete ethylation without the use of pressure vessels, has a high intensity of reaction, thus economizing material, avoids the necessity of recovering an expensive acid radical, may be handled and stored without loss due to low volatility, and is non-corrosive.

Mixed Dialkyl and Aryl-Alkyl Sulfates. There are two general methods for the preparation of mixed cellulose ethers, one being etherifying as with methyl sulfate to a partial substitution, followed by completing the etherification by the use of (say) ethyl sulfate, thus obtaining a methylethylcellulose, and the other the use of physically

1. U. S. P. 559392.
2. H. Wolff, Chem. Umschau, 1924, **31**, 87; abst. J. S. C. I. 1924, **43**, 525-B.
3. J. Taylor, I. E. C. 1927, **19**, 76.
4. J. Morgan and R. Soule, I. E. C. 1923, **15**, 587.
5. D. R. P. 302543.
6. U. S. P. 1505382. E. P. 147173.
7. Chem. Met. Eng. 1923, **29**, 319; abst. C. A. 1924, **18**, 222; J. S. C. I. 1923, **42**, 966-C. & I.; 997-A.
8. Chem. Met. Eng. 1921, **25**, 957.

admixed alkyl halides or sulfates in which two dissimilar alkyls have been combined with the acid radical. The patented processes of G. Young for methylethylcellulose formation[1], and of H. Dreyfus for methylbenzylcellulose production[2] are examples. There is still a third possibility in the substitution of the H of the three replaceable hydroxyls in cellulose by different groups, this possibility being the partial etherification to a monomethylcellulose, further ethylated to a monomethylmonoethylcellulose, and this finally benzylated to the maximum of etherification resulting in the formation of a methylethylbenzylcellulose. Such compounds have been described, but as yet, their constants imperfectly determined.

L. Bert[3] has prepared methyl-, ethyl-, *iso*propyl-, *n*-butyl- and *iso*amyl-ethyl sulfate by the action of ethyl chlorsulfonate on the corresponding sodium alkoxide. The observations of F. Bushong[4] on the *iso*propyl and *iso*amyl compounds confirmed the work of Bert. F. Thayer[5] has investigated methylethyl sulfate as an alkylating agent, being prepared by adding ethyl chlorsulfonate (1.3 equivalents) to sodium methoxide in dry ether. Yield, 19.7% of the theoretical. The alkylating power compared with methyl sulfate is inferior, but the methyl group has a more pronounced alkylating action than does the ethyl.

1. U. S. P. 1504178; abst. C. A. 1924, **18**, 3272; J. S. C. I. 1924, **43**, 743. E. P. 184825, 1921; abst. C. A. 1923, **17**, 878; J. S. C. I. 1922, **41**, 854-A; Kunst. 1923, **13**, 56; Chim. et. Ind. 1923, **10**, 542.

2. U. S. P. 1454959, 1454960, 1454961; abst. C. A. 1923, **17**, 2362; J. S. C. I. 1923, **42**, 600-A. E. P. 164384, 164385, 164386; abst. J. S. C. I. 1921, **40**, 540-A; C. A. 1922, **16**, 494; Chim. et Ind. 1922, **8**, 1081; Ann. Rep. S. C. I. 1921, **6**, 139.

3. Compt. rend. 1924, **178**, 1182; abst. J. C. S. 1924, **126**, i, 605; C. A. 1924, **18**, 1980. Chem. Zentr. 1924, II, 170.

4. Amer. Chem. J. 1903, **30**, 212; abst. J. C. S. 1903, **84**, i, 732; Chem. Zentr. 1903, II, 936; Jahr. Chem. 1903, **56**, 789. See also J. Nef, Ann. 1901, **318**, 43; abst. J. C. S. 1901, **80**, i, 626.

5. J. A. C. S. 1924, **46**, 1044; abst. C. A. 1924, **18**, 1980; J. C. S. 1924, **126**, i, 604; J. S. C. I. 1924, **43**, 536B. See P. Behrend, J. prakt. Chem. 1877, (2), **15**, 23; P. Claesson, ibid. 1879, (2), **19**, 231; O. Willcox, Am. Chem. J. 1904, **32**, 446.

A method has been patented by E. Wolf[1] for the preparation of these mixed esters containing different substituted radicals. If one molecule monochlormethyl ether is cooled to —5°, and after the addition of one molecule of sulfuric acid chlorhydrin is heated until the evolution of HCl ceases, the product then poured on ice, taken up with a neutral solvent as carbon tetrachloride and washed to neutrality, the lighter layer after separation being purified by rectification, it results in the formation of an ether of high purity. The product obtained is said to be identical with the chlormethyl methyl sulfate obtained by J. Houben and H. Arnold[2] by the action of dry HCl upon trioxymethylene at the ordinary temperature, the yield being 60% of theory. Wolf prepares methylpropyl sulfate by treating methylpropyl ether with sulfuric acid chlorhydrin as above, the product boiling at 125° at 7 mm. pressure.

Methylethyl sulfate boils at 190-200° at 742 mm.; ethylpropyl sulfate, a colorless oil, at 107-108° at 18 mm. pressure, density 1.140 at 16.5°. Ethyl-*n*-butyl sulfate boils at 117-118° at 20 mm., density 1.112 at 18°.

In the preparation of mixed cellulose ethers, it is customary either to partially etherify the cellulose in one step and then complete the etherification with a different radical, or to etherify in one operation by a physical admixture of etherifiants as methyl sulfate with ethyl sulfate.

Allyl Bromide, C_3H_5Br. *3-Brompropylen,* may be prepared by heating 1.3-dibrompropane with silver oxide on the waterbath[3], by distilling 1 mol. pure allyl alcohol with

1. U. S. P. 1101373; abst. C. A. 1914, **8**, 2922; J. S. C. I. 1914, **33**, 844; Mon. Sci. 1914, **81**, 185. Chem. Fab. dr. v. Kereszty and Dr. Wolf & Cie. Aust. 8495, 1913; abst. C. A. 1915, **9**, 513. Aust. P. 9624, 1913; Addn. to Aust. P. 8495; abst. C. A. 1915, **9**, 513.

2. Ber. 1907, **40**, 4306; abst. C. A. 1908, **2**, 399; Meyer Jahr. Chem. 1907, **17**, 228; J. C. S. 1907, **92**, i, 1000; Chem. Zentr. 1908, **79**, I, 17; Jahr. Chem. 1905, 1908, II, 304. Ber. 1908, **41**, 1565; abst. C. A. 1908, **2**, 2372; J. C. S. 1908, **94**, i, 533; Jahr. Chem. 1905-08, II, 2225. J. Houben, Ber. 1908, **41**, 3708; abst. C. A. 1909, **3**, 322; Jahr. Chem. 1905-08, II, 218. See also P. Hoering, Ber. 1908, **41**, 173; abst. C. A. 1908, **2**, 1419; Jahr. Chem. 1905-1908, II, 218.

3. B. Fortinski, J. Russ. Phys. Chem. Soc. 1913, **45**, 568; abst. Chem. Zentr. 1913, II, 1374.

3 mols. 48% HBr[1], by interaction of HBr in a boiling mixture of allyl formate and zinc[2], by treating bromine and allyl alcohol with sulfur dioxide and distilling[3]. L. Claisen and O. Eisleb[4] find the latter method gives a yield of 60-85%. Allyl bromide also results by heating allyl alcohol with phosphorous tribromide[5], or a mixture of potassium bromide and sulfuric acid[6], or by saturating allyl alcohol at 0° with HBr and boiling for several hours[7]. The Norris method[8] comprises distilling a mixture of HBr, sp. gr. 1.49, with allyl alcohol.

Allyl bromide boils at 71°, sp. gr. 1.459 at 0°/0°, and with concentrated HBr forms a mixture of propylene bromide and trimethylene bromide which may be separated by distillation[9]. Allyl bromide (see pp. 163, 208, 298) forms a compound with alkalicellulose (p. 305), is a celluloid and cellulose acetate solvent (p. 890) and is used in the preparation of allylcellulose (pp. 99, 163, 250, 298, 910). Such ethers as allylsugar, allylstarch and allyldextrin (p. 99, n. 1) are best prepared with allyl bromide as allylating agent. Other uses of allyl bromide are primarily in connection with the dyestuff industry[10].

Diazomethane. *Azimethylene.* CH_2N_2, is infrequently used as an etherifiant in the production of cellulose ethers

1. J. Norris, M. Watt and R. Thomas, J. A. C. S. 1916, **38**, 1076.
2. Chem. Fabr. Schering, D. R. P. 268340; abst. Chem. Zentr. 1914, I, 309.
3. F. Bodroux, Compt. rend. 1915, **160**, 206.
4. Ann. 1913, **401**, 27; abst. Chem. Zentr. 1913, II, 1859.
5. B. Tollens, Ann. 1870, **156**, 152.
6. H. Grosheintz, Bull. Soc. Chim. 1878, (2), **30**, 98; abst. J. C. S. 1878, **34**, 963.
7. W. Jacobi and G. Merling, Ann. 1894, **278**, ii, 1; abst. J. C. S. 1894, **66**, i, 162.
8. J. Norris, Amer. Chem. J. 1907, **38**, 633, 641.
9. F. Geromont, Ann. 1871, **158**, 369; abst. Jahr. Chem. 1871, **24**, 407; J. C. S. 1871, **24**, 697; Ber. 1871, **5**, 548; Chem. Zentr. 1871, **42**, 434. An excellent small-scale production method for allyl bromide formation is to flow into 200 cc. allyl alcohol, a chilled mixture of 200 cc. conc. sulfuric acid and 100 cc. water, and after standing several hours the liquid is poured upon 400 gm. powdered KBr and slowly heated until oil still passes over (O. Kamm and C. Marvel, J. A. C. S. 1920, **42**, 308). Yield, 92-96% of theory.
10. See U. S. P. 1219575, 1316804, 1336952, 1415700, 1444802, 1477113, 1482343.

(see p. 94, n. 8, 9; 95, n. 1). At the ordinary temperature it is yellow, odorless, poisonous gas, which strongly attacks the skin and mucous membranes, and has been used to a limited extent in the methylation of starch (p. 163, n. 4), and of the sugars (p. 733, n. 2).

Diazomethane may be prepared by the interaction of alkalis on nitrosomethylbenzamid[1]; by warming nitrosourethane with ether and KOH in methyl alcohol[2]. While a powerful methylating agent, converting hydroxyl groups (of which there are three in cellulose) into methoxyl, and alkylating primary and secondary bases, its poisonous nature has limited its use in carbohydrate methylation. Water converts it to methyl alcohol, iodine to methylene iodide, inorganic and organic acids to their methyl esters, HCl into methyl chloride, HCN into acetonitrile, and phenols into anisols. Diazoethane has not been used in the ethylation of carbohydrates.

Benzyl Chloride, *o-Chlortoluene,* isomeric with the three chlor-toluenes, is an important reagent by means of which numerous derivatives of benzyl alcohol have been prepared, and is the favorite etherifying agent for the benzylation of cellulose and other carbohydrates. It may be prepared by passing HCl into benzyl alcohol; by reacting on boiling toluene with chlorine[3]; from methylene chlorhydrin and benzene in carbon bisulfide solution in presence of zinc chlo-

1. H. v. Pechmann, Ber. 1898, **31**, 2640. It will be remembered that in the action of halogen on toluene at low temperatures, substitution is in the nucleus and at high temperatures in the side chain. Three compounds of the type $ClC_6H_4.CH_3$, the *o*-, *m*- and *p*-toluenes, and $C_6H_5CH_2Cl$, benzyl chloride, are possible and known. For instance, the action of chlorine on cold toluene results in the formation of *o*- and *p*-toluene chloride; by boiling toluene with chlorine, benzyl chloride is almost exclusively produced.

2. *Ibid.* Ber. 1895, **28**, 856.

3. S. Cannizzaro, Ann. 1853, **88**, 129; 1854, **90**, 252; 1854, **92**, 113. Ann. de Chimie, 1854, **40**, 234; J. pr. Chem. 1855, **66**, 161. Nuovo Cimento, 1855, II, 212; Compt. rend. 1855, **41**, 517; Ann. de Chimie, 1855, **45**, 468; Ann. 1855, **96**, 246; J. pr. Chem. 1856, **67**, 270. H. Sainte-Claire Deville, Ann. de Chimie, 1841, (3), **3**, 178; J. pr. Chem. 1842, **25**, 321; Ann. 1842, **44**, 304.

ride[1]; by chlorination of toluene in sunlight[2]; from benzylamine and nitrosyl chloride in ether at —15°[3]; by heating excess of toluene with sulfuryl chloride[4]; by chlorinating toluene in presence of iodine, ferric chloride or molybdenum chloride[5]; by chlorination of toluene by electrolytic chlorine[6]; by heating toluene with a mixture of lead and ammonium chlorides[7]; from *o*-toluenediazonium chloride by decomposition with cuprous chloride[8], or heating with excess of HCl[9]; or by the general methods as described by B. Lorges[10] and by F. Hobart[11].

Benzyl chloride may be produced commercially by processes as follows:

I. *Chlorination of Toluene by Bleaching Powder.* By heating to a high temperature an anhydrous mixture and bleaching powder with thorough commingling[12] and without the use of any acid, chlorination of toluene proceeds rapidly and uniformly, and with no undue amounts of undesirable side products. As an example, 200 of toluene is heated in a steam-jacketed iron kettle to about 90°, dry bleaching powder then slowly added, and the temperature gradually raised until it approximates the boiling point of toluene. When 200 of bleaching powder has been added, the mixture is held at 100-105° for one hour with continuous mixing, escape of toluene vapor being prevented by means of a

1. J. Schramm, Ber. 1885, **18**, 606.
2. G. Grasse-Cristaldi and C. Maselli, Gazz. Chim. Ital. 1898, **28**, 498; abst. J. C. S. 1899, **76**, i, 409; Jahr. Chem. 1898, **41**, 1243.
3. W. Solonina, J. Russ. Phys. Chem. Soc. 1898, **30**, 431; abst. Chem. Centr. 1898, **30**, 431.
4. A. Wohl, D. R. P. 139552, 160102, 162594.
5. E. Seelig, Ann. 1887, **237**, 130, 131, 151.
6. J. Cohen, H. Dawson and P. Crosland, J. C. S. 1905, **87**, 1035.
7. A. Seyewetz and M. Biot, Compt. rend. 1902, **135**, 1121; abst. Bull. Soc. Chem. 1903, (3), **29**, 221; Chem. Zentr. 1903, I, 283, 962; J. C. S. 1903, **84**, i, 157.
8. W. Wynne, J. C. S. 1892, **61**, 1072.
9. K. Gasiorowski and A. Wayss, Ber. 1885, **18**, 1939.
10. Rev. Chim. Ind. 1925, **34**, 10, 50; abst. C. A. 1925, **19**, 1700; Chem. Zentr. 1925, I, 2655.
11. Pharm. J. 1924, **113**, 635; abst. C. A. 1925, **19**, 1858; Chem. Zentr. 1925, I, 895.
12. C. Loomis, U. S. P. 1280612.

reflux condenser. The mixture is then cooled and allowed to settle, the oil being siphoned from the top. Oil adhering to the line residue is removed by steam distillation and added to that siphoned off. In this way 200-210 of oil are obtained, of sp. gr. 0.94-0.96 at 20°, containing 30-35% benzyl chloride and 70-65% toluene. These can be separated by fractional distillation, and the toluene chlorinated. A higher percentage of benzyl chloride may be obtained by using a larger proportion of bleaching powder, but benzal chloride and benzotrichloride are formed, not easily separated.

In the J. Conant process[1], dry bleaching powder of at least 35% available chlorine is mixed with 2 parts toluene, and sulfur dioxide or a mixture of sulfur dioxide and nitrogen next introduced by bubbling in at the bottom of the container. Considerable heat is evolved, but control of temperature is said to be unimportant as regulating the yield of benzyl chloride formed. When between 0.1-0.5 of SO_2 to 1 of bleaching powder has been introduced the reaction is completed. This process is said to produce but a trace of other chlorinated products, and no HCl is evolved.

In another method[2], toluene is treated at below 0° with hypochlorous acid in aqueous solution. For example, toluene 3 mol. is emulsified with a hypochlorite solution containing 1 mol. of active chlorine, the mixture cooled to —5°, and 0.5 mol. sulfuric acid gradually added. The product contains unchanged toluene, 60-70% of the theoretical quantity of benzyl chloride, with small quantities of benzal chloride and other substituted products, and is purified by distillation. Or[3], a slow stream of chlorine is run into toluene with violent agitation in the presence of a quantity of potassium or sodium chlorates.

1. U. S. P. 1233986; abst. C. A. 1917, **11**, 2580.
2. Levinstein, Ltd., H. Levinstein and W. Bader, E. P. 134250; abst. J. S. C. I. 1920, **39**, 9-A.
3. Soc. Chim. des Usines du Rhone, F. P. 483622; abst. C. A. 1918, **12**, 910. Swiss P. 77663.

II. *Chlorination with Sulfur or Phosphorous Chlorides.* Toluene and phosphorous trichloride are vaporized separately and intimately mixed in a closed container[1], adding sufficient to combine with only a portion of the toluene, then heating the mixture to 200° while subjected to the action of ultraviolet light. The benzyl chloride formed is condensed from the HCl and other residual components of the mixture and the latter, with the PCl_3 returned for further treatment. It is advised to use lead containers substantially free from arsenic, antimony or iron[2].

In the L. Kyrides process[3] instead of using a phosphorous halide, sulfur or sulfur chloride is employed, and a small amount of acetyl chloride. As illustrating the working of the process, 150 of dry toluene is admixed with 3 of sulfur chloride, heated to 90°, and by means of an efficient distributor, 75 of dry gaseous chlorine added. When the chlorine has all been added, a liquid is obtained which contains about 100 of benzyl chloride, most of which can then be recovered in a pure state by the usual methods. The addition of 3 parts acetyl chloride to the mixture of toluene and sulfur chloride is said to improve the quality and augment the yield.

III. *Chlorination of Toluene in Presence of Light.* In the C. Ellis method gaseous chloride and toluene in vapor form are passed through a heated tube containing pumice, porcelain or glass beads and phosphorous pentachloride[9], and exposed to the action of the rays from a mercury vapor lamp. Sufficient chlorine is used to combine with 25-50% of the toluene, benzyl chloride being formed in the tube which is maintained at a temperature above the boiling point of the toluene. By means of a mechanical arrangement HCl may be drawn off, and excess toluene returned to the still.

1. C. Ellis, U. S. P. 1146142; abst. C. A. 1915, **9**, 2423.
2. L. Kyrides, U. S. P. 1733268; abst. C. A. 1920, **24**, 382.
3. U. S. P. 1345373; abst. C. A. 1920, **14**, 2644.
4. U. S. P. 1202040; abst. C. A. 1917, **11**, 187.

G. Book and J. Eggert claim that in the chlorination of toluene at 105-110° with a chlorine stream of definite velocity[1], the composition of the reaction product is the same whether the reaction takes place in the dark or under definite conditions of lighting. In the patented process of H. Gibbs and G. Geiger and dedicated to the people[2], the reaction chamber is first swept clear of air by means of the introduction of CO_2, and is provided with a quartz mercury lamp emitting ultraviolet rays. Toluene is fed in at a speed of 60 gms. per minute into a vaporizer, the chlorine being simultaneously delivered at the rate of 46 gms. per minute. The products of reaction collect on the bottom of the chamber and are withdrawn periodically without the admission of air and purified, the HCl being led off through the top of the chamber and absorbed in water.

Properties. Benzyl chloride is insoluble in water, but by heating with water to 100-110° it is converted into benzyl alcohol[3]. Readily miscible with alcohol, ether and chloroform. Melting point, —48°[4], and boils at 175°[5]. Density 1.1135 at 4°/4°, 1.1040 at 15°/15°, and 1.0967 at 25°/25°[6]. Benzyl chloride is soluble in methyl, ethyl, propyl, butyl and amyl alcohols to the extent of 8.87%, 7.10%, 5.70%, 21.5%, and 4.88% respectively; in ether 23.1%, ethyl acetate 57.8%, chloroform 47.6% and benzene 69.7%[7]. It is a colorless liquid which exerts a powerful irritant action on the eyes and nose.

Uses. In addition to its use as a benzylating agent for the preparation of benzylcellulose and the benzylated carbohydrates (see pp. 4, 10, 39, 58, 91, 93, 171, 184, 190 ,194, 214, 245, 293, 295), it has been used as a cellulose ester

1. Zts. Elektrochem. 1923, **29**, 521; abst. C. A. 1924, **18**, 668; Chem. Zentr. 1924, II, 1741.
2. U. S. P. 1246739; abst. J. S. C. I. 1918, **37**, 52-A.
3. G. Niederist, Ann. 1879, **196**, 353.
4. E. Haase, Ber. 1893, **26**, 1053.
5. R. Schiff, Ann. 1883, **220**, 99.
6. W. Perkin, J. C. S. 1896, **69**, 1243.
7. H. v. Halban, Zts. physik. Chem. 1913, **84**, 129; abst. C. A. 1913, **7**, 3262.

precipitant (p. 133 n. 1; 170, n. 2), and for the pretreatment of cellulose (p. 655, n. 8). In addition, it has been proposed for the purification of anthraquinone[1] and benzanthrone[2], as a chlorhydrin solvent[3], for the manufacture of photographic films[4], finish remover[5], a paint component[6], and in the production of benzaldehyde[7], benzoic acid[8], nitrous acid[9], artificial resins[10], sodium bromide[11], benzyl nitrate[12], bibenzyl[13], benzaldehyde[14], and as a cellulose acetate solvent[15]. Benzyl chloride has also been patented for the manufacture of acetophenone[16], plastic component[17], as an insulating constituent[18], resin solvent[19], shellac substitute manufacture[20] and in the benzylation of dextrin[21], and cellulose (see pp. 39, 45, 58, 69, 171, 184, 204, 206, 207, 214, 233, 240, 244, 247, 257, 292, 293, 295, 302, 306, and topic *Benzylcellulose*).

The purity of benzyl chloride for the benzylation (not benzoylation) of carbohydrates should be carefully examined before use, for the commercial article generally contains moisture, benzal chloride, benzotrichloride, chlortoluenes, and unchanged toluene, and many of the anomalous results recorded in the benzylation of cellulose, undoubtedly are traceable to impurities contained in the benzyl chloride used.

1. U. S. P. 1420198.
2. U. S. P. 1365024.
3. U. S. P. 1394664.
4. U. S. P. 1411708.
5. U. S. P. 1147851, 1167640, 1169783.
6. U. S. P. 1189804, 1306221.
7. U. S. P. 1151255, 1272522, 1405261.
8. U. S. P. 1463190.
9. U. S. P. 1272522.
10. U. S. P. 1513802.
11. U. S. P. 1272522.
12. J. Nef, Ann. 1899, **309**, 126; abst. J. C. S. 1900, **78**, 4.
13. J. Michailenko and N. Protassowa, J. Russ. Phys. Chem. Soc. 1921, **53**, 347; abst. Chem. Zentr. 1923, III, 1014; C. A. 1924, **18**, 2338.
14. C. Benedetti, A. and W. Vanselow, U. S. P. 1405261.
15. Knoll & Co., D. R. P. 276013; abst. J. S. C. I. 1914, **44**, 916. D. R. P. 336476.
16. E. P. 5533, 1913. F. P. 361539.
17. U. S. P. 1513802. F. P. 518553. D. R. P. 301664, 336476, 346384.
18. D. R. P. 301664, 301713, 302521, 400312.
19. F. P. 537207, 568840.
20. E. P. 221205.
21. D. R. P. 93111.

The homologues of benzyl chloride[1], benzyl bromide[2], brombenzyl bromide[3], and phenylethyl chloride[4] are of but little interest in this connection.

Other Etherifying Agents. Ethylpropyl sulfate has been patented for the production of ethylpropyl starch[5]; and potassium ethyl sulfate[6], dipropyl sulfate[7], chlormethyl sulfate[8], and the iodides of *n*-propyl, *iso*-propyl, *n*-butyl, *iso*-butyl and *iso*-amyl[9] to a very limited extent. Ethyl chlorsulfonate[10] is a vigorous alkylating agent, and may be prepared by the action of phosphorous pentachloride on ethylsulfuric acid[11] or from ethyl alcohol and sulfuryl chloride[12]. It is seldom used in connection with the alkylation of cellulose. Chlormethyl sulfate[13] is applicable only in special cases.

Methyl-*p*-toluene sulfonate[14] and ethyl-*p*-toluene sulfonate[15] have been described as efficient etherifying agents for the carbohydrates.

1. M. Sommelet, Compt. rend. 1925, **180**, 1349; abst. Chem. Zentr. 1925, II, 399; J. C. S. 1925, **128**, 803. See Compt. rend. 1913, **157**, 1443; abst. Chem. Zentr. 1914, I, 462.
2. F. v. Konek and A. Loczka, Ber. 1924, **57**, 679; abst. Chem. Zentr. 1924, II, 145.
3. J. Shoesmith and R. Slater, J. C. S. 1926, **129**, 214; abst. Chem. Zentr. 1926, I, 2677.
4. J. Conant and W. Kirner, J. A. C. S. 1924, **46**, 232; abst. Chem. Zentr. 1924, I, 1182.
5. U. S. P. 1464153.
6. D. Hammick and J. Mullaly, J. C. S. 1921, **119**, 1802; abst. C. A. 1922, **16**, 678; Bull. Soc. Chim. 1922, **32**, 1029.
7. U. S. P. 1339947, 1464153, 1484249, 1506228.
8. J. Houben and H. Arnold, Ber. 1907, **40**, 4306; abst. C. A. 1908, **2**, 399; Meyer Jahr. Chem. 1907, **17**, 228; J. C. S. 1907, **92**, i, 1000; Chem. Zentr. 1908, I, 17; Jahr. Chem. 1905-08, II, 304.
9. M. Bogert and E. Slocum, J. A. C. S. 1924, **46**, 763.
10. F. Bushong, Amer. Chem. J. 1903, **20**, 212.
11. J. Nef, Ann. 1901, **318**, 43; abst. J. C. S. 1901, **80**, i, 626.
12. P. Behrend, J. pr. Chem. 1877,(2), **15**, 23; abst. Jahr. Reinen Chem. 1877, **5**, 148; J. C. S. 1877, **32**, 287; Jahr. Chem. 1877, **30**, 516.
13. J. Houben and H. Arnold, Ber. 1908, **41**, 1565; abst. C. A. 1908, **2**, 2372; J. C. S. 1908, **94**, i, 533; Jahr. Chem. 1905-08, II, 2225.
14. W. Rodionow, Bull. Soc. Chim. 1926, (4), **39**, 305; abst. Chem. Zentr. 1926, I, 2927.
15. F. Krafft and A. Roos, Ber. 1892, **25**, 2259; 1893, **26**, 2823.

CHAPTER VI

CELLULOSE ALKYL ETHERS

A prelude to the discovery, academic investigation and commercial exploitation of the alkylcelluloses, are the researches leading to the substitution of alkyl radicals in the simple sugars as indicated on page 2, but it was not until many years later that these methods of alkyl substitution were transferred to the carbohydrate group by the more or less incidental work of W. Suida on the examination of the effect of atomic groups of cellulose and textile fibers, primarily in connection with the dyeing process. It is noteworthy to bear in mind the salient property of cellulose—which stands out among the other primary materials of industry—of forming compounds of a multiplicity of varying properties, and hence of correspondingly diversified industrial application, both in the peaceful arts, and in the warlike pursuits by virtue of its propulsive force when in the nitrated condition.

A striking illustration of the versatility of a single class of cellulose compounds is in the ethers, specifically methylcellulose, which may be produced in the form of an ether perfectly soluble in cold water or hot water, or soluble in cold water and not in hot water, or insoluble in water but swelled thereby, or entirely unaffected by hot or cold water, but dissolving in an almost endless number of volatile solvents, solvent combinations, plastifying and softening bodies, and miscible with the inorganic and organic cellulose esters in all proportions by virtue of this wide solvent capacity. At the present time, industrial applications of the alkylcelluloses are limited almost entirely by their cost of production, or rather by the cost of the alkylating agent per unit weight, and the fact that such a large amount is required as compared with the weight of cellulose entering into the ether formation. The alkylation components are

very simple, being merely cellulose, alkali as sodium hydroxide, and methyl or ethyl chlorides or sulfates. All the entering reactants are obtainable in abundant quantity at a cost enabling competition with the cellulose nitrates and acetates with the exception of the alkylating agents. Let the necessary etherifying chemicals become available at competitive prices, and the enhanced value of the cellulose ethers over all cellulose esters in the number and cheapness of solvents and solvent combinations in which they are dissolvable (as mixtures of denatured alcohol and benzene or toluene) and it is predicted the cellulose ethers will supplant many of the cellulose esters in a large number of technical fields. Coupled with this most desirable solvent capacity in inexpensive dissolving combinations, is a high stability, low inflammability, and the fact that the cellulose ethers may be heated with water at 170° for many days without appreciable change, or with caustic potash solution of 25% strength without affecting their desirable physical properties.

It appears obvious that these compounds which have such a catalogue of good properties and such a wide diversification of indicated uses, must have a great future awaiting them, once they are capable of manufacture at the proper competitive prices. In the original patent of L. Lilienfeld issued in 1912, the ethylcellulose produced and described by him was soluble in such materials as turpentine oil, castor oil, linseed oil, olive oil, vaseline, paraffin oil, naphtha, stearine, beeswax, japan wax, lanolin and Chinese wood oil, in none of which twelve bodies is any industrially valuable cellulose or cellulose acetate dissolvable (see p. 19). Furthermore, no cellulose nitrate or acetylated cellulose is soluble in water, either hot or cold, to form any compound of technical usefulness, insofar as we are aware.

Theory of the Cellulose Ethers. The hydroxyl groups of cellulose—of which there are three in its simplest formula of $C_6H_{10}O_5$—deport themselves in all their relations similar to the hydroxyl groups in alcohols, not

only in the formation of ethers by the substitution of methyl, ethyl, benzyl, etc., radicals for hydrogen of the replaceable hydroxyl group, but by the substitution of acid radicals for the replaceable H of OH groups, forming the nitro- and acetyl-celluloses. Like the cellulose acetates they have no industrial application in the dry or undissolved conditions, thus differing sharply from the inorganic cellulose esters (nitrocelluloses), which are used in explosive combinations. But, in contrast to the cellulose esters, both from inorganic and organic acid radicals, they possess the very desirable property of being exceeding stable, being non-hydrolyzable by strong alkalis and unaffected by boiling water, most desirable properties which have been searched for in vain in the older and more firmly established cellulose nitrate and cellulose acetate arts. This rather sweeping statement is susceptible to but one important modification, which is that insofar as we are aware, there has not been found in the organic cellulose ester or cellulose ether fields, a plasticizing body which as closely approaches the ideal as does camphor in connection with the nitrocelluloses. But as research is being centered upon plastizants suitable for combination with the etherified celluloses, it becomes more and more obvious that etherified cellulose is opening up a much broader field than that of the other cellulose derivatives by virtue of the fact of its solubility and colloiding power with a much wider range of liquid and solid dissolving and softening bodies.

Whereas the earlier applications of the cellulose ethers were primarily addressed to the photographic film industry, recognition of the paramount importance played with the strict control of alkalicellulose formation and the steps prior to etherification as affecting the cellulose ethers themselves, coupled with a broadening of the field of research for suitable liquid and solid dissolvants in inducing peculiar and desirable properties for specific uses, has markedly increased the impetus for research in the past semidecade, and is indicative that the general field of thermo-

plastic materials, filaments, threads, yarns, textiles and coated fabrics has been definitely and permanently invaded in a systematic manner by this newer type of cellulose derivative. The entire gamut of nitrocellulose solvents and acetylcellulose dissolving bodies is being reviewed most meticulously as to their possible applicability in connection with the various degrees of cellulose etherification and cellulose ethers produced, not only the simple and compound methylated, ethylated and benzylated celluloses, but combinations of various dissimilar radicals therewith to produce mixed ethers, the addition of acid radicals thereto in the formation of cellulose ether-esters, and the physical blending of cellulose ether and cellulose ester to obtain especial properties optimum for use in all the places where the older known nitrocelluloses and acetylcelluloses have found application in the arts. There has been no recrudescence in the cellulose ether art, rather a steady augmentation of research and a broadening of possible fields for application. One has but to peruse the Chemical Annuals for the past ten years for a striking example of the truth of this statement. An official of the United States Patent Office in a position to know, has estimated that at the close of the year 1932 there were no less than fifteen hundred applications slumbering in the Patent Office archives having to do with some phase of cellulose ether activity—individual inventions still being actively prosecuted.

The well marked tendency to usurpation by the cellulose ethers in fields of technical usefulness heretofore held by the cellulose acetates and the nitrocelluloses in solution is emphasized by the following summary of desirable properties:

1. Extreme permanency, stability and neutrality. No acid radical to split off by exposure to the elements for a prolonged period. Heated with impunity in the presence or absence of water nearly to their melting points (above 200° usually). This results in an insulating power far surpassing that of all other known cellulose derivatives.

For example, the insulating power of an ethylcellulose in the shape of a cube having a volume of one cc. exceeds 1500 x 15.6 megohms.

2. The extraordinary suppleness and resistivity to protracted chemical and physical influences and the notable toughness and hardness of plastic masses produced from the solutions or jellies of cellulose ethers.

3. Their property of dissolving readily and to a high degree in an almost unlimited number of solvents and solvent combinations, including such cheap mixtures as denatured ethyl alcohol with benzene, toluene and xylene.

4. A very low hygroscopicity and hence negligible tendency to blush or fog when comparatively volatile solutions of the ethers are evaporated to dryness in an atmosphere of relatively high humidity.

5. Their relative non-inflammability, and ability to amalgamate themselves with a large number of halogen-containing and other liquid and solid inflammability-reducing combinations.

6. The desirable intrinsic properties of all other classes of cellulose derivatives combined do not exceed those of the cellulose ethers as developed up to the present time—and this art must be regarded at present as being but in its infancy, with possibilities and potentialities almost limitless.

Our knowledge in general of the cellulose ethers is based primarily upon the patent literature, the pure research which is the basis of these patents having been published in a minority of instances, as the result of which most of our available information on this subject comes from the issued patents rather than from purely scientific contributions.

Under the general acceptation that cellulose expressed in its simplest form has three replaceable hydroxyls, the hydrogen portion of which is susceptible to substitution with alkyl, aralkyl or aryl groups, we have in percentage composition of the substituent groups the following, as-

suming on a C_{12} formula for methyl, ethyl and propyl groups as examples, that from 1 to 6 of the available groups have been substituted, equivalent to ½ to 3 on a C_6 basis for cellulose:

Table II.

Cellulose Ether	Methoxyl	Ethoxyl	Propoxyl
Mono-	9.17%	10.23%	16.12%
Di-	17.61%	23.68%	28.93%
Tri-	25.68%	27.79%	39.34%
Tetra-	32.61%	41.28%	47.97%
Penta-	39.34%	48.49%	55.25%
Hexa-	45.58%	54.87%	61.46%

As might be expected, only under exceptional conditions and usually unintentionally have the cellulose ethers been prepared of the alkyl composition indicating a designated whole number of radicals have been replaced, and in those isolated instances it is questionable but what mixtures of ethers resulted, which *happened* to give one of the percentages as above stated. Like the older known acetylcelluloses, the cellulose ethers as manufactured commercially are mixtures of various numbers of substituent groups as is demonstrable by applying such purifying treatments as fractional precipitation from various solvent combinations and determining the alkyl group percentages in the various fractions. Analogous to the cellulose acetates, the cellulose ethers of maximum substituted groups are not of highest commercial utility, but based on a C_6 cellulose molecule those containing 2.5-2.8 radicals are technically most valuable. This is but a generalized statement susceptible to modification in many instances as evidenced by the fact, for example, that the introduction of not to exceed 1% of benzyl radical in an ethylcellulose soluble in or swollen by water, will greatly increase the resistivity of the mixed cellulose ether to the action of water, either hot or cold.

The properties of the cellulose ethers as normally expected, vary widely dependent upon the number and nature of substituent groups, and the conditions upon which the

groups were introduced into the cellulose aggregate. A (say) diethylcellulose prepared from normal cellulose may be basically different from a diethylcellulose obtained by the ethylation of an alkalicellulose, especially is this difference obvious in solubility and viscosity. There are those who have *studied* an art, and others who have *lived* it. Only the latter fully appreciate how essential for concordant and duplicable results, how important is minutia in detail when working with cellulose derivatives especially the cellulose ethers. A variation of 2% (for example) in the time of ageing of alkalicellulose or in ripening time in viscose produced therefrom, will cause readily perceivable changes in the final product (rayon).

None of the cellulose ethers can be said to be definitely characterized. Results have been published tending to show that upon careful practical precipitation a definite ether has been isolated, but such results are open to suspicion inasmuch as the alkoxyl content might be due to a percentage of a cellulose ether present both lower and higher in percentage to such a degree as to simulate the definite ether in percentage composition. That is, 5% of 3 and 5% of 1, is equivalent to 10% of 2, and a dialkylcellulose could readily have a proportionate amount of tri- and mono- therein, so the analytical figures would indicate 100% of a dimethylcellulose.

Methylcellulose. Our earlier knowledge of the methylcelluloses has been obtained incidentally in attempts to elucidate the structure and configuration of the cellulose molecule, and really begins in a comprehensive manner with the contributions of W. Denham and H. Woodhouse in 1913 (see pp. 24-30), extended in 1914 (pp. 30-33), and amplified in 1921 (pp. 33-37). Their results were checked by J. Irvine, W. Denham and E. Hirst in 1922 (p. 37), and only minor discrepancies reported.

They found that the exhaustive methylation of cellulose, when repeated 20 times, gives a product containing 43% methoxyl as against 45.6% methoxyl for trimethyl-

cellulose. The carbon and hydrogen values also agreed with $C_6H_7O_2(OCH_3)_3$, and as the finished ether preserved a fibrous structure, there appeared little likelihood that profound molecular alteration had taken place. The trimethylcellulose was heated with a large excess of methyl alcohol containing 1% HCl for 50 hrs. at 125-130°, this treatment effecting hydrolysis, depolymerization and conversion of the scission products into the corresponding methylglucosides. These were distilled in high vacuum to a total yield of 90% of theory. There were collected three fractions, the first two being trimethylmethylglucoside pure, and the third containing dimethylmethylglucoside in addition. From analysis it was determined that the small quantity of dimethylmethylglucoside in the third fraction agreed exactly with the deficiency of 2.6% in the methoxyl content of the trimethylcellulose used. No trace was found of tetramethylmethylglucoside. On hydrolysis of the first two fractions a yield of 89% of crystalline 2.3.6-trimethylglucose was obtained, thus affording proof that all the glucose residues in *a*-cellulose are identical in structure and the simplest possible formula satisfying this condition is that of an 1.5-anhydroglucose. It is necessary, however, to include one more glucose unit to satisfactorily account for the formation of cellobiose[1].

T. Ozawa[2] methylated wood pulp with concentrated NaOH and methyl sulfate, obtaining a heptamethylcellulose on a C_{24} cellulose, showing incomplete methylation equivalent to less than a dimethylcellulose on a C_6 cellulose basis. On the supposition that the impossibility of completely methylating carbohydrates with diazomethane might be due to the fact that the reaction system is heterogeneous, L. Schmid and B. Becker[3] attempted to effect the alkylation by converting the carbohydrate in liquid ammonia solution by means of alkali metals into the alcoholates, which then,

1. Chem. Trade J. 1922, **71**, 291; abst. C. A. 1923, **17**, 1713.
2. J. Chem. Ind. Japan, 1924, **27**, 884; abst. C. A. 1925, **19**, 894.
3. Ber. 1925, **58B**, 1966; abst. C. A. 1926, **20**, 744; Chem. Zentr. 1926, I, 56.

by double decomposition, should give the desired cellulose ethers. The methylation of inulin, lichenin, soluble starch and mannitol lead but to the introduction of one methyl group as against a possible maximum of three (p. 95, n. 1).

In an intensive investigation of the depolymerization of cellulose[1], E. Heuser and N. Hiemer (see p. 76, n. 5) methylated purified cotton, cellulose regenerated from cuprammonium solutions, rayon prepared by the cuprammonium process, hydrocellulose prepared by the action of HCl gas on regenerated cellulose, viscose precipitated by adding a ripened xanthate solution to boiling water, "cellulose A" of K. Hess and W. Weltzien, and "Cellodextrin I." By exhaustive methylation, products were obtained completely soluble in water and suitable for cryoscopic measurements. When pure Egyptian cotton is dissolved in cuprammonium hydroxide, reprecipitated with CO_2, and etherified with methyl sulfate and NaOH, a methoxyl content of 44.9% (trimethylcellulose=45.6%) is obtained after 22 operations. For the later methylations, a solution containing 50-60% NaOH and a large excess of methyl sulfate was used. The solubility in water of the methylcellulose increases to a maximum of 64% at 22.4% methoxyl, and then diminishes at 0° to 42% methoxyl. Solubility in glacial acetic acid remains nearly constant at about 33% between 10-32% methoxyl (dimethylcellulose=32.6% methoxyl), and then increases to 100% at 40.8%.

The end-product is also completely soluble in chloroform, dichlorethane, tetrachlorethane and pyridine. Cuprammonium stable fiber is more readily methylated, and after five methylations, contains 35.7% methoxyl. This dissolves to the extent of 80% in water at 15-17°, and is completely soluble at 8-12°. It is also entirely dissolvable by pyridine, and 50% soluble in glacial acetic acid. After purification by repeated dissolution in cold water and reprecipitation by heating, the methoxyl content rises to

1. Cellulosechem. 1925, **6**, 101, 125, 153; abst. C. A. 1926, **20**, 818; J. S. C. I. 1926, **45**, 502-A; Chem. Zentr. 1926, I, 1391.

37.5%. Cellulose regenerated from "viscose," or from cellulose acetate, or hydrocelluloses prepared from these by gaseous HCl, and cellulose dextrin prepared with sulfuric acid, are all more readily methylated, a methoxyl content of 35-40% being generally obtained after three methylations.

These products are all soluble in cold water, the highest temperature at which dissolution is complete varying up to 75° for cellulose dextrin. The softening temperature, which is about 350° for the product from pure cotton cellulose, varies down to 203° for the methylated cellulose dextrin. The molecular weights, obtained in aqueous solution cryoscopically, were found to be independent of the concentration. Concentrations varied between 0.12-1.9% and the freezing point depressions were 0.001-0.014°. The ash content (about 0.1%) was found to be without significance. The mol. wts. for methylated cuprammonium staple fiber were irregular, but the hydrocellulose prepared therefrom, having a corrected copper number of 6.8, gave a mol. wt. of 2700, corresponding with 1.3.5-dimethyl-anhydroglucose residues. The lowest mol. wt. was 800 for a hydrocellulose methylated (copper number 8), and 900 for a methylated cellulose dextrin (copper number 16.6).

Mol. wt. rises with diminishing hydration temperature (temperature of complete solution in water), and with increasing softening temperature, but is not directly related to the copper number. Since depolymerized cellulose is more readily methylatable than is normal cellulose, a trimethylcellulose would be more apt to be obtainable from the former than from the latter. After 9 methylations of hydrocellulose from viscose, the methoxyl is 45.42% (trimethylcellulose = 45.6%). The same methoxyl content is also obtained when dimethylcellulose from viscose cellulose is acetylated to dimethylcellulose monoacetate and then twice methylated, the ether being completely soluble in glacial acetic acid and chloroform, but insoluble in water. After 6 methylations, cellulose triacetate from cotton linters con-

tains 45.0% methoxyl, is soluble in glacial acetic acid and chloroform and mostly dissolvable in water.

E. Heuser, R. Schmitt and L. Gunkel[1] methylated HCl-lignin with methyl sulfate and obtained a maximum of 26.3% methoxyl, while E. Ungar[2] established that the lignin portion is methylatable with diazomethane. H. Urban[3] suspended lignin in water and methylated at 80-100° with methyl sulfate and KOH solution, a maximum in 15 methylations giving 28.31% methoxyl, his results being after 1, 3, 5, 7, 10, 12 and 15 methylations, 22.6%, 25.67%, 25.71%, 26.18%, 28.31%, 27.9% and 28.23% methoxyl respectively. By the successive methylation of cellulose, H. Urban obtained a maximum methoxyl content of 44.7% as against 44.6% maximum by W. Denham, and 43% by J. Irvine and E. Hirst, theory being 45.6%. The methylated cotton obtained was white, fibrous, forming highly viscous solutions with chloroform or tetrachlorethane which are clear; insoluble in water, alcohol, ether, ethyl acetate, acetone, carbon tetrachloride and carbon bisulfide. Sulfite cellulose also retains its fibrous structure and its light color upon methylation, which, however, proceeds very slowly. In 9 methylations a 41.2% methoxyl was reached, the ether being soluble in chloroform to a clear solution.

When methylated cotton (more than 40% methoxyl) was distilled under 1 mm. pressure at 300-350° there distils a light brown tar, and a darker tarry residue remains. The ether-soluble distillate was divisible into a fraction at 65-135° and a larger fraction coming over at 135-154°. Four-fold methylation of wood gave a 40% methoxyl content, which upon additional methylation reached a maximum of 41% methoxyl. P. Karrer[4] has described in

1. Cellulosechemie, 1921, **2**, 81; abst. C. A. 1922, **16**, 490; J. C. S. 1922, **122**, 325; Papier-fabrik. 1921, **19**, 81; Chim. et Ind. 1922, **8**, 141; Chem. Zentr. 1921, III, 1117.
2. Cellulosechemie, 1926, **7**, 113.
3. Cellulosechemie, 1926, **7**, 73; abst. C. A. 1926, **20**, 3080; J. S. C. I. 1926, **45**, 531-B.
4. P. Karrer and T. Lieser, Cellulosechemie, 1926, **7**, 1; abst. C. A. 1926, **20**, 1515; J. S. C. I. 1926, **45**, 267-B.

quite elaborate detail, bodies obtained by the methylation of viscose which he has named methylcellulose xanthates, but I. Sakurada and T. Nakashima[1] in repeating his work came to the conclusion that the ethers obtained are methylated celluloses rather than the methyl ester of cellulose xanthic acid or a methylated cellulose xanthate, and that the free alkali in viscose probably combines with available hydroxyl groups in the xanthate, and in this manner induces methylation of the cellulose.

H. Urban has shown that unchanged cotton may be methylated to a trimethylcellulose at 20°, and differs in several important aspects from those trimethylcelluloses prepared at substantially higher temperatures. In 1928 K. Freudenberg and E. Braun[2] described trimethylcellulose which contrasted to similar maximum methylated celluloses in dissolving to a clear, viscous solution in chloroform, tetrachlorethane and glacial acetic acid, and differing from the trimethylcellulose of K. Hess and W. Weltzien[3], as well as that of K. Hess and H. Pichlmayr[4] in that the original fibrous structure is preserved, is wholly insoluble in water and cannot be crystallized from organic solvents. It is formed from unbleached cotton with 93% yield of trimethylcellulose on theory, the 7% discrepancy being attributed primarily to mechanical losses, the methoxyl content after 3-4 methylations being 43-44%, and through further treatment rises to nearly 45%.

The methyl ether of 44.4% methoxyl gave with HCl in methyl alcohol a mixture of 91% of 2.3.6-trimethylmethylglucoside and 9% dimethylmethylglucoside, whereas a methyl ether that still lacks 1.2% methoxyl from a true trimethylcellulose should give a mixture of 90.4% trimethyl-

1. Sci. Papers Inst. Phys. Chem. Research (Tokyo), 1927, **6**, 197; abst. C. A. 1928, **22**, 683.
2. Ann. 1928, **460**, 288; abst. C. A. 1928, **22**, 3635; J. S. C. I. 1928, **47**, 399-A; Chem. Zentr. 1928, I, 1848.
3. Ann. 1925, **442**, 46; abst. J. C. S. 1925, **128**, i, 517; J. S. C. I. 1925, **44**, 238-B.
4. Ann. 1926, **450**, 29; abst. C. A. 1927, **21**, 174; J. S. C. I. 1927, **46**, 44-A; Chem. Zentr. 1926, II, 2892.

and 9.6% dimethyl-methylglucoside. Not a trace of tetramethylglucose was obtained, thus corroborating previous investigators upon this point. The methylcellulose is dissolved by etherified HCl at 30° within an hour, forming a syrupy compound considered to be a 2.3.6-trimethyl-1-chlorglucose, of which both an *a*- and a *b*- form are possible. It gives a well crystallized pyridinium salt, and by the action of sodium, forms pure trimethylglucose anhydride.

The trimethylcellulose thus obtained is so viscous in 2% chloroform solution as to be unpourable and has an immeasurably large molecular weight. They show there can be no reversible interconversion of trimethylcellulose and trimethylglucose anhydride, and that cellobiose must be a product of cellulose degradation, not a product of resynthesis from glucose.

E. Berl and H. Schupp[1] have published a detailed account of their investigations on the methylation and ethylation of various celluloses, methylation of cellulose (linters) with methyl sulfate and 15% NaOH at ordinary temperature affording first of all a monomethylcellulose, partly soluble in water, completely so in Schweitzer's reagent, and insoluble in the usual organic solvents. Further methylation of this produces methylcelluloses with gradually increasing methoxyl content, until trimethylcellulose is obtained after 25-28 methylations, this ether being insoluble in water and in Schweitzer's reagent. Solubility in water of the methylcelluloses diminishes gradually after the second methylation to water insolubility. In two of the cases examined, the methoxyl content of the water-soluble portion and of the original material was the same. That is, ability to dissolve in water is not determinable by the degree of methylation (i.e. methoxyl content). Solubility of the methylated products in Schweitzer's reagent diminishes appreciably with increasing methoxyl content, but two hy-

1. Cellulosechemie, 1929, **10**, 41; abst. J. S. C. I. 1929, **48**, 278-B; C. A. 1929, **23**, 4816; Chem. Zentr. 1929, II, 3088.

droxyl groups must be present in the cellulose molecule to give a completely soluble product.

Methylation of alkali-soluble cellulose (by previous treatment with 75% sulfuric acid) with methyl sulfate under a variety of conditions, gives cellulose ethers containing 19.7-30.71% methoxyl, according to the proportion of methyl sulfate used. Methylation proceeds at the ordinary temperature, but analogous ethylation requires an initial temperature of 50° for reaction to commence. K. Freudenberg[1] has given methods for preparing "water-insoluble" methylcellulose, but K. Hess[2] reports the methylcellulose ether dissolves in water at 0° after having been shaken with water or dissolved in methyl alcohol and chloroform (1:1).

W. Haworth[3] and J. Irvine[4] have announced the isolation of tetramethylglucose from fully methylated cellulose by hydrolysis, the latter showing that when cellulose is methylated on a large scale and the ether subjected to graded hydrolysis, only 2.3.6-trimethylglucose is liberated in the first instance, the 2.3.4.6-tetramethylglucose being derived from the more resistant fraction of the methylated cellulose.

Trimethylcellulose A. It has been shown that acetylation of cellulose with acetyl chloride gives a new triacetylcellulose (acetate A or triacetylcellulose A). Dried cotton cellulose containing 4-5 moisture, is shaken in a closed vessel with 11 times its weight of acetyl chloride at 17-20°, dissolution being effected in about 4 days. The product, after being allowed to lose contained HCl, is evaporated *in vacuo*, and the residue treated with chloroform and the latter evaporated. Pure triacetylcellulose A (cellulose triacetate A) is obtained by dissolving the product in

1. Ber. 1929, **62B**, 383; abst. J. S. C. I. 1929, **48**, 430-A; C. A. 1929, **23**, 3342.
2. Ber. 1929, **62B**, 924; abst. C. A. 1929, **23**, 4063; J. S. C. I. 1929, **48**, 684-A; Chem. Zentr. 1929, I, 2527.
3. Nature, 1932, **129**, 365; abst. J. S. C. I. 1932, **51**, 370-A.
4. J. S. C. I. 1932, **51**, 263-C. & I.

glacial acetic acid and precipitating with ether. As by-products, cellodextrin acetate and acetochlorcellobiose are formed[1].

Using methyl sulfate and hydrated barium hydroxide (which, unlike NaOH does not hydrolyze cellulose A [pp. 77, 116, 709]), there is obtained a product of 30-40% methoxyl, which is not affected by alkali, and on methylation with NaOH and methyl sulfate is converted into trimethylcellulose A (42-43% methoxyl). The latter is soluble in cold water, and when treated with HBr dissolved in glacial acetic acid, is converted into acetobromcellobiose, while with acetyl bromide containing HBr, gives a new acetobromglucose, m. pt. 60-70° as a white powder. The latter on hydrolysis is converted into celloglucosan, m. pt. 107-109°, similar to, but not identical with, ordinary glucosan[2].

In a continuation of their work on trimethylcellulose A and its scission, epitomized on pages 74-75 herein, K. Hess and W. Weltzien found the sequence of decomposition is cellulose to cellulose A to trimethylcellulose A to trimethylmethylglucoside (trimethylglucose-methylglucoside). Purified trimethylcellulose from cellulose A contained 45.1% methoxyl and m. pt. 230-237°, that from hydrocellulose 44.9% methoxyl, m. pt. the same. By the exhaustive treatment of natural cellulose or regenerated cellulose with methyl sulfate and NaOH at 5-60°, by precipitation with hot water and re-solution in cold water followed by precipitation with benzene or benzene-alcohol 1:1, trimethylcellulose A separates in a plainly crystallizable condition on concentration of its solution, especially those in chloroform-alcohol, or by slow concentration of its solutions in benzene-alcohol at 30°. Before the precipitation, the methylcellulose still shows a fibrous form to a large extent, although the fibers under the microscope, in contrast to the fibers

1. K. Hess, W. Weltzien, E. Messmer, E. Jagla, R. Singer, H. Jensen, A. Reh and F. Kunau, Ann. 1923, **435**, 1; abst. C. A. 1924, **18**, 1384; J. S. C. I. 1924, **43**, 88-B; Chem. Zentr. 1924, I, 751; J. C. S. 1924, **126**, i, 146.

2. K. Hess, Zts. Elektrochem. 1925, **31**, 613; abst. C. A. 1926, **20**, 663.

of the initial cellulose, appear greatly broken and eroded. The fiber character is first completely lost in the precipitation operations[1].

Their preferred method for the preparation of trimethylcellulose A is to first purify natural cellulose with chlorine dioxide and sodium sulfite until no further amount of reagent is consumed, then treat with 2% NaOH solution at boiling temperature and under exclusion of air, this operation being repeated until the typical swelling phenomena for raw cotton in cuprammonium solution had entirely disappeared. The methylation was carried out as previously indicated[2], the reaction temperature being kept under 55°. The crude methylcellulose formed is first washed with hot water, carefully air-dried, swollen with chloroform, then dissolved by the addition of alcohol (1:1), and the insoluble portion separated by centrifugalization. The residue is then treated as above, and this continued until eventually all passes into solution. After filtration through many layers of hardened filter paper under pressure, the methylcellulose is completely precipitated by copious addition of benzine-ether, washed with water and finally dried in the air. Before crystallization of the preparation, a further precipitation from benzene with petroleum ether is made. It is best to operate with 2-5% concentrations of the methylcellulose with slow evaporation at 30°. They regard trimethylcellulose A of highest purity as a definitely characterized chemical individual.

Trimethylcellulose prepared from natural cellulose, regenerated cellulose from viscose, cuprammonium cellulose, after one careful precipitation from benzene-benzine is readily crystallizable from chloroform-alcohol. If separation is too rapid the product deposits in the amorphous condition, but may be obtained crystalline by moistening with

1. K. Hess, C. Trogus and H. Friese, Annalen, 1928, **466**, 80; abst. C. A. 1929, **23**, 118; J. S. C. I. 1928, **47**, 1360-A; Chem. Zentr. 1929, I, 234.

2. K. Hess and W. Weltzien, Annalen 1925, **442**, 46; abst. J. C. S. 1925, **128**, i, 517; J. S. C. I. 1925, **44**, 238-B.

chloroform-alcohol and keeping for a few days. The crystalline form is retained after removal of the solvent. Like crystalline cellulose triacetate, crystalline trimethylcellulose gradually undergoes association in glacial acetic acid solution, the molecular weight (determined cryoscopically) increasing from about 300 to about 850 in 30 hrs.

In an investigation directed solely to crystalline trimethylcellulose[1] K. Hess and H. Pichlmayr found that endeavors to crystallize in the presence of ethyl benzoate or amyl acetate resulted in the precipitation of stiff jellies instead of crystalline masses, indicating that the power of crystallization and the tendency to swelling are throughout not mutually hindering to each other. Purification by digestion of trimethylcellulose in benzene at 65° has proved very advantageous as a method of purification, followed by precipitation by ethyl ether. To induce crystallization, it is recommended to prepare 10% solutions in chloroform-alcohol 1:1, which are slowly concentrated in glass vessels through which a current of dry air is circulated. In a few days spheroliths appear, which soon grow into crystal husks. The purified crystals are inclined to be soluble in chloroform, tetrachlorethane, benzene, nitrobenzene, chlorbenzene, glacial acetic acid, pyridine and tetralin; good solubility in hot ethyl benzoate or amyl acetate; difficultly soluble in hot methyl-, ethyl- and amyl-alcohol from which it precipitates in white flocks on cooling; insoluble in acetone, ether and petroleum ether; readily soluble in 50% mixtures of benzene-alcohol or chloroform-alcohol. Specific rotatory power (a) $^{20}_{D}$ —18.52° in benzene; —5.08° in pyridine; —4.34° in chloroform; —18.44° in water; and —9.81° in glacial acetic acid. A concentration of 0.1005% in acetic acid showed a fairly constant molecular weight of about 200 (calculated 204; limits 182-218) over a period of 47 hrs. The other concentrations showed greater variations; 0.812% varied 556-661; 0.389% from 304-721.

1. Annalen, 1926, **450**, 29; abst. C. A. 1927, **21**, 174; J. S. C. I. 1927, **46**, 44-A; Chem. Zentr. 1926, II, 2892.

Methylhydrocellulose. In 1922 E. Heuser and W. v. Neuenstein[1] published their work on the methylation of hydrocellulose from different sources and prepared in various ways. They regarded the hydrocellulose as produced by the method of E. Knoevenagel and H. Busch[2] as a pure product on account of being formed from cellulose in which the crystal valencies have already been resolved. Ordinary cotton cellulose upon repeated methylation gave a product corresponding with dimethylcellulose, completely insoluble in cold water and in organic solvents.

The product from the pure hydrocellulose of K. and B. with the same methoxyl content was completely soluble in these media and behaved as a uniform substance. The hydrocellulose of A. Girard yielded a mixed substance with properties partly the same as both of the above, in no case a trimethylcellulose being obtained. The dimethylhydrocellulose from the product of K. and B. yielded principally on acetylation dimethylcellulose monoacetate (monoacetyldimethylcellulose), soluble in organic solvents and with relatively low melting point. Molecular weight determinations gave inconclusive figures.

Best results[3] were obtained by using a hydrocellulose prepared by taking chopped viscose fiber of 6-10% moisture, passing dry CO_2 therethrough for 2 hrs. while confined in a closed flask, then a current of dry HCl fumes for 2-3 hrs. The flask was then tightly closed and left until a test portion was found soluble in 10% NaOH. For methylation, 5 gms. (1 mol.) of this hydrocellulose was dissolved in 50 cc. 10% NaOH solution (4 mols.), and after some hrs. 10 gms. methyl sulfate (3 mols.) added in small quantities with stirring. The temperature rose to 60° after 10

1. Cellulosechem. 1922, **3**, 89; abst. C. A. 1923, **17**, 875; J. C. S. 1923, **124**, i, 17; J. S. C. I. 1922, **41**, 977-A; 1923, **42**, 91-A; J. Text. Inst. 1923, **14**, 40-A.

2. Cellulosechem. 1922, **3**, 42; abst. C. A. 1922, **16**, 2779; J. C. S. 1922, **122**, i, 636; Chem. Zentr. 1922, II, 347.

3. E. Heuser and W. v. Neuenstein, Cellulosechem. 1922, **3**, 101; abst. C. A. 1923, **17**, 875; J. C. S. 1923, **124**, i, 95; J. S. C. I. 1923, **42**, 91-A.

min. Subsequent operations were performed without separating the methylated product, using the same proportions of reagents, but taking the NaOH in the form of a 25% solution instead of 10%. After the fifth operation, the major portion of the methylated cellulose remained insoluble in the saline liquid. An excess of alkali was added, and while hot the cellulose ether was collected, the precipitate dissolved in cold water, filtered to remove traces of undermethylated residue, and the ether which was precipitated, collected while hot and washed with boiling water. When completely methylated, this ether retained its solubility in cold water even after drying. Theoretical yields were obtained when the operations were performed with mechanical stirring, the maximum degree of methylation corresponding to 33.76% methoxyl. The dimethylcellulose monoacetate obtained yielded a compound (26% methoxyl, 17% acetic acid) having the approximate composition of dimethylcellulose acetate, m. pt. 110°, soluble in ethyl ether but insoluble in water; and a substance (23% methoxyl, 17% acetic acid), m. pt. 140°, insoluble in water but soluble in acetone.

In a later communication[1], the author's conception of dimethylhydrocellulose as a dimethyl derivative of a dimeric anhydrocellobiose is confirmed by cryoscopic determinations of the molecular weight of the substance in aqueous solution. The results obtained (737-773) agree well with the calculated value of 760 for $[C_{12}H_{16}O_6(OCH_3)_4]_2$. It is important to note, that with increasing concentrations, the mol. wt. of dimethylhydrocellulose does not rise over the value approaching the theoretical.

Properties of Methylcellulose. After repeated precipitation from benzene solution, or benzene-petroleum ether, of completely methylated cellulose, snow white, loose powders are obtained, which on careful evaporation crystallize from a mixture of chloroform-alcohol 1:1

1. E. Heuser and G. Jayne, Ber. 1923, **56**, 1242; abst. C. A. 1923, **17**, 3249; J. C. S. 1923, **124**, i, 657; J. S. C. I. 1923, **42**, 599-A.

in small needles arranged like snow flakes, which are double refracting when viewed under the polarization microscope. The crystals are solid. After several recrystallizations, the rotatory power in various solvents does not change, so that the methylcellulose crystals appear to be entirely homogeneous. If crystallization proceeds too rapidly, then the substance is obtained in double-refracting spherolites or as a gummy mass, which may be dissolved up and crystallized. By very slow crystallization, distinct needles may be obtained. Irrespective of the nature of the initial cellulose taken, crystals of methylcellulose obtained therefrom show the same degree of rotation.

J. Katz and P. Samwel[1] have studied the form of molecules of the cellulose ethers, by spreading them out in a mono-molecular layer. Cellulose ether dissolved in chloroform spreads readily on water and gives a monomolecular layer upon evaporation of the water. Its surface and thickness were determined at several pressures and extrapolated to zero pressure. The dimensions of the film were found: for ethylcellulose of high, low, or medium viscosity, from 60-66.5 sq. A. U. surface, 5.3-5.55 A. U. thickness; for methylcellulose, 59-61 and 4-4.3; from this is concluded that crystalline cellulose derivatives give values equal to those of technical products, and the latter of varying consistency give equal values, thus indicating that the micelles are string- or leaf-shaped, but not three-dimensional structures.

Viscosity determinations of trimethylcellulose solutions have not as yet been recorded, but H. Staudinger and O. Schweitzer[2] report that dibenzylcellulose exhibits abnormal behavior in *s*-tetrachlorethane, while methylcellulose (38% methoxyl) shows still more divergence from the Hagen-Poiseuille law in the same solvent.

Methylcellulose of maximum methylation (trimethylcellulose) dissolves or does not dissolve in water, depending

1. Naturwissenschaften, 1928, **16**, 592; abst. C. A. 1928, **22**, 3986; J. S. C. I. 1928, **47**, 937-A; Chem. Zentr. 1928, II, 963.
2. Ber. 1930, **63B**, 2317; abst. J. S. C. I. 1930, **49**, 1414-A. See P. Karrer and W. Fioroni; Ber. 1922, **55B**, 2854.

upon the method of preparation, especially as to the alkali-cellulose formation and the proportion of alkali contained therein. The ether, however, dissolves readily in ethyl acetate, glacial acetic acid, benzene, tetrachlorethane, chloroform, pyridine, and in chloroform-alcohol; insoluble in ether, in cold aliphatic alcohols, and usually in hot water.

Molecular Weight of Methylcellulose. E. Heuser[1] has made molecular weight determinations of various methylcelluloses containing 2-2.5 methoxyl groups, in aqueous solution by the cryoscopic method, the results obtained varying from 6000-8000 with cotton, to 900 with cellulose dextrin I. Molecular weights decrease with increasing hydration temperature, at which the methyl derivative is precipitated from aqueous solution on heating, and increase with increase of softening temperature. All the methylcelluloses used were water-soluble. His results are shown in the following Table:

Methylcellulose

Raw Material	No. Methoxy Groups	No. Methylations	Softening Temp.	Hydration Temp.	Mol. Wt. Min. and Maximum	Mean value of Reading	Degree Depolymerization
Cotton	2.0	5–10		about 350°	6000–8000	6–8000	30–40
Copperammonia cellulose pptd by CO_2	2.4	6		270–275°	4000	4000	20
Copperammonia staple fiber	2.4	5	8–12°	258–261°	1660–4990	3280	17
Hydrocellulose from above	2.4	5	12–15°	245–250°	2500–2920	2680	14
Regenerated viscose cellulose	2.5	3	8–12°	235–240°	2125–2390	2270	12
Saponified acetylcellulose "Cellulose A"	2.5	3	30–35°	240–245°	2100–2270	2210	11
Hydrocellulose I	2.3	3	48–53°	220–225°	1520–1630	1580	8
Hydrocellulose II	2.5	1	50–55°	200–205°	1150–1380	1260	6
Hydrocellulose III	2.1	–	55–60°	about 200°	700–800	800	4
Cellulosedextrin I	2.0	2	70–75°	200–205°	690–990	900	4

K. Hess[2] has found that in very dilute solutions, molecular weight determinations of trimethylcellulose in acetic

1. Zts. Elektrochem. 1925, **31**, 498; abst. J. C. S. 1925, **126**, 1387.
2. Ber. 1930, **63**, 518; abst. J. S. C. I. 1930, **49**, 456-A.

acid give too great depressions, increasing markedly with concentration.

Hydrolysis of Methylcellulose. J. Irvine[1] has shown that graded hydrolysis of methylated cellulose affords only 2.3.6-trimethylglucose in the first stage, and then 2.3.4.6-tetramethylglucose from the more resistant fraction. The latter is also obtained in 3-5% amount by similar hydrolysis of methylated amylose, one fraction of which gives a mixture of 2.3.4.6-tetra- (23-26%), 2.3.6-tri- (55-52%), and 2.3- and 2.6-di-methylglucose (21%). Approximately equal proportions of the 2.3- and 2.6-derivatives are obtained when the amylose is directly methylated, but the ratio is 24% and 76% respectively, when methylation follows preliminary acetylation. Hydrolysis of trimethylinulin with oxalic acid yields, in addition to trimethylfructoses, methoxy-5-methylfurfuraldehyde, tetramethylfructose and a trimethylanhydrofructose.

In a study of the action of hydrofluoric acid on carbohydrates[2], B. Helferich and O. Peters methylated the cellan of B. Helferich and S. Boettger[3] with methyl sulfate and KOH solution to a product containing 44% methoxyl, and $(\alpha)D$ 145.1 in chloroform. Hydrolyzed by 2% HCl in methyl alcohol there was obtained a mixture of methylated methylglucosides. By hydrolysis of the glucoside fraction (b. pt. up to 110° at 0.2 mm. pressure), 5% HCl gives a little 2.3.4.6-tetramethylglucose. The condensations in percent as determined by the diminution in reducing power, occurring when 2.3.4- and 2.3.6-trimethylglucoses and glucose are treated with anhydrous HF are 58, 59, 68 and 95 respectively.

F. Wood and A. Alexander[4] have made a study of the preferential absorption of alkali by partly methylated cellulose by the centrifuge method, 1-2 gms. of the partly methylated cellulose being dried at 105° and immersed in

1. J.S.C.I. 1932, **51**, 263-C. & I.; abst. J.S.C.I. 1932, **51**, 502-A.
2. Ann. 1932, **494**, 101; abst. C. A. 1932, **26**, 3486.
3. Ann. 1929, **476**, 150; abst. C. A. 1930, **24**, 720.
4. J. S. C. I. 1928, **47**, 357-T; abst. C. A. 1929, **23**, 3578; Chem. Zentr. 1929, I, 1065; Pulp & Paper Mag. 1929, July 25, 151.

NaOH solutions of various concentrations at 16° in a thermostat. After 3 hrs., or in the case of the more concentrated solutions after 12 hrs., the solid phase was carefully centrifuged for 2.5 min. at 7000 r.p.m., the wet solid being then immersed in water and titrated with *N*/HCl. The residual methylcellulose from this determination was washed with boiling water and its weight determined after drying at 105°. From these results, the composition of the aqueous NaOH in the material as shown:

(1) Great swelling takes place at 16° in the solutions of about 9% NaOH by weight, which is the region of concentration where solution effects are obtained with degraded cellulose by sufficiently lowering the temperature.

(2) The preferential absorption of NaOH is greatly diminished with methylated cellulose.

(3) There is apparently a horizontal portion between 15% and 22% NaOH by weight, but more points are required to substantiate this.

In determining the heat of reaction between partly methylated cellulose and NaOH solutions, an adiabatic arrangement is best for measurement of heat evolved in the reaction, but requires time for completion. The data obtained is based on the principle of measurement of water equivalent of the system by supplying heat electrically to produce the same thermal change as is produced by the heat of reaction to be measured. The results obtained are shown in the following Table:

Table IV. Evolution of Heat with NaOH, Cotton and Methylated Cellulose

(12-14% Methoxyl)

NaOH gms. per 100 cc.	Heat evolved per gm. cotton	NaOH gms per 100 cc.	Sp. gr.	Heat evolved per gm.
0.0	7.8	0.0	1.0	28 gm/cal
7.1	11.5	9.6	1.10	25
12.7	17.4	12.5	1.125	30.9
15.4	21.0	15.3	1.15	27.
19.4	26.0	18.9	1.18	33.
26.0	32.0	22.6	1.21	41.
35.0	35.0	26.7	1.24	49:44
		31.3	1.275	57:47

The major part of results was obtained in duplicate.

These results indicate that the greater dispersion of methylated cellulose results in a great increase in the heat evolution (for anhydrous materials), and that in spite of the large decrease in degree of dispersion brought about by the process of methylation, the preferential absorption of NaOH is considerably diminished at all concentrations of solution, and is concluded to be a function of the hydroxyl groups present.

Acetolysis of Methylcellulose. A product representing an intermediate stage in the acetolysis of cellulose to cellobiose and *iso*cellobiose has been described by K. Hess and H. Friese[1], and obtained by treating cellulose below —5° with a mixture of acetic acid and anhydride containing 2.5% sulfuric acid, the temperature being slowly raised and maintained at 30° for 2.5 days. After filtering and pouring into water, a white precipitate is obtained, which, after extraction with hot methyl alcohol, leaves pure hexa-acetylbiosan, m. pt. 258-259°. This is hydrolyzed by NaOH in methyl alcohol to biosan, decomposing about 270°, which may be re-acetylated to hexa-acetylbiosan by boiling acetic anhydride and pyridine, or acetolyzed to cellobiose and *iso*cellobiose.

Methylation of biosan with methyl sulfate and alkali gives hexamethylbiosan, m. pt. 210-215°, which is converted by HCl-methyl alcohol into 2.3.6-trimethylglucose,*ab*-methylglucoside, m. pt. 118-120°, from which by the action of aqueous HCl, 2.3.6-trimethylglucose, identical with that from cellulose or cellobiose, is obtained. T. Lieser[2] by treatment of methylcellulose[3] with a mixture of acetic acid and anhydride containing sulfuric acid at 25-30° for 7-20 days, obtained about 50% cellobiose octoacetate, indicating that some of the glucose anhydride units in the original product

1. Ann. 1926, **450**, 40; abst. C. A. 1927, **21**, 174; J. S. C. I. 1927, **46**, 44-A. See also Ann. 1927, **456**, 38; abst. J. S. C. I. 1927, **46**, 861-A.
2. Ann. 1930, **483**, 132; abst. C. A. 1931, **25**, 1498; J. S. C. I. 1931, **50**, 74-A.
3. T. Lieser, Ann. 1929, **470**, 104; abst. C. A. 1929, **23**, 3672; J. S. C. I. 1929, **48**, 799-A.

are not methylated, no methylcellobiose acetate being detected. It is assumed to be decomposed during acetolysis[1].

The acetolysis of trimethylcellulose supports the view that cellobiose is preformed in cellulose[2], for under mild treatment at low temperatures, fully methylated cellulose undergoes cleavage to a diacetylhexamethylcellobiose, which readily gives crystalline heptamethyl-*b*-methylcellobioside.

Acetone-soluble cellulose acetate can be completely methylated by treatment with methyl sulfate and 30% NaOH solution in acetone at 55°. Cellulose pulp and finely ground cellulose on similar methylation in two stages yielded trimethylcellulose, m. pt. 215-216°, $(\alpha)D$ —10.0 in chloroform, mol. wt. 2500 in camphor, various samples differing only in the viscosity of their solutions. Acetolysis of trimethylcellulose at 15°, followed by simultaneous de-acetylation and methylation[3] gives tetramethylmethylglucoside

1. He took 1.387 gm. dry cotton prepared by the alternating action of chlorine dioxide and 1% cold NaOH solution on raw yarn, this being acetolyzed with 5 cc. acetic anhydride, 5 cc. glacial acetic acid and 0.5 cc. strong sulfuric acid for 23 days at 23°. The mixture was then stirred into ice water, filtered, and the acetates stirred in ice water for some hours. After filtering off, washing, and drying to constant weight, 1.945 gms. of pure raw acetate was obtained. This was twice digested with cold alcohol, residue dissolved in chloroform, filtrate concentrated and treated with hot methyl alcohol. There crystallized out 0.62 gm. cellobiose octoacetate, m. pt. 220-222°, or 44.7% yield on theory.

In the acetolysis of methylcellulose, 1.723 gms. (9.12% methoxyl) were acetolyzed with 6.5 cc. each acetic acid and anhydride and 0.7 cc. sulfuric acid for 12 days, thermostatically controlled at 25°. The product was purified as above outlined, 1.42 gms. (82.4%) of acetate being obtained, and this was digested with 10 times their amount of cold methanol for 20 min. The undissolved material was filtered off, residue washed with cold methanol, then dissolved in chloroform and concentrated, finally treating with hot methyl alcohol. Upon cooling, cellobiose octoacetate crystallized out, m. pt. 218-220°, yield 45% of theory.

Decrease of methoxyl content during acetolysis was demonstrated by acetolyzing 1.389 gms. methylcellulose (7.20% methoxyl) with 5 cc. each acetic acid and anhydride and 0.5 cc. sulfuric acid for 23 days at 23°, the deep red solution being worked up as above. Found 2.44% methoxyl, 50.2% acetyl. When this crude acetate was acetolyzed again as above there was obtained 1.71% methoxyl.

2. W. Haworth, E. Hirst and H. Thomas, Nature, 1930, **126**, 438; abst. C. A. 1931, **25**, 203; J. S. C. I. 1930, **49**, 1415-A.

3. *Ibid.* J. C. S. 1931, **134**, 821; abst. C. A. 1931, **25**, 3828; J. S. C. I. 1931, **50**, 941-A.

(15%), heptamethyl-*b*-methylcellobioside, b. pt. 208-220° at 0.02 mm. pressure, m. pt. 117-118°, mol. wt. 620 in camphor, and hydrolyzed to a mixture of tetramethylglucopyranose and 2.3.6-trimethylglucopyranose. From the residue is obtained a methylated cellodextrin, m. pt. 151-152°, mol. wt. 855 in camphor, not methylated by silver oxide and methyl iodide, but yielding on acetolysis and methylation, tetramethyl methylglucopyranoside (30%) and heptamethyl-*b*-methylcellobioside (25%).

Methylcellulose and X-Ray. Studies of methylcellulose with X-ray have shown the properties of the cellulose micelle reacting as a permutoid with great energy. Nearly all cellulose derivatives may be prepared from normal cellulose without losing the fiber structure of the original cellulose if the product has not passed into solution, and it has often been found in operating under suitable conditions, that the fiber period of the original cellulose is substantially conserved, even in the derivative, especially the cellulose ethers. From investigations of polymorphism phenomena, it is evident that substituted micelles of cellulose are capable of existence in an extraordinarily large number of possible lattice types, in many instances admitting of a definite explanation of the numerous physical and chemical properties of these derivatives.

X-ray diagrams of cellulose, cellulose esters and cellulose ethers, even with but the comparatively fragmentary indexing now existing in many instances, are yet sufficiently comprehensive to allow of certain definite qualitative statements to be made, which undoubtedly will become quantitative with further study. As an illustration, J. Trillat[1], from a study of the position of the interferences and the blackening of the X-ray diagram of acetylcellulose, has made

1. Rev. gen. Colloides, 1928, **6**, 57; abst. C. A. 1928, **22**, 4244; 1929, **23**, 971. Rev. gen. Colloides, 1928, **6**, 177; abst. Pulp & Paper Mag. 1929, July 25, p. 151. 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.

deductions as to the commercial applicability of this ester of great interest.

R. Herzog and B. Lange[1], working with methylcellulose prepared by the method of H. Urban[2], and in which the methylcellulose obtained gave highly viscous clear solutions with chloroform and tetrachlorethane but was insoluble in water, alcohol, ether and pyridine, have studied the influence of concentration, temperature and solvent upon the state of dispersion of cellulose derivatives, using chloroform and tetrachlorethane as solvents. The methyl ether was dissolved at 12.5°, allowed to stand until equilibrium had been established (until the polarization angle no longer showed any marked variation with time), sealed in glass cylinders in order to avoid changes in concentration and to exclude any possible atmospheric action, warmed to 40° and kept in a thermostat. The depolarization of the solutions was then measured, the results obtained being shown in the four diagrams in Fig. 4.

It was found that the depolarization itself is dependent of concentration, so that a decrease of the depolymerization angle may be due to concentration change. The decrease of particle size by "dissociation" took place so slowly that in the first 15 min. after dilution, no change was observable. It will be noted from the results that variation of depolarization with time does not begin before about 15 min., and that the initial values of depolarization of the concentrated and dilute solutions are but little different, being already in the range where the depolarization is almost independent of concentration.

It has been shown by K. Hess and C. Trogus[3] that attempts to interpret X-ray diagrams of cellulose on the basis of a cellobiose unit are of doubtful value. They have produced diagrams of trimethylcellulose and a number of other

1. Proc. World Eng. Cong., Tokyo, 1931, **31**, 501; abst. C. A. 1931, **25**, 5554; J. S. C. I. 1931, **50**, 1087-B.
2. Cellulosechemie 1926, **7**, 73; abst. C. A. 1926, **20**, 3080.
3. Ber. 1928, **61B**, 1982; abst. C. A. 1929, **23**, 5315; J. S. C. I. 1928, **47**, 1225-A; Chem. Zentr. 1929, I, 46.

cellulose derivatives in the original communication. The diagram of methylcellulose shows a maximal intensity, the identity period of which differs within narrow limits in individual samples. This intensity corresponds with net-place distance of about 4.5 A. The relatively indistinct interferences of cellulose, its esters and ethers may be at-

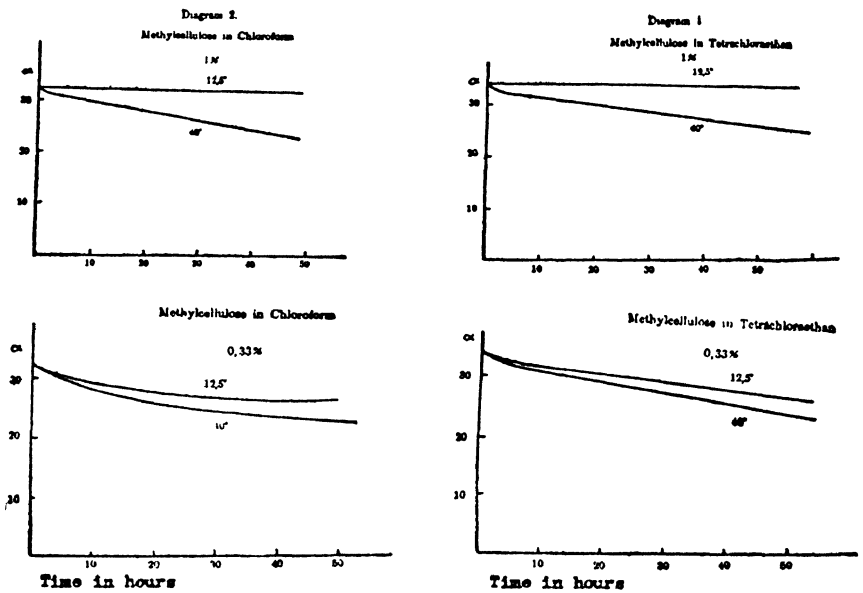


Fig. 4. Depolarization of Methylcellulose.

tributed to an arrangement of masses of a glucosan-like complex, held together by what is known as directed associative forces. According to H. Mark and G. v. Susich[1], X-ray examination of methylcellulose has shown that Hess and Trogus' deduction of the values 21.3 and 25.6 A. for two of the periods of identity of the elementary cell rests on a mis-interpretation of the X-ray diagram, the most probable value being 10.1-10.5 A. for the period of identity along the axis of the fiber.

1. Z. physikal. Chem. 1930, **9B**, 157; abst. C. A. 1930, **24**, 5480; J. S. C. I. 1930, **49**, 1098-A.

Table V. Translation Lattice for Methylcellulose

Point	*d* in Å		Index	Intensity	Remarks	Identical Interference Points
	Found	Calculated				
A_0	25.6	25.6	010	nedium strong	focusing	1
A_1	21.3	21.3	100	medium strong	diagram	1
A_2	12.8	12.8	020	strong		1
A_3	11.5-9.03	10.91-9.29	120;210;110	very strong	.....	4
A_4	8.5	8.52	030	medium strong	indistinct	1(?)
A_5	7.1	7.04	300	weak	.....	1
A_5	5.2	5.16-5.12	410;050	weak	.....	2
A_6	4.88-4.02	4.73-4.01	340;250;430;060;160;510;350;440;520	very strong	.....	9
A_8	3.48	3.48-3.52	540;600;610	weak	.....	3
A_9	3.28	3.26-3.31	460;630;550	weak	.....	3
A_{10}	2.28-2.21	2.27-2.20	2,11,0;930;860;690;3,11,0;940	weak	.....	6
A_{11}	2.03	2.04-2.01	880;5,11,0;10,4,0	very weak	indistinct	....
I_0	present, but indistinct			weak	.....	(?)
I_1	5.92	5.97-5.82	301;311	medium-strong	.....	2
I_2	4.88	4.92-4.71	241;331;401;411	medium-strong	.....	4
I_3	4.1-3.9	4.17-3.89	431;061;501;511	strong	.....	4
I_4	3.47	3.47-3.49	451;071;361	medium strong	.....	3
I_5	3.08	3.05-3.13	181;551;631;371	strong	.....	4
I_6	2.80	2 84-2.76	721;381;651;731;091	strong	.....	5
I_7	2.67	2.69-2.64	571;291;741;481;661	strong	.....	5
II_0	5.65	5.65	002	medium strong	.....	1
II_1	5 06	4 89-5.18	022;212;202;122	medium strong		3
II_2	4 32	4 34-4 29	232;312	very strong	.....	2
II_3	3.59-3.37	3.64-3.34	342;252;432;062;502;162;512;352	strong	.....	8
II_4	3.08	3 08-3.04	452;702,362;172	medium strong	.....	4
II_5	2.80	2 82-2.76	552;632;372;082;182;	weak	.....	5
II_6	2 54	2.54	732,092	very weak	.....	2-6(?)
II_7	2.12	2 14-2.10	1,11,2;922;2,11,2;932	very weak	.....	4
III_0	3.70	3.78	003	very weak	.....	1
III_1	3 74-3.35	3.73-3.32	013;103;113;023;123;203;213;033;223;133,303	very strong		11
III_2	2 88-2.64	2.89-2.63	433;063;503;163;513;353;443;523;263;533;073,453	medium strong	.....	12
III_3	2.22	2.27-2.21	733;093;193;293;483;573;743	weak	indistinct	7
IV_0	2.84	2 84	004	weak	.....	1
IV_1	2 74-2.55	2.74-2.57	124;204;214;034;134;304;314;234;044;324;144	weak		11
IV_2	2.34-2.24	2.34-2.22	164;354;514;524;534;454;074;364;174	weak	.....	9
V_0	present, but indistinct					
V_1	1.88-1.82	not calculated				

In a further study, C. Trogus and K. Hess[1] used two forms of trimethylcellulose, one preserving the natural fiber

1. Z. physikal. Chem. 1929, **5**B, 161; abst. J. S. C. I. 1929, **48**, 1222-A. See also C. Trogus and K. Hess, Z. physikal. Chem.

structure of ramie, and the other corresponding with the mercerized fiber. The diagrams of both agree with *a* 21.3, *b* 25.6 and *c* 11.3 A., the diagonal helical axis being lacking in both. Within the limitations of technique, the diagram to be expected from the net plane distances is experimentally corroborated. Details of the results obtained are shown in Table V.

K. Freudenberg[1] has shown that trimethylglucose anhydride shows no tendency to polymerize to trimethylcellulose.

Distillation of Methylcellulose. J. Reilly[2] has distilled methylcellulose under pressure ranging from 0.5-18 mm., and obtained about 50% of product which is apparently a methylated glucosan containing approximately the same methoxyl content as the methylcellulose distilled. In addition, water and gases are formed, there being obtained 43.4% CO_2, 28.9% CO, 0.15% oxygen, 3.1% unsaturated hydrocarbons and 23.2% methane[3].

1929, **4**B, 321; abst. C. A. 1930, **24**, 2287; J. S. C. I. 1929, **48**, 1222-A; Chem. Zentr. 1929, II, 1912. Ber. 1928, **61**B, 1982. Zts. physikal. Chem. 1930, **9**B, 160; abst. C. A. 1930, **24**, 4929; J. S. C. I. 1930, **49**, 1098-A.

1. Annalen, 1928, **461**, 130; abst. J. S. C. I. 1928, **47**, 743-A; C. A. 1928, **22**, 3292.

2. Helv. Chim. Acta, 1921, **4**, 616; abst. C. A. 1921, **15**, 3464; Bull. Soc. Chim. 1922, **32**, 616; J. C. S. 1921, **120**, i, 545; Chem. Zentr. 1921, III, 946.

3. He prepared four methylcelluloses containing 23.6-44.6% methoxyl, the latter being almost pure trimethylcellulose. He prepared methylated celluloses of 25.3% (A), 28.1% (B), 33.4% (C) and 43.7% methoxyl (sample D) and dry distilled each under reduced pressure. Two distillates of each were collected, one at 60°, the second below zero. 26 gms. A distilled 0.5 hr. at 10-15 mm. pressure yielded 51% of a paste (60°), 32% of liquid below 0°, 7% residue, 10% volatile. The paste was soluble in water and in ethyl alcohol and had 24.3% methoxyl. Hydrolyzed by dilute sulfuric acid it reduced Fehling's solution, gave a deep red osazone, and had 19.4% methoxyl. When 25 gms. of B were distilled at 10-15 mm., it yielded 51.2% of paste, 32.5% liquid, 9.4% residue and 6.9% volatile. When the first paste fraction was redistilled at 10 mm., and 4 fractions collected, the distillate with maximum methoxyl was 32.3% corresponding to dimethyllevoglucosan. This hydrolyzed in 1% sulfuric acid, neutralized and evaporated *in vacuo*, yielded a hard, friable mass, corresponding by analysis to dimethylglucose.

Manufacture of Methylcellulose. Under the topic "Manufacture of Alkylcellulose" (see p. 1416) are given methods for alternatively producing methyl- or ethyl-celluloses of varying physical constants, especially in relation to solvent values. Perhaps the mildest method of methylating carbohydrates is by the use of diazomethane, but the methylation is carried only to the lower ethers[1], M. Nierenstein[2] having obtained from cotton cellulose a methylated product of 1.5-4.2% methoxyl. Amino acids, their hydrochlorides or esters are not methylated by the action of diazomethane in ether solution, being recovered unchanged[3].

Treatment of cellulose *B* with nitroso-methylurethane in methyl alcohol affords a monomethylcellulose[4], insoluble in organic solvents, which swells in NaOH solution. Similar treatment of cellulose gives products containing 0.75-0.87% methoxyl. Hydrolysis of the methylated cellulose, first with 75% sulfuric acid at the ordinary temperature and then with hot 8% sulfuric acid, gives dextrose and 2-methylglucose. This last compound is also obtained by hydrolysis of 3.4.6-triacetyl-2-methylmethylglucoside, obtained by the methylation of 1-chlor-3.4.6-triacetylglucose with 10% HCl.

T. Lieser[5] has described the preparation of monomethyldicellulose, cotton being first converted into cellulose xanthate, and purified with methyl alcohol. Immediately after purification, it is suspended in cold absolute methyl alcohol, and with stirring, nitrosomethylurethane in methyl alcohol is added drop-by-drop. Diazomethane is at once formed. Under constant cooling and stirring, the reaction

1. L. Schmid, Ber. 1925, **58**, 1963; abst. C. A. 1926, **20**, 743; Chem. Zentr. 1926, I, 890.
2. Ber. 1925, **58B**, 2615; abst. C. A. 1926, **20**, 1390; J. S. C. I. 1926, **45**, 154-A; Chem. Zentr. 1926, I, 2195.
3. A. Geake and M. Nierenstein, Zts. physiol. Chem. 1914, **92**, 149; abst. C. A. 1914, **8**, 3563; J. C. S. 1914, **106**, i, 1146.
4. T. Lieser, Ann. 1928, **464**, 43; abst. C. A. 1928, **22**, 4792; J. S. C. I. 1928, **47**, 742-B.
5. Ann. 1929, **470**, 104; abst. C. A. 1929, **23**, 3672; J. S. C. I. 1929, **48**, 799-A.

is allowed to proceed for 5 hrs., the product filtered, mercaptans washed out with alcohol, then with water. Methoxyl 9.13% as against theory 9.18%. Monomethyldicellulose is colorless, of the appearance of cotton cellulose, swells in caustic soda but without dissolving and is water-insoluble.

If one part monomethyl-dicellulose is hydrolyzed by stirring with 3-4 parts 75% sulfuric acid and left at room temperature for 20 hrs., then diluted with water to an 8% acidity, and boiled 2 hrs. under reflux, a monomethylglucose (13.92% methoxyl) results.

Ethylcellulose. The chemical deportment of triethylcellulose is closely related to that of trimethylcellulose. Both form crystalline compounds, both may be alkylated to substantially the tri-alkyl stage. In glacial acetic acid solutions triethylcellulose shows dissociation and association phenomena entirely analogous to the trimethylated celluloses, so that the glucosan character shown in all other cellulose derivatives holds true for the triethyl ethers. By means of HCl in methyl or ethyl alcohol, triethylcellulose may be substantially quantitatively resolved into the corresponding glucosides, that from triethylcellulose yielding triethylglucose, probably a 2.3.6-derivative, similar to the 2.3.6-trimethylglucose from trimethylcellulose.

Notwithstanding the fact that triethylcellulose like the corresponding trimethyl derivative may be obtained in crystalline condition, elastic films are obtained therefrom upon rapid evaporation—a phenomenon of peculiar interest that such crystallizable preparations should leave coherent films upon evaporation. In contrast to trimethylcellulose, triethylcellulose is insoluble in hot or cold water and readily goes into solution in chloroform, benzene, toluene, xylene, acetic anhydride, glacial acetic acid, dioxane, ethyl benzoate, ligroin and petroleum ether,—the latter two more readily when an equal volume of ethyl alcohol is present.

According to S. Uschakov and I. Schneer[1], the optimum conditions for the formation of ethylcellulose are the employment of 6 mols. ethyl chloride to 1 of cellulose, heating of the mixture for 18 hrs. at 120-130°, and mercerization with 50% NaOH solution. The degree of ethylation increases as the water content of the cellulose decreases, but too highly ethylated compounds have undesirable properties. Increasing the amount of ethyl chloride used and decreasing the water content give a lower viscosity in the final product. The viscosity also decreases from 20 to 5 when the amount of ethyl chloride is raised from 6 to 35 mols., while treatment of the finished material with water or ammoniacal ethyl alcohol under pressure does not cause an appreciable diminution in viscosity. Ethylcellulose is of maximum resistance to dilute sulfuric acid, ammonia and water when the ethoxyl content is about 45%.

E. Berl and H. Schupp[2] have made an elaborate study and comparison of methyl- and ethyl-cellulose, and from their work the following generalizations may be drawn:

1. As to the influence of time upon the degree of ethylation, the ethoxyl content rises to its nearly attainable maximum—according to the reaction conditions—after a short time, without perceptibly increasing later, it being difficult to reach the complete ethylation stage represented by a triethylcellulose.

2. The less the amount of cellulose caused to react upon a definite constant amount of ethyl chloride while the other reaction conditions remain the same, the higher the alkylation degree of the isolated products. By employment of the mol. proportion cellulose to ethyl chloride = 1:48, the ethoxyl content rises to the triethyl stage.

3. At higher temperatures, higher ethoxyl values are obtained than at lower temperatures, other constants being the same.

1. Plast. Massi, 1931, **1**, 17; abst. C. A. 1932, **26**, 3373; J. S. C. I. 1932, **51**, 370-A.
2. Cellulosechemie, 1929, **10**, 41; abst. C. A. 1929, **23**, 4816.

4. The etherification of the hydroxyl groups in cellulose upon the alkylation degree is dependent upon the concentration of the lye.

5. The indifference of ethylcellulose to Fehling's solution indicates that a formation of aldehydic groups does not occur by the alkylation procedure.

6. When etherifying at comparatively low temperatures (60-80°) ethyl products are obtained which dissolve only partially in alcohol. Increase in temperature and alkali concentrations gradually reduces the proportion of alcohol-insoluble ethylcellulose. Soluble ethylcelluloses with more than 2.5 ethoxyl groups are completely soluble in alcohol, pyridine and ether, easily soluble in chlorinated hydrocarbons as chloroform and dichlorethylene, and in benzene, toluene and xylene.

7. In further ethylation of water-soluble ethylcelluloses, the water solubility gradually diminishes as also does it in Schweitzer's solution, and a ready solubility in a wide range of organic solvents appears.

8. Depolymerization of diethylcellulose by acetolysis is possible without the splitting off of ethyl groups.

9. Heating of diethylcellulose for hours with 15, 30 and 60% NaOH solution has no effect on the ethoxyl content.

10. There is a strong diminution in viscosity of solutions of ethylcellulose upon repeated alkylation, the degrading influence of the alkylating agent coupled with increase in alkyl content causes simultaneous progressive splitting of the cellulose complex, which expresses itself in materially increased friction of the solutions. The inner friction of cellulose ethers from unchanged cellulose is extraordinarily greater than that of the ether prepared under the same experimental conditions, and from cellulose degradation products of the same alkyl content—a proof that the preliminary treatment of cellulose with acids is combined with a degradation of the highly complex cellulose aggregate.

11. Aqueous, alcoholic and chloroformic solutions of alkylcellulose showed not the slightest rotation of polarized light.

12. The solubility of ethylcelluloses of varying ethoxyl content in named solvents is very enlightening. With water, the ether of 26.955 ethoxyl was soluble, 46.42% ethoxyl, insoluble in hot or cold water. With pyridine, soluble with all. Alcohol, 26.95% insoluble, 46.42% difficultly soluble, 47.23% soluble, 50.67% insoluble. Chloroform, dichlorethylene, benzene. 26.95% all insoluble, the others all soluble.

13. Maximum of ethylation of dimethylcellulose is 2-methyl-0.5-ethylcellulose which is soluble in benzene, chloroform, dichlorethylene and glacial acetic acid, but insoluble in alcohol, ether, acetone or pyridine.

14. As to the stability of ethylcellulose with alkalis, an ether of 42.2% ethoxyl was heated 4 hrs. with 15%, 30% and 60% NaOH solution, the ethoxyl after this treatment being 42.35, 42.98, and 42.03% respectively.

According to C. Dreyfus and G. Miles[1] flexibility of the cellulose ethers, especially ethylcellulose, may be materially augmented by the addition of zinc chloride. It is recommended to prepare a solution of ethylcellulose suitable for film manufacture, using as a solvent equal parts of ethyl alcohol and acetone, to which is added from 2-10% of zinc chloride (based on the weight of ethylcellulose), and cast the film from this solution. H. Hopkins and J. Segur[2] reduce the viscosity of ethylcellulose by adding gasolene thereto. They take an ethylcellulose soluble in butyl alcohol but not soluble in gasolene and prepare an 8% solution in butyl alcohol, the solution having a viscosity of 2.75 poises. 50% gasolene based on the butyl alcohol is then added, and it is found that the viscosity has been reduced to 1.44 poises. However, in preparing a solution of ethylcellulose containing butyl alcohol and benzine in the pro-

1. U. S. P. 1611169; abst. C. A. 1927, **21**, 496.
2. U. S. P. 1855744; abst. Plastics, 1932, **8**, #7, 292.

portions of ethylcellulose 8, butyl alcohol 33 and benzine 67, it is found that the alcohol and benzine have combined solvent power in excess of the sum of the separate solvent powers.

The water sensitivity of cellulose ethers has been studied by E. Doerr[1], who reports that the sensitivity decreases from complete solubility to very slight absorption of water with increasing molecular weight of the alcohol radical, and with increasing saturation of the cellulose hydroxyl groups. The sensitivity of the insoluble ethers is conveniently measured by the increase in length of a strip when immersed in water. According to A. Mentzel[2], structural parts of electrolytic cells are made of cellulose ethers as ethylcellulose, mixed, if desired, with alkali-resistant materials such as asbestos or meal. C. Stark[3] has reviewed the issued patents dealing with ethylcellulose.

Crystalline Triethylcellulose. In 1927 K. Hess and A. Mueller[4] reported the synthesis of crystallized ethylcellulose, having many of the properties of methylcellulose crystals, and obtained by the ethylation of cellulose A, regenerated cellulose from viscose and the cellulose obtained from copperammonium rayon. Samples obtained from these three sources all sintered at 230-240° and melted at 240-255°. The yields were 73, 64 and 84% respectively on theory. Slowly crystallized from 0.2% solution in benzene it separates in fine needles, but if separation is too rapid an amorphous powder or elastic film is obtained, which, however, may be redissolved in benzene, and crystals obtained from the evaporation therefrom. Unlike trimethylcellulose[5], crystalline triethylcellulose is insoluble in water. By the cooling of hot solutions in amyl acetate, *cyclo*hexanone and other solvents, it separates in a gelatinous form. The crystals which are quite difficult to obtain,

1. Cellulosechemie, 1932, **13**, 85; abst. J.S.C.I. 1932, **51**, 637-B.
2. E. P. 372451; abst. J. S. C. I. 1932, **51**, 732-B.
3. Kunstoffe, 1932, **22**, 107; abst. C. A. 1932, **26**, 4170.
4. Ann. 1927, **455**, 205; abst. C. A. 1927, **21**, 2982.
5. K. Hess and H. Pichlmayr, Ann. 1926, **450**, 29.

are plainly visible to the unaided eye, and which as a result of their anistropy lift off particularly well in the polarization microscope.

If the ethylcellulose is rapidly precipitated out of a solution as from glacial acetic acid, with water or alcohol, or from pyridine, nitrobenzene or tetralin with alcohol, it appears in white flocks, which under the polarization microscope are recognizable only as individual clumps of minute, double-refracting granules. Like trimethylcellulose, crystalline triethylcellulose is precipitable from hot triacetin solutions as a jelly-like mass. If a sufficiently concentrated solution in chloroform is quickly evaporated, there at first remains behind a syrup, which on complete evaporation of solvent forms an elastic film, which is not as elastic as those made from lower ethylated celluloses, although hardly breaking on bending. It appears remarkable that films made from such a crystallizable preparation should admit of forming a film coherent under the conditions of formation.

The specific rotation of triethylcellulose as compared with trimethylcellulose is shown as follows:

Table VI. Rotation of Trimethyl and Triethyl-cellulose.

Solvent	Trimethylcellulose		Triethylcellulose
Benzene	$(a)_D^{20}$	—18.5	+26.1
Pyridine		— 5.1	+49.1
Chloroform		— 4.3	+24.4
Glacial Acetic acid		— 9.8	+11.5
Water	$(a)_D^{0}$	—18.4	.....

An especial peculiarity of triethylcellulose in contrast with the corresponding methyl ether, is the relatively high *positive* rotatory powers, those of trimethylcellulose being *negative*. Crude triethylcellulose crystals may be purified by dissolving the preparation after vacuum drying, in 10 times their weight of glacial acetic acid, filtering, diluting with an equal volume of methyl alcohol, and the

solution allowed to run into ice water in a thin stream while stirring. The separated white precipitate is filtered, washed with water and dried in a desiccator. If the crystals are not entirely white, solution with methyl alcohol for some hours removes the small amount of color so that the crystals upon evaporation become perfectly white. No change in rotatory power was observed during the various purification steps. By precipitation from glacial acetic acid solutions, the yield is lowered by about 10-15%.

Crystalline triethylcellulose is readily dissolvable in the cold in chloroform, benzene, toluene, xylene, glacial acetic acid, acetic anhydride, ethyl acetate, ethyl benzoate, dioxane, ligroin and petroleum ether. When warm, it dissolves in tetralin, aniline, glycerol, benzyl alcohol, *cyclo*hexanone, amyl acetate and triacetin. It is insoluble in hot or cold water as well as cold or warm methyl alcohol, ethyl alcohol or acetone. The triethylcellulose from cellulose A and from copperammonium cellulose dissolves on digestion while warm in ether, but the triethylcellulose from viscose is not taken up by ether. If, however, it is dissolved in tetralin with warming and again precipitated with cold methyl alcohol, and dried, it then dissolves smoothly and readily as with the other two preparations.

In a subsequent communication[1] crystalline triethylcellulose was prepared from cotton by direct ethylation, the properties agreeing with the crystalline ether previously prepared, and through hydrolytic splitting gave triethylethylglucoside in 94% yield of the theoretical, and by hydrolysis of this, a 2.3.6-triethylglucose (?) was obtained. Best crystals are obtainable from evaporation of 0.2-0.5% strength in benzene-alcohol (2:1), the proportion to be kept exact. If the solution is allowed to evaporate slowly from a flat bottom dish protected against atmospheric moisture, the ethylcellulose separates on the walls of the vessel in

1. K. Hess and A. Mueller, Ann. 1928, **466**, 94; abst. C. A. 1929, **23**, 1118; J. S. C. I. 1928, **47**, 1360-A; Chem. Zentr. 1929, I, 235.

very fine needles arranged in the form of rays, which are strongly refractive.

Propylcellulose. O. Leuchs in 1917, first proposed the use of propylcellulose in the arts[1], his varnish comprising this ether dissolved in benzene, the method of preparation being to heat alkalicellulose with benzene 9 and propyl bromide 11 with stirring in a closed vessel for 60-80 hrs. at 100°, a solution of propylcellulose being formed which is filtered from undissolved particles, precipitated by water and dried. The propyl ether is an amorphous, solid substance, soluble in benzene, or a mixture of benzene, alcohol and chloroform.

G. Young[2] has described propyl-, butyl- and amyl-cellulose which differ from that of O. Leuchs in being insoluble in methyl or ethyl alcohol or benzine. Depending upon whether *n*-propyl chloride or *iso*-propyl chloride is used as alkylating agent, *n*-propylcellulose or *iso*-propylcellulose results. An intimate mixture of 2 parts cellulose, 2-3 of NaOH and 1.5 of water (equivalent to 40% NaOH solution), is allowed to react together and an excess of propyl chloride added, preferably in the ratio of 20 mol. wt. of chloride to 1 mol. wt. of cellulose, excess of alkyl chloride being eventually recovered by distillation. The etherification is carried out in one stage in an autoclave at not exceeding 130°, the reacting materials being stirred meanwhile. The propyl ether obtained is washed with water, purified by solution in glacial acetic acid, with subsequent precipitation in water, filtering and drying. If a mixture of the isomeric propyl chlorides is used in stoichiometrical or other ratio quantities, a *n*-propyl-*iso*-propylcellulose results. By employing a mixture of methyl, ethyl, propyl,

1. U. S. Serial No. 185198, filed Aug. 8, 1917; official letter Aug. 28, 1917; L. Lilienfeld, E. P. 12854, 1912, and 6035, 1913, cited against applicant. Nine claims.

2. U. S. P. 1504178; abst. C. A. 1924, **18**, 3272; J. S. C. I. 1924, **43**, 743-B; Chem. Zentr. 1925, I, 2050. E. P. 184825; abst. C. A. 1923, **17**, 878; J. S. C. I. 1922, **41**, 854-A; 1924, **43**, 743-B; Chem. Zentr. 1923, II, 591; Kunst. 1923, **13**, 56; Chim. et Ind. 1923, **10**, 542. F. P. 555279; abst. Chem. Zentr. 1923, IV, 681.

butyl and amyl chlorides in the above process, mixed ethers as methylethyl-, methylpropyl-, methylbutyl-, methylamyl-, ethylpropyl-, ethylbutyl-, ethylamyl-, propylbutyl-, propylamyl, or butylamyl-cellulose are obtained. Young does not give specific physical constants of the ethers producible under his process.

Propylcellulose has been patented for use in an insulating composition[1], as celluloid substitute[2], for films and plastics[3]. *b*-Naphtholamyl ether[4], on account of its insolubility in water, high boiling point and stability to light, has been advocated as a plasticizer for propylcellulose.

Dihydroxypropylcellulose. Oxyalkyl- and hydroxyalkylcelluloses have been described by L. Lilienfeld[5], insoluble in water but dissolving in aqueous alkalis, being ethers in which one hydroxyhydrogen atom of cellulose is replaced by an oxyalkyl or hydroxyalkyl group, and readily obtained by the reaction between cellulose and a halo-hydrin, particularly a monohalo-hydrin of a poly-alcohol, in the presence of an alkali. Industrial indications are shown in the following five examples:

1. *Films.* 100 parts of a 1.2-dihydroxypropylcellulose insoluble in water but soluble in dilute alkalis (obtained by

1. Siemens-Schuckertwerke G. m. b. H., E. P. 157119; abst. C. A. 1921, **15**, 1954; Chem. Zentr. 1921, II, 784; Kunst. 1923, **13**, 8. This patent is an addition to E. P. 156527; abst. C. A. 1921, **15**, 1772. Swiss P. 97643; abst. Chem. Zentr. 1923, IV, 424; Kunst. 1924, **14**, 90.

2. E. P. 6387, 1913; 3370, 1914. F. P. 459972. D. R. P. 357707. Aust. P. 61055. Dan. P. 28835.

3. 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. 73001; abst. Kunst. 1917, **7**, 222. Aust. P. 62809, 1913; abst. Chem. Ztg. 1913, **37**, 1499. Hung. P. Appl. L-3294; abst. Chem. Ztg. 1913, **37**, 11. Ital. P. 173413, 183582.

4. E. Zuehl, E. P. 17948, 1900; abst. J. S. C. I. 1900, **19**, 954; 1901, **20**, 926. U. S. P. 700884, 1902; abst. J. A. C. S. 1902, **24**, 520; Mon. Sci. 1903, **59**, 6. E. P. 8945, 1909; abst. J. S. C. I. 1909, **28**, 1271.

5. U. S. P. 1722928; abst. C. A. 1929, **23**, 4572. E. P. 231808; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 913-B; Chem. Zentr. 1926, I, 274. Australia P. 5422, 13743.

acting upon cellulose with *a*-monochlorhydrin in the presence of alkali), or hydroxyethylcellulose (obtained as above only with ethylenechlorhydrin) are dissolved in 900-1200 of 5-8% NaOH with stirring, being afterwards coagulated by 10% sulfuric acid, or 25% strength acetic acid, or 30% strength ammonium chloride or 20% tannin, or 40% formaldehyde. The solidified film is thoroughly washed with water and dried. The flexibility may be augmented by treatment with a softener as glycerol.

2. *Artificial Filaments.* A solution as above is extruded through orifices, washed with water, and toughened if desired by immersion in formaldehyde solution. A mixture of equal volumes of viscose (containing 8-12% cellulose) and solution of 1.2-dihydroxypropylcellulose may be spun into filament form.

3. *Dressing for Textile Materials.* A woven fabric as cotton, is impregnated by spreading or padding, in a unitary or plurality of coatings, with a solution as above described. After the material has been dried and steamed if desired, it is introduced into a precipitating bath, then washed and dried. A softening agent as soap solution, Turkey-red oil or glycerol may be added, and pigments or starch incorporated. The finished textile when embossed, or glazed with fluted, riffled or engraved rollers produces a damask effect.

4. *Printing on Textiles.* 100 parts of propylcellulose solution are mixed with powdered mica 6-10, or lampblack 4, or zinc oxide 8-10, and printed on cotton fabric, which is dried, precipitated, washed and dried.

5. *Book Cloth.* A porous textile as calico is coated one or more times with the solution as above, until the fabric pores are completely filled. After calendaring, the fabric is passed through a precipitating bath, washed, dried and finally embossed (see p. 169, n. 1; 205, n. 4).

Butylcellulose. Amylcellulose. These two alkylated celluloses differ but little from propylcellulose (see previous topic), except decreased solubility in water, both hot and

cold, due to the larger magnitude of the substituent alkyl group. Their specific properties have been but little studied. The difficulty of reacting with alkyl halides with increasing weight of alkyl, has also detracted from technical interest in these two cellulose ethers.

E. Desparmet[1] prepared butylcellulose (?) by the action of butyl chloride upon cellulose in the presence of a base as pyridine, dimethylaniline or diethylaniline, and G. v. Frank and W. Caro[2] have described the formation of *iso*-amylcellulose oxalate. Butylcellulose has been proposed as an ingredient in insulating material[3], in combination with caoutchouc[4], and with methylhexalin and *p*-coumarone as an enamel[5]. The composition of G. Padgham[6] comprises plasticized nitrocellulose produced by mixing a solution of collodion and amyl stearate with one consisting of "Neutroleum" which is cyclohexyl acetate and 5% of a 1 to 1 mixture of butyl acetate and butylcellulose to which pale mineral oil is added. A butylstarch linoleate has been patented[7].

Valuable lacquer layers, films and plastic masses it is claimed may be formed by the addition to butylcellulose of certain nitrogen-containing bases which are non-volatile or volatile with difficulty, as the substituted guanidines. These include triphenylguanidine, the biguanidines, tetramethylthiouran disulfide, *b*-naphthylbiguanid, benzylaniline,

1. F. P. 664932; abst. C. A. 1930, **24**, 961.
2. Ber. 1930, **63B**, 1532; abst. C. A. 1930, **24**, 4270; British Plastics, 1930, **2**, #17, 229.
3. Siemens-Schuckertwerke G. m. b. H., E. P. 157119; abst. C. A. 1921, **15**, 1954; Chem. Zentr. 1921, II, 784; Kunst. 1923, **13**, 8. This patent is an addition to E. P. 156527; abst. C. A. 1921, **15**, 1772. Swiss P. 97643; abst. Chem. Zentr. 1923, IV, 424; Kunst. 1924, **14**, 90.
4. D. R. P. 301088; H. v. Euler, abst. Wag. Jah. 1917, II, 252.
5. Swiss P. 97643; abst. Chem. Zentr. 1923, IV, 424; Kunst. 1924, **14**, 90.
6. E. P. 347597; abst. J. S. C. I. 1931, **50**, 672B. There is an error in L. Lederer, E. P. 19107, 1906, p. 2, line 14 from top, "butylcellulose" should be butyrylcellulose, i.e., cellulose butyrate.
7. I. G. Farbenindustrie, E. P. 334897; abst. Brit. Plastics, 1931, **2**, 317; J. S. C. I. 1930, **39**, 1146-B. F. P. 695323; abst. C. A. 1931, **25**, 2866.

dibenzylaniline, carbazol, *N*-ethylcarbazol and aminobenzoic acid esters[1]. The choice of bases to be used is that they shall form perfectly homogeneous masses with the particular cellulose ether used. It has been shown that these stability-prolonging compounds are efficacious, even in small amounts relative to the proportion of cellulose ether present. As an example, butylcellulose 7 is dissolved in a mixture of ethyl acetate and benzene each 11, toluene 5, xylene and alcohol each 10, ethylglycol 9, and 0.15-0.2 parts of *N*-ethylcarbazol. The lacquer layer or film produced from the above is said to be about five times as stable as the carbazol-free butylcellulose composition. For the manufacture of opaque butylcellulose lacquers, the above lacquer may be mixed with zinc oxide 10, organic pigment dyes, and 1-2% parts dibutyl phthalate.

Properties of the Alkylcelluloses. The outstanding properties of these cellulose ethers are their extreme permanency, neutrality, and ability to withstand alkaline and other hydrolytic treatments, being thus sharply differentiated in this respect from the cellulose esters, both those containing inorganic (cellulose nitrate) and organic (cellulose acetate) acid radicals. They withstand heating, whether water is present or not, and are resistant to *hot* liquids containing either alkalis or acids. Their permanency exceeds that of all simple and mixed cellulose esters, and all hitherto known conversion products and derivatives of cellulose.

Another distinguishing feature is their great resistance to chemical and physical influences, and the notable toughness, hardness and yet pliability of threads and films produced therefrom, and this resistance is accompanied by a ready and complete solubility in an almost unlimited number of solvents, solvent combinations, high boilers, softeners, plastifiers and extensibility-inducing bodies. Another important and valuable characteristic is their relative in-

1. I. G. Farbenind. E. P. 342288; abst. C. A. 1931, **25**, 4725; J. S. C. I. 1931, **50**, 404-B; Brit. Plastics, 1931, **3**, #26, 44. D. R. P. 538110.

combustibility and their low specific gravity. It follows that the multiplicity of solvents and especially inexpensive solvent mixtures (as alcohol and benzene or benzine) for the ethers of cellulose, permit of treating these ethers combined with an extraordinarily large number of flexilizing and colloiding media.

In general, the alkylcelluloses are white, amorphous powders or granular masses in which the interior of the granule is often hard, corneous and less opaque than the exterior, and which conform in their chemical behavior to the known organic alkyl ethers. On account of their comparative chemical inertness they are not saponified by water, but are decomposed by hydriodic acid with formation of alkyl iodide and regeneration of hydrated cellulose. Irradiation of methylcellulose and ethylcellulose in the solid form leads to the formation of a considerable quantity of insoluble matter with a diminution in viscosity of solutions prepared therefrom[1]. However, ultraviolet treatment does not materially reduce the viscosity of the solutions—a sharp differentiation in this respect from acetylcellulose and nitrocellulose liquid compositions.

Mechanical Properties of Alkylcellulose. The tearing strength and total stretching of cellulose ethers simple and mixed, as determined by M. Hagedorn and P. Moeller[2] is as follows:

Table VII. Tearing Strength and Total Stretching of Cellulose Ethers.

Cellulose Ether	Tearing Strength, kg. per sq. mm.	Total Stretching in %
Ethyl	5.5-6.5	25-30
Propyl	5.5-6.0	25-30
Butyl	3.0	27
Benzyl	5.0-6.0	25-30
Mixed Ethers:		
Ethyl-butyl	6.0-6.5	30
Ethyl-benzyl	6.0-6.5	12
Propyl-benzyl	5.0	18
Butyl-benzyl	4.5	28

1. L. Clement and C. Riviere, British Plastics, 1932, **3**, #34, 121.

1. Cellulosechem. 1931, **12**, 29; abst. J. S. C. I. 1931, **50**, 436-B; Brit. Plastics, 1931, **3**, #28, 180; Nitrocellulose, 1931, **2**, 39; C. A. 1931, **25**, 5982.

A method for augmenting the electric disruption strength resistance of cellulose ether film has been worked out by M. Ow-Eschingen[1] who finds that the dielectric character is increased by soaking the film with an oil of high disruptive strength as paraffin oil or transformer oil, the process being carried out *in vacuo*, and subsequently under a pressure above atmospheric.

In the preparation of dielectric films of cellulose ethers[2], it is recommended to superpose a cellulose ether film on a cellulose ester film before all the solvent has evaporated from either, so that they may be coalesced by pressure and heat, without the passage of any impurities from one film to another. It has also been found[3] that the electric charge of fibers of cellulose ethers, which is generated during their transformation into textiles, may be reduced by treating the fibers with mixtures of oils and fats, to which an oil-soluble organic base has been added.

Solubility of the Alkylcelluloses. The lower methylated celluloses are dissolvable in water, but with increase of alkyl in combination with cellulose, this water solubility by imperceptible gradations passes to an insolubility accompanied by a swelling effect, which in turn gives way to a straight insolubility in water as the percentage of alkyl increases in the cellulose aggregate. This statement is subject to considerable fluctuation depending primarily upon the nature and composition of the alkalicellulose etherified, the proportion of alkali to cellulose and to etherifiant, and the temperature and length of time of the etherifying operation. This solubility characteristic is somewhat analogous to the organic esters as cellulose acetate, where it will be remembered that continued partial hydration of an acetylcellulose insoluble in acetone but soluble in chloroform, gradually leads to an acetone soluble ester as acetic acid is progress-

1. E. P. 281663; abst. C. A. 1928, **22**, 3528; J. S. C. I. 1928, **47**, 824-B; Chem. Zentr. 1928, I, 1600.
2. E. Pfiffner, E. P. 267917; abst. C. A. 1928, **22**, 1237; Chem. Zentr. 1927, II, 521; Kunst. 1929, **19**, 112.
3. Aceta Ges., E. P. 346912; abst. Silk J. 1931, **8**, #88, 56.

ively saponified off, and if this hydration is allowed to extend beyond the stage of solubility in pure acetone which simultaneously is also the stage of plasticity in warm alcohol-free chloroform, a solubility in acetone containing gradually larger amounts of water is shown, until eventually a product is obtainable soluble in water with turbidity, which turbidity may be cleared up by continued hydration treatment. In both cellulose ethers and esters, a lower acyl or alkyl content shows a tendency to dissolve or swell in water.

Those less highly alkylated cellulose ethers which are dissolvable in cold water are usually insoluble in hot water, and there have been described cellulose ethers soluble in ice water, but precipitable in water at room temperature. There is no known corresponding analogue to this with the cellulose esters.

M. Hagedorn and P. Moeller[1] have critically investigated the solubility of the cellulose ethers in comparison with the solubility of the cellulose esters, both simple and mixed. The results obtained are embodied in Table VIII, and involve 208 separate determinations. It is to be noted that the cellulose ethers all have solubilities of a higher order than do the cellulose esters. The solubilities of the mixed ethers, while not the mean of the solubilities of a physical mixture of the individual ethers in stoichiometrical proportions, yet are of a very similar degree. However, there is this sharp differentiation to be borne in mind, and that is the effect of very small proportions of a higher alkyl or aralkyl when combined with a lower alkylcellulose as modifying the sensitivity of the lower alkyl to water, whether it be solubility, colloiding or merely an intumescing effect. The formation of a methylethylcellulose in which the ethoxyl is less than 2% exerts a marked effect on a methylcellulose as diminishing the effect of water thereon, and especially is this effect apparent in a methylbenzylcellulose in which

1. Cellulosechem. 1931, **12**, 29; abst. J. S. C. I. 1931, **50**, 436-B; Brit. Plastics, 1931, **3**, #28, 180; Nitrocellulose, 1931, **2**, 39; C. A. 1931, **25**, 5982.

Table VIII. Solubility of the Cellulose Ethers and Esters in Various Solvents.

	Water	Alcohol	Ether	Acetone	Ethyl Acetate	Benzine	Benzene	Chlor-hydrocarbons
Methylcellulose	only sol. cold	insol.	insol.	insol.	insol.	insol.	insol.	insol.
Ethylcellulose	swells easy	sol.	sol.	sol.	sol.	swells easy	sol.	sol.
Propylcellulose	swells easy	sol.	swells easy	swells	sol.	swells hot	sol. hot	sol.
Butylcellulose	swells easy	sol.	swells easy	swells	sol.	swells hot	sol. hot	sol.
Benzylcellulose	insol.	swells weakly	swells weakly	sol.	sol.	swells hot	sol.	sol.
Ethylbutylcellulose	swells easy	sol.	swells easy	swells easy	sol.	swells	sol.	sol.
Ethylbenzylcellulose	insol.	sol	swells weakly	swells weakly	swells easy	insol.	swells easy	sol.
Propylbenzylcellulose	insol.	swells weakly	swells easy	almost sol.	sol.	insol.	sol.	sol.
Butylbenzylcellulose	insol.	swells weakly	swells easy	almost sol.	sol.	insol.	sol.	sol.
Cellulose Esters								
Formate	swells easy	insol.	insol.	insol.	insol.	insol.	insol.	insol.
Acetate	insol.	insol.	insol.	swells easy	insol.	insol.	insol.	insol.
Propionate	insol.	insol.	insol.	sol. hot	sol. hot	insol.	insol.	sol.
Butyrate	insol.	swells easy	swells easy	sol.	sol.	insol.	sol.	sol.
Valerate	insol.	swells easy	swells hot	sol.	sol.	insol.	sol.	sol.
Capronate	insol.	insol.	sol.	sol.	sol.	swells easy	sol.	sol.
Pelargonate	insol.	insol.	swells by heat	sol. hot	sol.	insol.	sol.	sol.
Laurate	insol.	insol.	sol.	swells easy	sol.	sol. hot	sol.	sol.
Stearate	insol.	insol.	swells weakly	swells weakly	swells easy	swells	sol.	sol.
Naphthenate	insol.	swells weakly	sol.	swells	sol.	sol.	sol.	sol.
Acetoproprionate	insol.	insol.	insol.	sol.	sol.	insol.	insol.	sol.
Acetobutyrate	insol.	insol.	insol.	sol.	sol.	insol.	insol.	sol.
Acetolaurate	insol.	insol.	swells	sol. hot	sol.	swells weakly	sol. hot	sol.
Acetobutyrolaurate	insol.	insol.	swells weakly	sol.	sol.	insol.	sol.	sol.
Butyrolaurate	insol.	insol.	swells	sol.	sol.	insol.	sol.	sol.
Naphthenate-laurate	insol.	swells	sol.	swells	sol. hot	sol.	sol.	sol.
Naphthenate-oleate-laurate	insol.	swells	sol.	swells	sol. hot	sol.	sol.	sol.

the entering benzyl group is but about 1%. In both examples, the comparatively insignificant addition chemically of the ethyl or benzyl to the methylcellulose, exerts a retarding effect in the action of water thereon entirely out of proportion to the percentage of higher molecular size radical introduced.

In referring to Table VIII one observes the comparatively high water-sensitivity of the cellulose ethers, which in the case of the lower members shows the peculiarity of being soluble in cold water, and, analogous to many of the proteins, is coagulated through warming. However, this analogy is not strictly comparable in that the cellulose ethers precipitated by warming, may be filtered off and dissolved in other solvents, an impossibility with the coagulated proteins without decomposition. This property of differential solubility has been taken advantage of widely in the arts, as will appear in discussing the technical applications of the cellulose ethers in this work. It is to be remembered that the well-known number of cellulose ethers is less than that of the cellulose esters, but an entirely new field has been opened up and discussed under the topic Cellulose Ether-Esters, whereby combination of acid radical with a partially etherified cellulose leads to the production of an entire series of new bodies, whose solubilities and other physical constants have as yet, been imperfectly investigated, but which hold forth many interesting technical possibilities. One reason why this cellulose ether-ester field has not been more thoroughly explored up to the present time is undoubtedly the trouble involved in their preparation, as two opposite processes are involved and which must be combined, i.e., formation of the ethers in an *alkaline* medium, and of the esters under exclusion of alkali.

In order to increase the porosity and receptivity of the alkylcelluloses, especially for dyestuffs, certain salts in aqueous solution, as zinc chloride or calcium thiocyanate, or solvents as acetone, acetic acid, ethyl alcohol or chlorinated aliphatic hydrocarbons may be used, the solvent power of

which may be diminished or attenuated to any desired degree by the addition thereto of miscible cellulose ether non-solvents[1]. L. Lilienfeld[2] has described the formation of alkylcelluloses soluble in water below 16°, but insoluble at temperature above. The water-soluble methylcelluloses have been proposed for such uses as emulsions[3] and as a homogenizer for rubber pastes[4].

In order to lessen the effect of water on the cellulose ethers, the water-soluble alkylcelluloses may have added thereto a water-insoluble ethylcellulose, bakelite, latex, linseed oil or benzyl alcohol[5]. And it has been shown[6] that ethylcellulose insoluble or only slightly soluble in water at temperatures below 10°, but which swell up or dissolve in water at such temperatures, may be made by treating ethyl ethers soluble at 16° with ethyl sulfate and NaOH in such manner that the ratio of alkali to the water content of the reaction mixture is within the limits of 0.1-0.25, the importance of the process depending upon the fact that it avoids the necessity of using organic solvents. Likewise[7], the water solubility may be overcome by the addition of aldehydes during etherification, formaldehyde, acetaldehyde and benzaldehyde being suitable. Exemplification of the method is indicated in the following two examples:

1. 500 cc. 40% formaldehyde solution are treated with 20% NaOH solution, and brought to 95°. Into this is im-

1. British Celanese, Ltd., and W. Dickie, E. P. 351999; abst. J. S. C. I. 1931, **50**, 880-B. See also E. P. 348589.

2. D. R. P. 488781; abst. C. A. 1930, **24**, 2290.

3. Imperial Chemical Industries, Ltd., and M. Wyler, F. P. 683728; abst. Cellulose, 1930, **1**, 270.

4. I. G. Farbenindustrie, E. P. 305490; abst. C. A. 1929, **23**, 4848; J. S. C. I. 1930, **49**, 730-B; Chem. Zentr. 1929, I, 2929. F. P. 668907; abst. C. A. 1930, **24**, 1764.

5. *Ibid.* E. P. 252176; abst. C. A. 1927, **21**, 1548; J. S. C. I. 1928, **47**, 154-B; Chem. Zentr. 1927, I, 1091; Kunst. 1929, **19**, 90. F. P. 615876.

6. L. Lilienfeld, U. S. P. 1505043; abst. C. A. 1924, **18**, 3272; J. S. C. I. 1924, **43**, 784-B. E. P. 181395; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1923, **42**, 1126-A; Chem. Zentr. 1922, IV, 963. Aust. P. 101021. Can. P. 248229; abst. C. A. 1925, **19**, 3491. Can. P. 248230, 252955.

7. I. G. Farbenindustrie, D. R. P. 538686; abst. Chem. Zentr. 1932, I, 2914.

mersed methylcellulose for 0.5 hr., the reacting mixture allowed to drip off, then dried 2 hrs. at 70-100°. The strength of the methylcellulose is unchanged. The optical properties, resistance to temperature, and dissolving power in organic solvents are likewise not modified. The solubility power in water at 12° is lowered to 4%.

2. Ethylcellulose soluble in water at 10° is immersed in a mixture of acetaldehyde 10 and acetic anhdride 1, and allowed to remain 30 min. After washing and drying, the cellulose ether has become resistant to cold water.

If it is desired to produce an ethylcellulose insoluble in water at 16° or above, but swelling or dissolving in water below this temperature[1], an alkali-insoluble cellulose body is etherified under such conditions that there is present for one part by weight of cellulose, 0.6-3 parts NaOH, the amount of alkali always exceeding the weight of water present. Or[2], the ethylcellulose may be treated with nitric acid insufficient for esterification to increase the solubility. The ethyl alcohol solubility of an ethylcellulose may be raised by increasing the temperature of ethylation, otherwise proceeding in an identical manner. If ethylcellulose but partially soluble in alcohol is producible at 60-80° etherification temperature[3], the solubility may be made complete by merely raising the temperature to 100-120°.

N. Kocher has shown[4] that sensitivity of ethylcellulose to water may be decreased by treatment of the ether, preferably in film form, with water near the freezing point,

1. L. Lilienfeld, E. P. 181393; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1924, **43**, 51; Ann. Rep. S. C. I. 1924, **9**, 153; Caout. et Gutta. 1923, **20**, 11687; Faserstoffe, 1924, **6**, 20; Chem. Zentr. 1924, II, 963. Can. P. 220831; abst. C. A. 1922, **16**, 2989; Faserstoffe, 1922, **4**, 143.

2. C. Dreyfus and L. Lee, E. P. 319691; abst. C. A. 1930, **24**, 2599; Cellulose, 1930, **1**, 150; Silk J. and Rayon World, 1930, **6**, 68.

3. E. Berl and H. Schupp, Cellulosechemie, 1929, **10**, 41; abst. J. S. C. I. 1929, **48**, 278-B; C. A. 1929, **23**, 4816; Chem. Zentr. 1929, II, 3088.

4. U. S. P. 1437810; abst. C. A. 1923, **17**, 879; J. S. C. I. 1923, **42**, 91-A; Chem. Zentr. 1923, II, 1122.

and J. McBurney and E. Nollau[1] have pointed out that livering or jelling (incipient precipitation) of cellulose ethers in solution may be prevented by the addition thereto of 0.1-0.5% oxalic, phosphoric, malic, citric, tartaric, formic, acetic or boric acids. Solubility may also be augmented by treating the cellulose before etherification with hydrofluoric acid[2] (see topic "Pretreatment of Cellulose"). Glacial acetic acid and vitriol in small amounts when applied to ethylcellulose increase the solubility for volatile solvents and extend the range of bodies which exert a solvent action on the cellulose ether[3].

In a study of the aliphatic ketones as solvents, J. Park and H. Hofmann[4] report that ethylcellulose is soluble in acetone, methylethyl ketone, methylpropyl ketone, methylbutyl ketone and methylamyl ketone, but give no method of preparation or other distinguishing characteristics of the ethylcellulose used. An idea of the multiplicity of solvents in which an alkylcellulose will dissolve when produced according to a definitely outlined process is shown in the last paragraph on page 19.

A peculiar phenomenon is observable with the cellulose ethers which has no counterpart, insofar as aware, with the cellulose esters, either inorganic or organic, and that is the ability of an ether insoluble in two solvents, dissolving in a *mixture* of the solvents. As an example, ethylcelluloses are known which are insoluble in benzene alone or in ethyl alcohol. Their ethoxyl content ranges 42-45%. If a 10% ethylcellulose in suspension in benzene be added to a 10% suspension in ethyl alcohol, a transparent solution results, either at room temperature, or usually facilitated by warming. This ratio of benzene to alcohol is

1. E. P. 278696; abst. C. A. 1928, **22**, 2673; J. S. C. I. 1928, **47**, 866-B; Chem. Zentr. 1928, I, 989.
2. British Celanese, Ltd., E. P. 308348; abst. C. A. 1930, **24**, 239; J. S. C. I. 1930, **49**, 610-B; Chem. Zentr. 1929, II, 813.
3. I. G. Farbenindustrie, E. P. 277111; abst. C. A. 1928, **22**, 2464; J. S. C. I. 1927, **46**, 860-B; Plastics, 1928, **4**, 508; Chem. Zentr. 1928, I, 445.
4. I. E. C. 1932, **24**, 132.

50:50. Likewise there are known ethylcelluloses which are insoluble both in benzene or in alcohol, and which do not dissolve, or at least only partially in benzene-alcohol 50:50, but which pass into solution in the proportion 9:1. Other combinations are also known in which both methyl- and ethyl-cellulose exhibit this peculiar solvent propensity. A favorite (because relatively inexpensive) solvent combination is benzene, or toluene or xylene with ethyl alcohol 9:1, but the physical characteristics of the alkylcellulose must be known before deciding on the use of a particular aromatic hydrocarbon in conjunction with alcohol, on account of the variations in evaporative speed of the hydrocarbon. Benzene and alcohol boil at substantially the same temperature, whereas toluene, and especially xylene boil substantially higher, hence (say) in a xylene-alcohol mixture, increment of xylene increases as the solvent portion evaporates. No alkylcellulose of technical importance is soluble in aliphatic hydrocarbons alone. Treatment to reduce viscosity of an alkylcellulose usually increases both the solubility in a given solvent in which it may have been partially soluble, or induces solving effect in other liquids in which where before the viscosity-reducing treatment, the ether was insoluble.

Tendency to jellify in contact with finely divided metals as aluminum powder in bronzing liquids is much less with the alkylcellulose than with the cellulose ethers. Solubility may also be augmented in several instances, by passing ozone into a solvent holding a cellulose ether in suspension, but such ozonized solutions have a deficient stability[1], and are more prone to changes by light or ultra-violet treatment. The effect of stabilizers on solubility is discussed in Chapter XII.

The overwhelming complexity of direct and incipient solvent action recorded for the cellulose ethers, and the sometimes directly contradictory data published by investigators of unimpeachable integrity, makes definite, clear

1. C. Malm and A. Andersen, U. S. P. 1857562.

cut and logical generalizations and deductions well nigh impossible insofar as advancing a general scheme of solvent action, as will more clearly appear in Chapter XII, when dealing with the solvents individually, as homologues or isologues, by groups, or by their chemical constitution and physical constants. He who is able to formulate a lucid system explaining the heterogeneous solvent data now found in the technical and patent literature concerning the etherified celluloses, must be of super-astute intellectuality.

Plasticity of the Alkylcelluloses. The natural plasticity of ethyl- and methyl-cellulose is appreciably greater than with the cellulose acetates, although the property of heat moldability, usually accompanied by pressure, is seldom taken advantage of in the arts, in the absence of contributing products. The solubility of these ethers in vegetable oils as castor and olive finds no counterpart with the acetyl- or nitro-celluloses. The thermoplasticizing, flexibility-inducing and extensibility-contributing bodies suitable for incorporation with the cellulose ethers covers a much wider range than those brought forward as useful adjuncts to the acetated celluloses. Their classification, physical constants and selective adaptability in the presence or absence of volatile solvents and solvent combinations are taken up in Chapter XII. In general, the plasticizers may be used in amounts up to 100% by weight with methylated and ethylated cellulose, and it is noteworthy to remember that the majority of plasticizing bodies suitable for incorporation with the nitrocelluloses, are also applicable for admixture with the alkylcelluloses. The elasticity of plastic materials having a base of ethylcellulose, in general is increased by attaching thereto, or physically admixing therewith, a layer of the same or a different cellulose ether relatively poor in plastifiant.

Viscosity of Alkylcellulose. In general, the viscosity of solutions of cellulose ethers varies with the degree of modification of the cellulose used for etherification, an unmodified cellulose giving a higher viscosity, which is but

another way of stating that the viscosity varies directly with the degree of cellulose depolymerization[1]. However, there are a number of contributing factors involved in the depolymerization such as concentration of alkali to cellulose, time of ripening of alkalicellulose, and temperature and length of time of etherification. Likewise the viscosity is variable within wide limits depending upon whether and how much pressure was used in etherifying as is necessary when working with methyl chloride or ethyl chloride, both of which are gases at room temperature, or whether the etherification is conducted by methyl sulfate or ethyl sulfate as alkylants, both of which are liquid normally.

A given alkylcellulose in solution may be reduced in viscosity in several ways, as:

1. Treatment with neutral bodies, usually of a plastifying-inducing capacity as tricresyl phosphate, diethyl phthalate, dibutyl tartrate, chloroform, acetone or the aromatic hydrocarbons or alkyl-substituted hydrocarbons[2].

2. Heating the solution, preferably under pressure.

3. Bringing the ether in contact with dilute acids, the ether being either in the moist solid state or in solution, until the reduction in viscosity desired has been attained.

4. Treatment of the dry cellulose ether with an acid gas as hydrochloric acid and afterwards washing to neutrality[3]. Before washing, the etherized cellulose may be "seasoned" by exposure in the atmosphere or in the presence of an inert gas, until the viscosity reduction has been reduced to the point required.

5. The cellulose before etherification may be subjected to mechanical distintegration as by dry grinding or by wet beating[4].

1. L. Clement and C. Riviere, Rev. gen. Colloides, 1924, **2**, No. 3, 11; abst. C. A. 1924, **18**, 3714; Chem. Zentr. 1924, II, 24.

2. C. Dreyfus, F. P. 673029; abst. C. A. 1930, **24**, 2292; Kunst. 1931, **21**, 17. A. Wacker Ges. fur Elektrochemische Ind., E. P. 342391; abst. C. A. 1931, **25**, 5557; J. S. C. I. 1931, **50**, 388-B. A. Ascherl and W. Gruber, U. S. P. 1834040.

3. Imperial Chemical Industries, E. P. 313091.

4. P. Waentig, Text. Forsch., 1921, **3**, 154; abst. Chem. Zentr. 1922, II, 99; J. S. C. I. 1922, **41**, 409-A.

6. Exposure to ultra-violet light. Slow process and not very satisfactory.

7. Over-ripening of the alkalicellulose. Efficient but a dangerous procedure the tensile strength of filament or film made therefrom may be reduced as the result.

8. Ethyl alcohol in conjunction with 0.1% acetic acid, aided by light reduces viscosity of alkylcellulose solutions, and the acidity may afterwards be overcome in such a solution by titration to neutrality with ammonium hydroxide, the small amount of ammonium acetate introduced exerting apparently no effect.

9. Addition of water in relatively small amounts to some alkylcellulose solutions gradually reduces the viscosity[1].

10. P. Seel[2] lowers the viscosity characteristics of ethylcellulose by making a solution of faint acidity, and then incubating at 65° until the viscosity has dropped to the point desired.

Structure-viscosimetric measurements of cellulose derivatives have been made in organic solvents by Y. Nisizawa[3], using an overflow viscosimeter, and show that ethylcellulose in acetone, benzyl alcohol and mixtures of ethyl alcohol and ethyl ether exhibits structure viscosity, as a rule the structure viscosity increasing with the addition of a medium having a pronounced solvent power. The designation "structure-viscosity" has been suggested by W. Ostwald for the anomalous viscosities occurring in colloidal systems, and expressed by a sharp rise in viscosity with small flowing viscosities, the lower the viscosity or the smaller the pressure, the stronger being the connection between individual structural parts in the solution. The results obtained are shown in Tables IX and X.

1. H. Dreyfus, F. P. 683076; abst. C. A. 1930, **24**, 4632.
2. U. S. P. 1635013; abst. C. A. 1927, **21**, 2985; J. S. C. I. 1927, **46**, 774-B; Plastics, 1927, **3**, #11, 608; Chem. Zentr. 1927, II, 2025. See also U. S. P. 1548938, 1679903.
3. Kolloid Zts., 1931, **56**, 59; abst. J. S. C. I. 1931, **50**, 1008-A.

Table IX. Ethylcellulose Solution (Benzene 41 cc. + Alcohol 30 cc.)

	10% Solution Capillary #6				6.7% Solution Capillary #6			3.3% Solution Capillary #5			
	p	Δ_6'	η_5'	η_1'	p	Δ_1'	η_1'	p	Δ_{30}''	η_{30}''	η_1'
1	4770				4800			4830			
2	3770	1000	4,13	20,65	3830	970	4,35	3950	880	4,86	2,43
3	2945	825	4,03	20,15	3040	790	4,30	3190	760	4,64	2,32
4	2310	635	4,04	20,20	2415	625	4,28	2570	620	4,64	2,32
5	1804	506	4,01	20,05	1915	500	4,28	2070	500	4,65	2,33
6	1410	394	4,00	20,00	1520	395	4,28	1660	390	4,67	2,34
7	1100	310	4,00	20,00	1205	315	4,29	1340	320	4,66	2,33
8	859	241	3,99	19,95	959	246	4,27	1085	255	4,69	2,35
9	669	190	3,93	19,65	756	203	4,22	879	206	4,68	2,34
10	518	151	3,87	19,35	600	156	4,35	710	169	4,60	2,30
11	401	117	3,90	19,50	480	120	4,52	570	140	4,57	2,29
12	312	89	3,98	19,90	388	92	4,57	460	110	4,87	2,44
13	244	68	3,97	19,85	310	78	4,47	375	75	5,17	2,59
14	189	55	3,98	19,90	249	61	4,53	305	70	4,89	2,45
15	149	40	4,08	20,40	200	49	4,52	250	55	5,15	2,53
16	116	33	3,93	19,65	160	40	4,57	208	42	5,20	2,60
17	90	26	4,28	21,40	130	30	5,00	170	38	5,08	2,54
18	74	16	4,77	23,85	108	22	5,03	141	29	5,53	2,77
19	59	15	4,92	24,60	87	21	4,57	119	22	5,67	2,34
20	50	9	5,25	26,25	70	17	4,82	99	20	5,65	2,83
21	40	10			58	12	5,52	84	15	6,00	3,00
22					49	9	5,45	71	13	6,75	3,38
23					40	9	5,35	63	8	8,40	4,20
24					34	6		56	7	8,03	4,02
25								49	7	8,17	4,09
26								44	5	9,77	4,89
27								40	4		

Table X. Ethylcellulose Solution (Benzene 55 cc. + Alcohol 15 cc.)

	10% Solution Capillary #6				6.7% Solution Capillary #6			3.3% Solution Capillary #5			
	p	Δ_6'	η_5'	η_1'	p	Δ_1'	η_1'	p	Δ_{30}''	η_{30}''	η_1'
1	4700				4810			4650			
2	3890	810	5,20	15,60	3820	990	4,28	3670	980	4,24	2,12
3	3205	685	5,20	15,60	3020	800	4,25	2920	750	4,34	2,17
4	2660	545	5,35	16,05	2400	620	4,27	2320	600	4,37	2,19
5	2210	450	5,50	16,50	1900	500	4,27	1860	460	4,42	2,21
6	1855	355	5,75	17,25	1510	390	4,31	1480	380	4,39	2,20
7	1565	290	6,05	18,15	1200	310	4,33	1185	295	4,47	2,24
8	1338	227	6,42	19,26	956	244	4,36	950	235	4,47	2,24
9	1148	190	6,60	19,80	761	195	4,39	760	190	4,47	2,24
10	990	158	6,75	20,25	610	151	4,48	610	150	4,52	2,26
11	855	135	6,87	20,61	489	121	4,64	490	120	4,55	2,28
12	741	114	7,06	21,18	395	94	4,68	395	95	4,57	2,29
13	645	96	7,14	21,42	321	74	4,94	317	78	4,73	2,37
14	560	85	7,23	21,69	265	56	5,25	261	56	4,93	2,47
15	490	70	7,55	22,65	220	45	5,19	211	50	4,64	2,32
16	430	60	7,82	23,46	180	40	5,45	170	41	4,80	2,40
17	380	50	7,84	23,52	154	26	6,16	140	30	5,00	2,50
18	333	47	7,58	22,74	130	24	6,06	114	26	4,97	2,49
19	292	41	8,00	24,00	111	19	7,15	94	20	5,55	2,78
20	260	32	7,79	23,37	99	12	9,00	80	14	5,73	2,87
21	230	30	8,84	26,52	89	10	9,35	66	14	5,50	2,75
22	208	22	9,25	27,75	80	9	9,40	56	10	6,60	3,30
23	185	23	9,25	27,75	72	8		49	7		
24	168	17	9,87	29,61							
25	151	17	10,80	32,40							
26	140	11	13,30	39,90							
27	130	10	13,71	41,13							
28	121	9	16,15	48,45							
29	115	6	21,90	62,70							
30	110	5									

Observe that with a larger proportion of benzene, the viscosity in the region of greater velocity of flow is diminished, but the structural viscosity region in all three solutions, begins at higher pressure and shows a sharper rise.

In an investigation of the influence of small quantities of water on the viscosity of ethylcellulose solutions in anhydrous solvents[1], H. Suida found that traces of water (0.01-0.09%) added to ethylcellulose vacuum dried at 60° in 2% concentrations in dry benzene, reduce the viscosity very markedly, for instance, from about 16 min. for 0.01% water to 3 min. 35 sec. for 0.09% water, after one day, as compared to the dry solution. After 14 days, when the water content was 0.01%, the viscosity was 8 min. 47 sec. and, when the water content was 0.09%, the viscosity decreased to 3 min. 16 sec. Dry benzene solutions of ethylcellulose with alcohol from 0.5%-90% showed a greater decrease in viscosity due to alcohol than to water (after one day from 20 min. 36 sec. for alcohol-free benzene solution, to 36 sec. for benzene solution containing 90% alcohol. The water effect, moreover, is limited to a small range of concentration because of the separation of cellulose derivatives from solution. Changes in viscosity of ethylcellulose solutions with time of[2] standing are due to absorption of moisture. All viscosity determinations were made at 18°. He found that cellulose and its derivatives give no genuine solutions, since the dispersion takes place not up to the molecules, as with the crystalloids, but as a rule, up to the micelles. It has been known for some time that the addition of stronger polar liquids to solutions of cellulose deriv-

1. Cellulosechemie, 1931, **12**, 310; abst. C. A. 1932, **26**, 3104.
2. See W. v. Neuenstein, Kolloid Zts. 1927, **41**, 362. F. Baker, Journ. Chem. Soc., 1913, **103**, 1653. E. Mardles, Kolloid Zts. 1929, **49**, 4, 11; J. S. C. I. 1923, **42**, 207; J. C. S. 1925, **125**, 2240. A. Highfield, Ph. Ch. Zt. 1926, **124**, 248. G. Esselen, I. E. C. 1920, **12**, 801. K. Werner and H. Engelmann, Zts. ang. Chem. 1929, **42**, 438. S. Sheppard, E. Carver and R. Houck, Colloid Symposium Monograph, 1928, **5**, 243. W. Ostwald, Kolloid Zts. 1928, **45**, 56. O. Blueh, Pharm. Zt. 1926, **27**, 226. I. Sakurada, Kolloid Zts. 1929, **48**, 97; 1930, **49**, 52, 178. M. Hagedorn and P. Moeller, Cellulosechem. 1931, **12**, 29. G. Barr and L. Bircumshaw, Trans. Faraday Soc. 1921, **16**, 72.

atives in general and to the cellulose ethers specifically, is of great influence upon the solubility and hence upon the viscosity of the solutions, and this is evident from the difficult reproducibility of the viscosity of solutions of ethylcellulose in the usual solvents.

The change in viscosity with addition of ethyl alcohol to anhydrous benzene solutions of ethylcellulose is significant, in that the viscosity value of a 2% anhydrous solution in benzene decreases to a minimum with a content in the solution of 40% anhydrous alcohol, and then amounts to only a trifle more than 1/40 of the viscosity of the alcohol-free solution. Ethyl alcohol has a dipolar moment of 1.35, while ethyl alcohol only apparently lowers the viscosity more than water, which shows a higher dipolar moment, since on the one hand, about 1% alcohol produces the same lowering of viscosity as 0.07% water, but on the other hand, the viscosity-lowering action of water is limited lower, through the mixture occurring with about 0.08% water.

This amazing influence of the slightest traces of water on the viscosity of organosols of this kind, also gives meaning to the oft-observed, but little understood fluctuations in viscosity on standing of cellulose ether solutions. Lowering in viscosity is also observable in solutions which are stored in vessels not entirely tight.

B. Rassow and M. Wadewitz[1] have shown that in general, it is not the result of the degree of heating but of the length of the heating when permanent changes in viscosity are produced in the drying of cellulose derivatives. H. Pringsheim, W. Kusenack and K. Weinreb[2] have demonstrated the lowering of viscosity occurring on the heating of cellulose esters, while J. Katz[3] has mentioned that a drying of cellulose at 105° in an oven was insufficient for a removal of the "swelling-water," a complete removal of

1. J. prakt. Chem. 1923, **106**, 266; abst. C. A. 1924, **18**, 1568.
2. Papier Fabr. 1927, **25**, 785; abst. C. A. 1928, **22**, 2837.
3. Die Chemie der Cellulose und Ihrer Begleiter, 1928, 660.

the water taking place only when the drying is carried out in a stream of hydrogen at 140°[1].

I. Sakurada[2] investigated the action of trivial amounts of water in an alcohol-benzene mixture which served as swelling agent for acetylcellulose, and found that only small amounts of water increase the swelling, but also that the addition of pure benzene influences the swelling and viscosity more strongly than the addition of alcohol, which is readily explainable by the minimal dipolar moments of the benzene.

To *increase* the viscosity of an alkylcellulose solution[3], the acetone may be extracted with either water or a mixture of water-acetone to dissolve out the lower viscosity derivatives, i.e., those ethers of low viscosity which dissolve in or are swollen by water.

The variation in viscosity of aliphatic ketones as solvents of cellulose derivatives has ben reported upon[4], the following table (applied to nitrocellulose) showing the relative variations in 20% solutions at 25°, the viscosity being given in poises: Acetone, 1.4, methylethyl ketone 2.0, methylpropyl ketone 3.4, methylbutyl ketone 7.5, methylamyl ketone 12.0, ethyl acetate 3.0, and *n*-butyl acetate 9.1.

The rotatory power and optical indifference of ethylcellulose solutions have been studied by K. Hess and E. Messmer[5].

Viscosity Reduction of Cellulose Ethers. Methods for reducing the viscosity characteristics of the inorganic (nitrocellulose) and organic (acetylcellulose) esters of cellulose are many, and may be classified as follows: (1) Employment of a maximum high temperature in esterification;

1. H. Ost and F. Westhoff, Chem. Ztg. 1909, **33**, 197; abst. C. A. 1909, **3**, 1394; J. S. C. I. 1909, **28**, 325; J. C. S. 1909, **96**, i, 210; Chem. Zentr. 1909, I, 1231.
2. Kolloid Zts. 1930, **49**, 178.
3. I. G. Farbenindustrie, A. G., E. P. 321651; abst. C. A. 193v, **24**, 2882; J. S. C. I. 1930, **49**, 99-B; Cellulose, 1930, **1**, 198. D. R. P. 511019; abst. C. A. 1931, **25**, 1379.
4. J. Park and H. Hofmann, I. E. C. 1932, **24**, 132.
5. Ber. 1921, **54**, 834.

(2) prolonging the time of reaction; (3) restricting the water in the esterizing bath, or in the case of the acetates, the water used in partial hydration; (4) increasing the temperature during esterification, or of hydrolysis; (5) increasing the quantity of condensing agent used; and (6) treatment of the formed ester, either in the solid state or in solution with acids, alkalis, steam and/or pressure.

As solvent recovery in lacquers, fluid coating compositions and the formation of films and filaments is often not attempted, especially in connection with the use of brush and spray lacquers, the total cellulose in solution becomes of great technical importance from price considerations, since it is dissipated during use. Reductions in viscosity of nitrocellulose are based primarily upon the disclosures of C. Piest[1], W. Tucker[2], M. Fric[3], T. Chandelon[4], H. Nishida[5], H. Ost[6], F. Baker[7], and W. Gibson[8], and on the patented processes of F. Lehner[9], Kunstfaeden Ges.[10], T. Chandelon[11], E. Berl[12], G. Dietl[13], K. Kishi[14], H. Turgand[15], J. Potter[16], O. Carlsson and E. Thall[17], E. Pitman[18], J. Clancy[19] and E. Flaherty[20]. Reduction in viscosity of the cellulose acetates is indicated on pp. 212, 524, 536, 561, 595, 615, 811, 813, 815, 899, 910, 924 and 984 herein. The recently issued pro-

1. Zts. Schiess Sprengst. 1910, **5**, 40, 409; Zts. ang. Chem. 1911, **24**, 968; 1913, **26**, 24.
2. I. E. C. 1921, **13**, 623.
3. Comp. rend. 1912, **154**, 31.
4. Bull. Soc. Chim. Belg. 1914, **28**, 24.
5. Caout. et Guttap. 1914, **11**, 8103.
6. Zts. ang. Chem. 1911, **24**, 1892.
7. J. C. S. 1913, **103**, 1653.
8. J. C. S. 1920, **117**, 479. For data on lowering the viscosity of cellulose derivatives, see A. Bresser, Industria chimica, 1931, **6**, 93.
9. U. S. P. 713999. F. P. 243612.
10. U. S. P. 866768. E. P. 27527, 1906. F. P. 371544. Belg. P. 195899.
11. E. P. 11941, 1911.
12. D. R. P. 199885.
13. E. P. 15029, 1905. F. P. 356323. Belg. P. 185822.
14. F. P. 473986.
15. F. P. 344845.
16. U. S. P. 1201758.
17. U. S. P. 1375208. E. P. 136141.
18. U. S. P. 1535438, 1636319.
19. U. S. P. 1439293.
20. U. S. P. 1629999.

cess of C. Dreyfus and G. Schneider[1] involving the use of hydrogen dioxide and iron salts is especially noteworthy.

The theoretical aspects of viscosity changes in cellulose derivatives and the details of structure viscosity measurements are contained in the contributions of Y. Nisizawa[2], A. Drinberg[3], H. Staudinger[4], K. Hess and I. Sakurada[5], and L. Clement and C. Riviere[6].

The practical reduction in viscosity of cellulose ether solutions may be classified under the heading of (1) treatment with acid, or (2) with alkali or alkaline base, (3) with ozone, or (4) water, or (5) heat, or (6) by evaporation, as in the following processes:

(1) *Viscosity Reduction by Acid Treatment,* as indicated by the following seven methods, the viscosity of cellulose ethers is diminished without affecting the solubility by treatment with a hot aqueous mineral acid of relatively low concentration, or a hot solution of an acid salt in water, with exclusion of swelling agents and solvents[7]. Or

1. U. S. P. 1851665.
2. Kolloid-Z. 1931, **56**, 59; abst. C. A. 1931, **25**, 5554, 5761, 5982.
3. Zhur. Prikladnoi Khim. 1931, **4**, 293; abst. C. A. 1932, **26**, 357.
4. H. Staudinger, K. Frey, R. Signer, W. Starck and G. Widmer, Ber. 1930, **63B**, 2308; abst. J. S. C. I. 1930, **49**, 1415-A.
5. Ber. 1931, **64B**, 1183; abst. J. S. C. I. 1931, **50**, 828-A.
6. Rev. gen. Colloides, 1924, **2**, #3, 11; abst. C. A. 1924, **18**, 3714.
7. A. Wacker Ges. f. Elektrochem. Ind., E. P. 342391; abst. C. A. 1931, **25**, 5557; J. S. C. I. 1931, **50**, 388-B. U. S. P. 1834040 of A. Ascherl and W. Gruber. D. R. P. 531981; abst. C. A. 1932, **26**, 304. It should be borne in mind that processes have been proposed for diminishing the viscosity of cellulose ethers, but only at the expense of the mechanical properties of the product, leading to more or less degraded ethers. This deterioration is shown by changes in solubility, caused by an essential diminution of the micelle and a marked degradation. This effect has been purposely used as a means of augmenting the solubility of sparingly soluble etherified celluloses, as by treatment with depolymerizing agents. It is well known that the solubility of the cellulose ethers may be increased by treatment with mineral acids of suitable concentration, with or without the addition of a body exercising a swelling action on the ether, as by treatment with glacial acetic acid in the presence of a relatively small amount of sulfuric acid. In the above process, for instance, it is maintained that the mechanical properties of the product remain satisfactory, although a profound diminution in viscosity is attained, degradation is avoided as evidenced by the unchanged solubility of the cellulose ether operated upon.

the cellulose ether may be treated with hot aqueous acetic acid without the use of hydrolytically acting agents as mineral acids. Duration of treatment depends upon concentration of the acid, temperature and total cellulose ether solids per unit volume, if in solution. The following four examples are illustrative:

(a) Ethylcellulose 1, having a primary viscosity of 800, is heated for 0.5-6 hrs. at about 95° with 5-20 of acetic acid 80%, the diminution in viscosity being (40% ethoxyl cellulose ether used dissolved in dichlorethylene-alcohol): viscosity after 15 min. treatment, 445; after 5 hrs., 62; after 6 hrs., 50. The solution, either hot or cold, is precipitated with water, washed and dried.

(b) One part ethylcellulose of primary viscosity of 150, suspended in 5-20 parts of 30% acetic acid and heated for 3 hrs., preferably while stirring at the boiling point, the viscosity is reduced to 115.

(c) One part ethylcellulose viscosity 665, when heated for an hour with 10-30 parts 2% HCl, gave a viscosity of 116.

(d) One part ethylcellulose as in (c), heated for 3 hrs. with 5-20 parts sodium acid sulfate of 2% strength. Viscosity after treatment, 316.

The process of P. Seel is somewhat similar[1], the cellulose ether as ethylcellulose, of high viscosity when dissolved in solvents, usually ethyl alcohol-benzene (1:1), producing a heavy, molasses-like dope of slight acidity, approximately equivalent to a hydrogen-ion concentration of *pH* 5.0, is made into film and stored or "incubated" at 65° from days up to several months. The film is tested for viscosity periodically, and when found reduced to the point desired, is dissolved in the above solvent combination and used as a lacquer or for film composition.

1. U. S. P. 1635013; abst. C. A. 1927, **21**, 2985; J. S. C. I. 1927, **46**, 774-B; Chem. Zentr. 1927, II, 2025; Plastics, 1927, **3**, #11, 608.

Or[1], the cellulose ether in the dry state or in solution, may be treated with a mixture of waste nitrating acid, as a mixture of sulfuric acid 13%, nitric acid 7%, nitrogen oxides 1-2%, viscosity reduction being carried out at room temperature by allowing the cellulose ether and acid mixture to stand in contact with each other for several days. When viscosity reduction has diminished to the point desired, the ether is washed neutral, dried and is then ready for use.

The invention of the Imperial Chemical Industries[2] involves treating the cellulose ether with an acid gas until the ether has absorbed sufficient to cause a slow, internal transformation and resulting viscosity decreases to the point desired. The following two examples indicate the *modus operandi* of the process:

(a) Any convenient charge of cellulose ether, preferably air dried, is placed in a container with stirring device, and a stream of HCl gas passed through while the charge is in motion, the temperature being maintained at about 25°. The total amount of gas absorbed varies within the limits 0.1-5% of the weight of the cellulose ether. When the viscosity is reduced to the point required the charge is quenched in water, washed to neutrality and dried.

(b) 500 parts cellulose ether, dried at 95-100°, or viscosity 30,000 centipoises at 25° as determined by the ball-fall method, the cellulose ether being in a 12% xylene solution, is placed in a container with agitating and heating arrangement, and HCl gas passed in until 0.3% (based on the weight of the cellulose ether) has been absorbed, heating being continued at 100° until the desired viscosity diminution results. After 2 hrs. heating, the neutral cellulose ether gave a viscosity of 400 centipoises.

1. C. Prachel and L. Branchen, U. S. P. 1679943; abst. C. A. 1928, **22**, 3777; Plastics, 1929, **5**, #1, 26; J. S. C. I. 1928, **47**, 810-B; Chem. Zentr. 1928, II, 1639. See U. S. P. 1548938, 1635013.

2. E. P. 313091; abst. C. A. 1930, **24**, 960. U. S. P. 1864554, E. Reid, is the same.

In the method of D. Traill and A. Levesley[1], a high viscosity ethyl- or benzyl-cellulose is heated under pressure with dilute acid into an undegraded ether of low viscosity, e.g., 0.1-5.0 c.g.s. units in 10% solution in toluene-ethyl alcohol (4:1).

J. Altwegg and C. Maillard[2] operate upon the crude cellulose ether by the addition thereto of a mineral acid, a combined bleaching and viscosity reduction taking place simultaneously. Their method is indicated by the three following examples:

(a) 15 cc. of 8° Be. HCl are poured into a liter of acetic acid containing 100 gms. crude ethylcellulose, and after thoroughly mixing, the mass is allowed to stand 30 min. at ordinary temperature, after which the ester is precipitated and washed free from reactants.

(b) 50 parts crude ethylcellulose (40% ethoxyl) are dissolved in alcohol 500 at 93°, and 15 of 35° Be. sulfuric acid added with stirring. After standing for an hour at 20-25° the mixture is poured into water, filtered and washed to neutrality.

(c) Methylcellulose may replace ethylcellulose in Ex. (a).

The method of viscosity reduction of O. Leuchs[3] is by the utilization of sulfuric acid, phosphoric, oxalic acids, or a mixture of zinc chloride and HCl, as exemplified in the two following examples:

(a) One part by weight of ethylcellulose (47-48% ethoxyl), which only undergoes swelling in benzene or alcohol-benzene, is introduced into a mixture of alcohol-water-sulfuric acid (3:3:1.5) and thoroughly stirred. At first, the mass simply swells up but after a time, depending upon the temperature of the mixture, complete solution is ef-

1. Can. P. 320779. E. P. 357123; abst. J. S. C. I. 1931, **50**, 1107-B.

2. U. S. P. 1599508; abst. J. S. C. I. 1926, **45**, 1010-B; F. P. 603791; abst. C. A. 1926, **20**, 3567; J. S. C. I. 1926, **45**, 739-B; Ann. Rep. S. C. I. 1926, **11**, 131; Caout. et Guttap. 1927, **24**, 13425.

3. U. S. P. 1767382. E. P. 277111; abst. C. A. 1930, **24**, 4307.

fected. The solution is then precipitated with water, washed and dried. The cellulose ether is then readily soluble in benzene and benzene-alcohol and of diminished viscosity. By prolonging the action of the acid for 12-24 hrs., the solubility is still more increased, viscosity decreasing with increase in solubility.

(b) One part ethylcellulose as in (a) above is treated with about 10 parts glacial acetic acid containing 0.1% sulfuric acid, and treatment effected as above.

The British Celanese, Ltd.[1], makes use of nitric acid, either before or after the cellulose derivative has been formed, about 10% strength being used. In addition to diminishing the viscosity by nitric acid treatment, an improved color and increased clarity is said to result by this treatment.

(2) *Viscosity Reduction with Alkali.* In the method of A. Nathansohn[2], a cellulose ether or ester, preferably in solution, is treated with a basic compound as pyridine, quinoline or aniline in the presence of phosphorous oxychloride, the ratio being 350 pyridine, 100 phosphorous oxychloride. Phosphorous pentachloride, phosphorous sulfochloride or diethylaminophosphine chloride may be employed.

A favorite method of diminishing viscosity in nitrocellulose solutions is by the addition of ammonium or sodium hydroxides thereto, especially the former. Societe Clement & Riviere have applied this method to the treatment of benzylcellulose[3], from 0.1-0.2% ammonia gas being introduced with the cellulose ether, the latter preferably in solution.

(3) *Viscosity Reduction with Ozone.* This process, primarily applied to the organic cellulose esters, is also equally applicable to the cellulose ethers. The cellulose derivative is placed in a vessel at approximately room temperature, and a slow stream of ozone of 2-3% concentration

1. E. P. 319691; abst. Cellulose, 1930, **1**, 150; C. A. 1930, **24**, 2599.
2. F. P. 683251; abst. C. A. 1930, **24**, 4631.
3. F. P. 675086; abst. C. A. 1930, **24**, 2882.

passed through at the rate of about one liter of gas per minute for about 15 minutes. This induces a distinct bleaching action, but an imperceptible diminution in viscosity. However, by passing the gas for 75 minutes in a test run, viscosity was reduced from 120,000 to 26,000 centipoises, and after 2 hrs. to 3,700 centipoises. The ozonizing treatment is prolonged until the degree of viscosity and bleaching desired has been obtained[1].

(4) *Viscosity Reduction by Addition of Water.* This process, evolved by H. Dreyfus[2], and intended primarily for application to cellulose ether and ester solutions for filament formation, is based on the observation that when acetone is used as solvent, the addition of water thereto in amounts well under that required for precipitation purposes, causes a substantial reduction in the viscosity of the solution. Filaments obtained by extrusion from such solutions may be drawn out to produce filaments of exceptionally fine denier, or thin films or ribbons may be similarly produced.

(5) *Viscosity Reduction by Dissolving and Heating.* Methyl-, ethyl- or benzyl-cellulose is dissolved in a mixture of benzene, toluene, ether, methyl or ethyl alcohols, acetone or other solvents, either at their boiling points, or the cellulose ether and solvent combination is placed in a closed container and heat applied. In an illustrative example in which 6 gm. cellulose ether was dissolved in 100 gms. benzene, the viscosity was reduced from 100 to under 5, when compared with glycerol as 100 as standard. While in the heated condition, the cellulose ether may be incorporated with plasticizing bodies (triphenyl phosphate, tricresyl phosphate, diethyl phthalate, dibutyl tartrate) and synthetic resin bases (phenol-aldehydes, diphenol-propane-aldehyde, phenol-furfural, aniline-furfural, acetone-furfural)

1. C. Malm and A. Andersen, U. S. P. 1857562.
2. E. P. 328636; abst. J. S. C. I. 1930, **49**, 656-B.

to produce plastics, molding compositions and celluloid substitutes[1].

(6) *Viscosity Reduction by Solvent Evaporation.* The cellulose derivative in dilute solution is spread in a thin layer on the outer surface of a liquid which is not miscible with the solution[2] and after the film becomes solid from evaporation of solvent and absorption into the other liquid, the film may be removed and will be found to be considerably reduced in viscosity after re-solution in (say) acetone. A cellulose ether may be dissolved in butyl tartrate, spread in a thin solution or brushed or poured on a constantly renewed aqueous surface. After the film has hardened and substantially all the contained solvent has been removed, it is dried, and re-dissolved if desired.

Or[3], the organic cellulose derivatives may be dissolved in an organic liquid as acetone containing up to 4% (on the weight of the cellulose compound) of a substance which is a non-solvent for the cellulose derivative but dissolves in the cellulose solvent, increasing its electrical conductivity. Suitable bodies are aluminum chloride, sulfate or resinate; copper, zinc or magnesium oleate; or triethanolamine or analogous organic base. After the solution has stood at room temperature for a few days a marked diminution in viscosity is apparent.

Stability of Alkylcellulose. The cellulose ethers possess a higher degree of stability, neutrality and indifference to water or the action of alkaline or acid agents than any of the other cellulose derivatives. This includes heating to high temperatures, both with and without water.

A number of bodies have been proposed to increase the natural stability of the cellulose ethers. Inasmuch as many of them have solvent or thermoplasticizing properties,

1. C. Dreyfus, F. P. 673029; abst. Kunst. 1931, **21**, 17. F. P. 673030; abst. C. A. 1930, **24**, 2316.
2. H. Mark, D. R. P. 521720; abst. C. A. 1931, **25**, 3481; Chem. Zentr. 1931, II, 352.
3. Brit. Celanese, Ltd., E. P. 366110; abst. J. S. C. I. 1932, **51**, 336-B.

they are more properly taken up in connection with dissolvants in Chapter XII. As an instance, it has been found that the stability of films, plastic masses, lacquer layers and artificial fibers may be improved by the addition thereto of inorganic bases as zinc oxide, lead oxide, white lead, or aluminum oxide, in conjunction with sulfoxides or disulfoxides as diphenylsulfoxide. Substituted thiazoles as, mercaptobenzothiazole, 5-methylmercaptobenzothiazole or dehydrothiotoluidine may also be added to increase the stability[1], an example being:

20 parts ethylcellulose dissolved in 72 parts benzene and 8 parts alcohol, with addition of 0.4-0.5 parts dehydrothiotoluidine. The film obtained from this solution shows, compared to the thiazole-free film, a much increased stability. The stabilizer in the above example may be replaced by 0.3 parts each dehydrothiotoluidine and *p*-aminobenzoic acid.

Clarity of alkylcellulose solution may be improved, according to R. Brownlow who has patented a process for so doing[2], by the introduction into the solution of liquids soluble in or miscible with water as phosphorous oxychloride or sulfur oxychloride, of especial advantage when the cellulose ether is to be used in film form as for the wrapping of such commodities as foodstuffs or confectionery, or as strip material adapted for use as supports for photographic emulsions. Metallic halides as calcium chloride or zinc chloride may be employed in association with the oxychloride, nonmetallic vessels being employed in all the operations. One part zinc chloride and 2 parts sulfur oxychloride may be used, the total amount being not over 5% of the weight of the methyl- or ethyl-cellulose employed.

Molecular Size of Cellulose Ethers. By the methods of I. Langmuir and E. Adams, the area per molecule of etherified celluloses and the thicknesses of the films formed in

1. L. Rosenthal, E. Messmer and R. Hebermehl, D. R. P. 537626.
2. E. P. 322464; abst. C. A. 1930, **24**, 2881; J. S. C. I. 1930, **49**, 184-B; Brit. Plastics, 1930, **1**, 447.

water have been determined for various amorphous and crystalline ethylcelluloses and methylcelluloses[1], from solutions in benzene, chloroform, chloroform-alcohol 9:1, and methylene chloride-alcohol 9:1. The number of hydroxyl groups per molecule cellulose which were substituted varied from 2.25 to 3. The areas in square A.U. and the thickness in A.U. were for ethylcellulose 63.5-66 and 2.25-3, and for methylcellulose 59-61 and 4.1-4.3. The thickness of film corresponds with ordinary organic mols., values for the amorphous and crystalline products agreeing very well. The marked difference in area and thickness of film for alkylcellulose are attributed to differences in orientation of the mols. in the surface. It appears from the fact that the thickness of film is independent of viscosity and was the same for the amorphous and the crystalline preparations, that the micelles of these substances have a thickness of one or two C-chains.

Depolymerization and Acetolysis of Alkylcellulose. According to K. Hess and W. Wittelsbach[2], acetolysis under very mild conditions of ethylcellulose uniformly confirms the deduction, that when degradation has proceeded sufficiently far, the ethoxyl number of the ethyldextrin acetates produced should be less than that of the ethyl dextrose. H. Ost and his pupils[3] have proven from the acetolysis of cellulose (which topic see) that 4 glucose residues are obtained per 1 cellobiose residue, but one must obtain substituted glucose in the decomposition of cellulose esters, even when decomposition proceeds so smoothly that a splitting off of the substituents is avoided.

1. J. Katz and P. Samwel, Ann. 1929, **472**, 241; abst. C. A. 1929, **23**, 5378; Chem. Zentr. 1929, II, 2176. Naturwissenschaften 1928, **16**, 592; abst. C. A. 1928, **22**, 3986; J. S. C. I. 1928, **47**, 937-A; Chem. Zentr. 1928, II, 963.

2. Zts. Elektrochem. 1920, **26**, 232; Paper, 1920, **27**, No. 13, 13; No. 26, 32; C. A. 1921, **15**, 1619; 1922, **16**, 2221; J. C. S. 1920, **118**, i, 532; J. C. S. Ann. Rep. 1920, **17**, 67; J. S. C. I. 1920, **39**, 512-A; Bull. Soc. Chim. 1921, **30**, 1332; Chem. Tech. Uebers, 1921, **45**, 200.

3. Ann. 1913, **398**, 323; abst. C. A. 1913, **7**, 3836.

This conclusion is confirmed by a study of the acetolysis of ethylcellulose in presence of a small amount of sulfuric acid and at comparatively low temperatures. The acetolysis of an ethylcellulose containing 2.5 ethyl groups per glucose residue proceeds with intermediate formation of substituted dextrins (penta- to di-saccharides), and splitting off of ethylglucose acetate. Whereas the ethoxyl content of the glucose portion at the commencement corresponds to a triethyldiacetylglucose, the dextrin portions show a lower ethoxyl value. Only with an extensive decomposition of the dextrin to glucose, does the average ethoxyl content of the glucose portion also sink. The decomposition of ethylcellulose through hydrolysis gives acetyl-ethyldextrin and diacetyl-triethylglucose.

An intrinsic difference between the acetolysis of cellulose and that of ethylcellulose is shown in the temperatures required on mixing the initial material with the acetolyzing mixture. With cellulose, a quick rise to 130-140° is noted, whereas no such sharp rise with ethylcellulose takes place, even when the same acetolyzing mixture is used as with cellulose. From the easier acetolysis of ethylcellulose, it is believed hydrolysis of the ethyl groups does not take place, or at least only to an inconsiderable measure.

In a study of the depolymerization of cellulose and its transformation into a biose-anhydride, K. Hess[1] determined the action of acetyl bromide on ethylcellulose by placing 13.5 gms. of the ether (43% ethoxyl) in a closed flask for 8 days with 50 gms. acetyl bromide. The materials dissolved immediately on bringing the substances together. The dark brown solution when worked up, yielded a large amount of bromacetylglucose. There was also obtained brominated ethylated sugars from which the halogen could not be removed by silver carbonate.

In continuing their earlier work on the acetolysis of

1. Ber. 1921, **54**, 2867; abst. C. A. 1922, **16**, 1400.

ethylcellulose, K. Hess and W. Wittelsbach[1] obtain as a final product of the reaction, a tetraethylbiose anhydride. Thus, 2 hrs. acetolysis gave a product with 35.81% ethoxyl, 15.2% acetic acid, sintering at 166°, and melting 196-205°. Molecular weight in freezing 1.93% acetic acid, 440. Depolymerization of cellulose to celluxose occurs, and with great readiness. They took 52.2 gms. dry ethylcellulose (2 ethoxyl groups), dissolved in a mixture of 75 cc. glacial acetic acid and 75 cc. acetic anhydride with stirring, allowed to stand at 18° for 15 hrs., until a homogeneous solution resulted. Then a mixture of 25 cc. glacial acetic acid, 25 cc. acetic anhydride and 5.32 gms. 96% sulfuric acid were added at —5°, and the molecular weights obtained after 2, 5, 24, and 144 hrs. In each instance, the determinations indicated a tetraethylbiose anhydride.

It appears that reliable conclusions as to the constitution of cellulose from the products of the acetolysis of alkylated celluloses can only be drawn when alkylation has been conducted in such a way as to exclude the probability of the disruption of glucosides or ether-like linkages[2]. Under these conditions the limit of alkylation is reached when two ethyl groups per C_6 cellulose have been taken up. The resulting diethylcellulose is an individual substance, and when subjected to acetolysis a far-reaching depolymerization occurs with the absorption of one acetyl group for each $C_6H_8O_3(OC_2H_5)_2$, and without the generation of a free aldehyde group. The acetylated product is readily hydrolyzed by methyl alcoholic ammonia, and gives a product of the same empirical composition as the starting material and with a molecular weight in dilute solution of 800-900, rapidly increasing with increasing concentration. The sub-

1. Ber. 1921, **54**, 3232; abst. C. A. 1922, **16**, 2027; J. C. S. 1922, **122**, i, 116; J. S. C. I. 1922, **41**, 94-A; Bull. Soc. Chim. 1922, **32**, 461; Caout. et Gutta. 1922, **19**, 11334; Ann. Rep. S. C. I. 1922, **7**, 136.

2. K. Hess, W. Wittelsbach and E. Messmer, Zts. ang. Chem. 1921, **34**, 449; C. A. 1922, **16**, 490; J. C. S. 1921, **120**, i, 710; J. S. C. I. 1921, **40**, 688-A; Bull. Soc. Chim. 1922, **32**, 56; Chem. Tech. Uebers, 1921, **45**, 327; Paper Trade J. 1922, **74**, 49; Textile Ber. 1922, 43.

stance, therefore, contains at least four dextrose residues, and since free aldehyde groups are absent, it must be assumed that these structural units are held together by another linking system than the "glucoside" linkage in the original ethylcellulose. Although with different preparations, isolated at different stages of the acetolysis, approximately identical molecular weights were found, differences in optical rotation and melting point indicate that the depolymerization is accompanied by isomerization. The further acetolysis of the substance resulted in the formation of acetyl-ethylated hexoses, which on hydrolysis gave a syrup, from which triethylglucose was isolated in crystalline form, and which appeared to be merely a mixture of this with diethylglucose, the latter predominating. The presence of other ethylated glucoses in the syrup, and the proportions of di- and tri-ethylglucose which it contains vary considerably.

The acetolysis of methylcellulose with a mixture of acetic acid and acetic anhydride[1] containing sulfuric acid at 25-30° for 7-20 days, gives about 50% cellobiose octoacetate, indicating that some of the glucose anhydride units in the original product are not methylated. No methylcellobiose acetate could be detected, being probably decomposed during acetolysis.

E. Heuser and N. Hiemer have comprehensively studied the degree of polymerization of alkylated celluloses, a synopsis of their conclusions being found on pages 76-77 herein.

Spectrographic Properties of Alkylcellulose. B. Rassow and W. Aehnelt[2] have made a spectrographic investigation of the cellulose ethers in conjunction with cellulose acetate, using an ethylcellulose of 45.88-46.05% ethoxyl (triethylcellulose requires 45.92% ethoxyl), the ether being soluble in chloroform-alcohol 9:1, easily soluble in alcohol-

1. T. Lieser, Ann. 1930, **483**, 132; abst. J. S. C. I. 1931, **50**, 74-A.

2. Cellulosechem. 1929, **10**, 169; abst. C. A. 1930, **24**, 3711; J. S. C. I. 1930, **49**, 10-A.

benzene 1:1, methylene chloride and perchlorethylene, soluble after some time in chloroform, and swelling in absolute alcohol and in absolute ether, the absorption curve of a 4% solution in chloroform-alcohol 9:1 being: 1.0, 3950; 1.5, 3250; and 2.0, 2750, between the limits 2200-400 A. by the Baly-Hartley method[1]. Ethylcellulose has practically the same effect on light absorption as has acetylcellulose.

According to H. Mark and G. v. Susich[2], X-ray investigation of methylcellulose has shown that the deductions of K. Hess and C. Trogus[3] of the values 21.3 and 25.6 A. for two of the periods of identity of the elementary cell, rest on a misinterpretation of the X-ray diagram, the most probable value being 10.3 ± 0.2 A. for the period of identity along the axis of the fiber. J. Young and F. Spiers report[4] in the determination of space groups in certain carbohydrates, that the process of methylation does not appreciably alter the *c*-spacing, the spacing of 4.5 A. in the principal dimensions being of frequent occurrence. R. Herzog[5] has shown that cellulose, hydrocellulose and viscose in parallel arrangement show Roentgen diagrams similar to the crystal particles arranged along one axis, whereas nitro-, acetyl- and ethyl-cellulose are amorphous.

H. Gardner and C. Knauss[6] have made tests of the relative light frequency of cellulose ether dissolved in benzene and toluene with the following plasticizers added thereto: ethyl acetylglycollate, ethyl *m*-toluenesulfonamide, diethyl, diamyl and dibutyl phthalates, hexol, *p*-toluenesulfonamid, tricresyl phosphate, *o*-chloracetanilid, and *o*-acetanisidine, each with 1% (on the weight of the lacquer) of dicyandiamine or urea added. Best results were ob-

1. Kayser's Handbook on Spectroscopy, **3**, Chapt. 3.
2. Zts. physik. Chem. 1930, **9B**, 157; abst. C. A. 1930, **24**, 5480.
3. Zts. physik. Chem. 1929, **5B**, 161; abst. J. S. C. I. 1929, **48**, 1222-A. See also C. Trogus and K. Hess, Zts. physik. Chem. 1929, **4B**, 321. K. Hess and C. Trogus, Ber. 1928, **61B**, 1982.
4. Zts. Krist. 1930, **78**, 101.
5. Cellulosechem. 1921, **2**, 101; abst. C. A. 1922, **16**, 1663; J. S. C. I. 1922, **41**, 8-A.
6. Am. Paint & Varnish Manufrs. Assoc. Circ. 1928, No. 338, 657; abst. C. A. 1929, **23**, 276; J. S. C. I. 1928, **47**, 888-B.

tained with tricresyl phosphate. The fluorescence of acetyl- and nitro-cellulose films has been investigated by J. McNally and W. Vanselow[1].

A radio-active, luminous ethylcellulose in filament form has been described[2], and obtained by treating titanium oxide with radium bromide and admixing this with the cellulose ether in acetone or other solvent. It is claimed that filaments so produced exhibit a remarkable and beautiful phosphorescent glow when brought into a darkened room. Other phosphorescent bodies as barium sulfide, calcium sulfide and chlorophene may be added. H. Dreyfus takes textiles composed of or containing cellulose ethers[3], and treats them with zinc sulfide and a small proportion of a promoter, such as magnesium chloride containing a small quantity of a copper compound, the phosphorescent material being in a very fine state of subdivision. The cellulose ether, if in a softened or swollen condition, absorbs a larger proportion of the self-luminous product.

Phosphorescent and luminous compositions containing cellulose derivatives have also been described by J. Beavis[4], produced with the aid of resins, neutral rosin or rosin esters, copal, sandarac, dammara and dammar. The phosphorus composition is ground with the resinous body and added in desired amounts to the cellulose derivative in solution. The phosphorescent salts employed are calcium, strontium, magnesium or barium sulfides, or complex mixtures containing both sulfides of the alkaline earth metals or of aluminum, together with a proportion of salts of bismuth, thorium, thallium, uranium and the alkali metals.

Inflammability of Alkylcellulose. All the cellulose ethers are non-explosive, and no more combustible than the

1. J. A. C. S. 1930, **52**, 3846; Eastman Kodak Co. Abridged Sci. Pub. 1930, **14**, 186; abst. C. A. 1931, **25**, 33.
2. H. Gardner, U. S. P. 1791199; abst. C. A. 1931, **25**, 1673; Chim. et Ind. 1931, **25**, 1217.
3. E. P. 340636; abst. Silk J. 1931, **7**, #82, 37; #83, 54. F. P. 704564; abst. C. A. 1931, **25**, 4718.
4. E. P. 299228; abst. C. A. 1929, **23**, 3167; J. S. C. I. 1929, **48**, 64-B; Chem. Zentr. 1929, I, 1052.

cellulose acetates. Careful determinations have indicated that the inflammability of ethylcellulose of maximum ethylation is about 90% of that of maximum acetylated cellulose. The inflammability diminishes with increase in the number of alkyl groups substituted in cellulose, and cellulose ethers of the same number of alkyls of higher molecular weight, appear to be less flammable than those of lower alkyl molecular magnitude.

A large number of inflammability-reducing bodies has been proposed for incorporation with the cellulose esters and ethers to attenuate their burning capacity. They may be roughly divided into three classes, (1) those which are solvents or plastifiers and produce colorless solutions or masses, (2) those having little or no solvent action but which do not interfere with the transparency of the cellulose ether when added thereto, and (3) inorganic pigments which produce an opacity by virtue of their insolubility. There are also volatile solvents as the haloid substituted aliphatic hydrocarbons which diminish inflammability in cellulose ether solutions, but which become dissipated when the solutions are evaporated to dryness.

The subject is treated *in extenso* in Chapter XII, a few examples being indicated hereas as showing the scope and general nature of the bodies which have been proposed for this purpose. Many of the delustering bodies discussed in that topic in Chapter XIII are fire-retardants by virtue of the pigments contained therein, and incorporated to produce a subdued luster to the cellulose ether filament or textile. In order to diminish the speed of burning of cellulose ethers in general, it has been found that compositions which permit of a self-sustaining combustion by the application of a flame at ordinary temperature, may be inhibited in or prevented from burning under normal temperature, provided there is present a heat-absorbing compound capable of taking up through decomposition or volatilization, the major portion of the heat that would be necessary to raise the

components to the point at which ignition may be initiated or sustained.

The incorporation has been suggested[1] of bromine substituted derivatives of catechol, resorcinol, hydrochinone, pyrogallol, cresol or thymol, tribromphenol being especially useful. Brom-camphor[2], as well as brom-benzene, -toluene, -xylene, -mesitylene, -ethylbenzene, -cumene and -cymene[3] have also been advocated. Triphenyl phosphate with hydrated magnesium carbonate[4] or calcium sulfate[5], combine solvency and opacity of the added fire-retardants.

Bromine substituted acidylated aromatic amines have received patent protection in this field[6], as acetyl-4-brommethyl-, acetyl-2.4.6-tribrommethyl-, diacetyl-2.4.6- (or 2.4.5-) tribrom- or acetyl-2.4.6-tribrommethyl-anilid; diacetyl-3.5-dibrom-2-toluidid, diacetyl-1.3.6-tribrom-2-naphthalid and benzoyl-2.4.6-tribromanilid. Substituted aromatic esters[7] have also been brought forward for this purpose, examples being trichlor (or brom or iodo)-phenyl (-cresyl, -xylenyl or -naphthyl) formate, acetate or propionate—in all, 36 different esters.

Divisibility of Alkylcellulose. Substances insoluble or only slightly soluble in water as the cellulose ethers may be brought into a state of extremely fine dispersion in water, which includes stable suspensions as well as colloidal solu-

1. S. Carroll, U. S. P. 1716418; abst. C. A. 1929, **23**, 3807; J. S. C. I. 1930, **49**, 413-B; Plastics, 1930, **6**, #1, 26.
2. *Ibid.* U. S. P. 1716419; abst. C. A. 1929, **23**, 3807; J. S. C. I. 1930, **49**, 413-B; Plastics, 1930, **6**, #1, 26.
3. *Ibid.* U. S. P. 1716420; abst. C. A. 1929, **23**, 3807; J. S. C. I. 1930, **49**, 413-B; Plastics, 1930, **6**, #1, 26.
4. C. Burke, U. S. P. 1633067; abst. Plastics, 1927, **3**, 542; J. S. C. I. 1927, **46**, 775-B. DuPont Viscoloid Co., E. P. 289936; abst. C. A. 1929, **23**, 944; J. S. C. I. 1928, **47**, 478-B.
5. G. Leysieffer, E. P. 206770; abst. C. A. 1924, **18**, 1199; Kunst. 1925, **15**, 27; Ann. Rep. S. C. I. 1924, **9**, 147; Chem. Zentr. 1924, I, 981. F. P. 562667; abst. Chem. Zentr. 1924, II, 2623; Kunst. 1925, **15**, 122.
6. British Celanese, Ltd., and A. Daly, E. P. 319073; abst. C. A. 1930, **24**, 2599; J. S. C. I. 1930, **49**, 53-B; Brit. Plastics, 1930, **1**, #10, 447.
7. C. Dreyfus, U. S. P. 1838078.

tions[1], if they are dissolved or dispersedly suspended in organic solvents which are not miscible with water, and the resulting solutions or suspensions mixed with water in the presence of sulfonic acids or sulfonic acid salts of organic compounds, especially those which possess high wetting power, sodium sulfanilate being excepted. Excellently suitable are the products resulting from the action of *iso*-propyl alcohol or *n*- or *iso*-butyl alcohol or cyclohexanol upon naphthalenesulfonic acids, and also their condensation products with aldehydes. These include diamylnaphthylaminesulfonic acid, benzylsulfanilic acid, butylsulfanilic acid, butylaminonaphthalenesulfonic acid, diethylmetanilic acid, and sodium stearoanilidosulfonate.

The application of the process is indicated in the following:

1. 1 part colophony is dissolved in 1 part heavy benzine. This solution is converted into a mass having the consistency of ointment by stirring it into a solution of sodium *iso*propylnaphthalenesulfonate to which glue has been added, the mass being then diluted with water. In this manner a very stable emulsion of the resin is obtained, excellently adapted for dressing or finishing fabrics.

2. 1 part nitrocellulose lacquer or copal varnish prepared with water-insoluble solvents and colored with a dyestuff insoluble in water, is treated with the aqueous solution of a mixture of sodium butylnaphthalenesulfonate and glue. A colored emulsion of the lacquer is obtained which can be used for dyeing, finishing or dressing.

3. 2 parts lacquer prepared from water-insoluble solvents and containing Indanthrene brilliant violet RK in colloidal distribution, are treated with 3 parts of 40% solution of sodium dibutylsulfanilate, and diluted with water.

The preparation of methyl-, ethyl- and benzyl-cellulose masses in a very fine state of comminution as pastes, especially those cellulose ethers of fibrous structure, may be

1. I. G. Farbenindustrie, E. P. 264860; abst. J. S. C. I. 1928, **47**, 648-B; Chem. Zentr. 1927, II, 330.

accomplished in an economical manner and uniform products obtained therefrom[1], if the etherized cellulose is subjected once or several times to mechanical tearing by friction rollers, in the presence of non-solvents or solvent mixtures of low dissolvability, insufficient in power to dissolve or gelatinize the cellulose ether. The structure can almost be destroyed in this manner, as by passage through a pair of closely arranged rotating friction rollers followed by further comminution by grinding. The comminuting effect may be enhanced by arranging the rollers so that they rotate in opposite directions, and at the same time are laterally displaced in opposite directions.

Refer also to topic "Emulsions."

Electrodeposition of Cellulose Ethers. The invention of S. Sheppard and C. Beal for the electrical deposition of cellulose ethers[2] has for its object the production of an electrically deposited coating of maximum uniformity. Sometimes the coatings deposited become uneven and have undesirable thin spots or pits which impair them, due usually to locally generated currents and small electromotive forces which prevent or reduce the deposit of material at certain points. This may be overcome according to the patentees, by rendering the surface upon which the cellulose ether is to be deposited, electro-conductive by previous coating with a layer of colloidal material permeable to the dispersion medium of the emulsion, and adapted to form a diffusing path for the electric current at such surface.

The coated surface is then brought into contact with the emulsion and the depositing current passed through the coated surface and the emulsion. It has been found that water-insoluble ethylcellulose will deposit particles to form a coating having the desired properties more readily, if a suitable solvent or coalescing agent is present in the

1. I. G. Farbenindustrie, E. P. 330957; abst. C. A. 1930, **24**, 6013; J. S. C. I. 1930, **49**, 814-B; Nitrocellulose, 1931, **2**, 104.
2. E. P. 251271; abst. J. S. C. I. 1927, **46**, 850-B; Chem. Zentr. 1926, II, 3080.

droplets, or in the liquid containing the droplets[1]. The ethylcellulose is dissolved in a mixture of benzene-alcohol 1:1 to a 30% solution of the cellulose ether, stirred into an aqueous bath to form an emulsion, and electrodeposited. Where water-insoluble cellulose ether solvents are used as acetylene tetrachloride or benzene, they remain in the droplets in useful quantities, for when the droplets are electrodeposited there is sufficient solvent present to act as a coalescing agent, enabling the particles to be brought together as a uniform or blended coating.

In the electrodeposition of a cellulose ether on anodes from aqueous solutions[2], the coating sometimes becomes impaired by oxidation from nascent oxygen liberated at the anode when high current densities are employed. Under these conditions the process is apt to be slowed down by polarization at the anode, due to liberated oxygen, bubbles of oxygen tending to inhibit the continuity and smoothness of the deposit. These difficulties may be substantially avoided by having present in the anode zone during the deposition, a metal which has a greater affinity for nascent oxygen than has the deposited cellulose ether. Examples of suitable metals are zinc, cadmium and magnesium. The anode surface upon which the cellulose ether is to be deposited may be coated with the metal, or the whole article upon which the anode surface is located may be of the desired metal.

The liberation of oxygen at the anode may be wholly or partially counteracted by chemically combining the oxygen at the time when it tends to be electrolytically libe-

1. L. Eberlin and C. Beal, U. S. P. 1589327, 1589328; abst. J. S. C. I. 1926, **45**, 793-B; Chem. Zentr. 1926, II, 1344.

2. C. Beal and L. Eberlin, U. S. P. 1589324; abst. Plastics, 1926, **2**, 366; J. S. C. I. 1926, **45**, 793-B; Chem. Zentr. 1926, II, 1343. U. S. P. 1476374; abst. J. S. C. I. 1924, **43**, 104-B; Ann. Rep. S. C. I. 1925, **10**, 411; 1926, **11**, 400. E. P. 251979; abst. Kunst. 1929, **19**, 90; Chem. Zentr. 1926, II, 3080.

rated[1]. The oxygen is removed by means of a reducing agent as a sulfur compound (sodium or ammonium sulfite, thiosulfate or hydrosulfite) which reacts with the oxygen to release products compatible with the deposited metal and with the emulsion. These sulfo-bodies combine with the liberated oxygen to form polythionates which assist in maintaining dispersion of colloidal sulfur in the emulsion.

Useful coatings containing both rubber and cellulose ether may be simultaneously electrodeposited upon conducting surfaces of objects, by first providing separate emulsions of unvulcanized rubber, of vulcanizing material as sulfur, and of cellulose ether. Or rubber latex having about 30% rubber therein may be used, preferably stabilized by rendering alkaline with ammonia[2]. The sulfur emulsion is readily prepared by mixing 20% of comminuted sulfur into a 0.5% solution of glue in water by means of a high speed colloid mill. The other emulsion is prepared by dissolving 50 parts water-insoluble ethylcellulose in 150 parts of benzene-alcohol 1:1, the solution being then stirred into the aqueous bath containing the colloid and emulgent, and then homogenized. Turkey red oil is a good emulgent in this connection.

Strengthening Cellulose Ethers. The strength and elasticity of cellulose ethers, especially in film and filament form[3], may be increased by incorporating in the solution of the etherized cellulose, a cementing substance either as such, or in the form of its components, or of an intermediate product which solidifies by polymerization, condensation or auto-oxidation to form the desired cementing material. The cementitious component may be a synthetic

1. S. Sheppard and L. Eberlin, U. S. P. 1580795; abst. J. S. C. I. 1926, **45**, 639-B; Ann. Rep. S. C. I. 1926, **11**, 400; Chem. Zentr. 1926, II, 501. E. P. 253085; abst. J. S. C. I. 1927, **46**, 62-B; Chem. Zentr. 1926, II, 1796. E. P. 253091; abst. Chem. Zentr. 1926, II, 1796.

2. *Ibid.* U. S. P. 1589332; abst. J. S. C. I. 1926, **45**, 794-B; Chem. Zentr. 1926, II, 1344. U. S. P. 1589330; abst. J. S. C. I 1926, **45**, 794-B; Chem. Zentr. 1926, II, 1344.

3. I. G. Farbenindustrie, E. P. 294485; abst. C. A. 1929, **23**, 2032; Silk J. 1928, Nov., 90; Chem. Zentr. 1929, I, 171; Kunst. 1929, **19**, 67.

resin or product of linseed oil oxidation, or produced by means of bodies which enter into chemical combination with the hydroxyl group or ether radicals of the cellulose.

Films may be made from a solution of ethylcellulose to which linseed oil has been added, or to a solution of cellulose ether is added urea and hexamethylenetetramine, films cast from this solution being subsequently heated. There is a difficulty in operating this process, in that in the drying step there is a separation of water due to the resin condensation, and this water disturbs the required hardening of the gel. It has, however, been observed that the cellulose ether may be strengthened by means of a cementing substance as the condensation product from urea or phenol and formaldehyde[1], and without causing the cellulose ether to lose its characteristic solubility in organic solvents, the only difference between the solidified and non-solidified cellulose ether is that the former has a higher viscosity, indicative that the size of the particles of the material has been increased by the adhesive nature of the cementing substance. Correspondingly, the cellulose ether shows a higher strength by pretreatment in this manner. The following examples illustrate the invention:

1. 17 gms. finely pulverized ethylcellulose soluble in benzene are allowed to stand 12 hrs. in 200 cc. of a solution of 2.5 gms. of a condensation product of crude cresol and formaldehyde, soluble in water, in 1000 cc. of water, and after thorough pressing, are dried 3 hrs. at 140°. From the pretreated cellulose ether thus obtained, products may be obtained by dissolving it in 140 cc. benzene and working up in the usual manner. Such a film has a strength about 25% higher and an extensibility about 21% greater than that made from a film of the untreated cellulose ether.

2. 17 gms. ethylcellulose are treated as in Ex. 1, and left 12 hrs. in contact with 200 cc. solution of 2.5 gms. each urea and hexamethylenetetramine in 1000 cc. water. After

1. I. G. Farbenindustrie, E. P. 293350; abst. C. A. 1929, **23**, 1750; Silk J. 1928, **5**, #53, 108; Chem. Zentr. 1928, II, 2206.

thorough pressing the material is heated 3 hrs. at 140°. From the cellulose ether thus pretreated and dissolved in 140 cc. benzene, films or fibers may be made of 36% augmentation in strength.

Cellulose Glycol Ethers. Cellulose Chlorhydrins. Hydroxyalkylcellulose. The Farbenfabriken vorm. F. Bayer & Co.[1] were the first to describe a process for the production of glycolcellulose, their method being to treat hydrocellulose, oxycellulose or cellulose hydrate with ethylene oxide or its homologues or analogues. Cellulose is treated with an excess of ethylene oxide in a closed vessel. According to the temperature, time of treatment and proportion of reactants to cellulose, the resulting cellulose ether possesses a fibrous structure although there is an increase in weight and reactivity, or else the cellulose swells to many times its original volume, forming a gelatinous mass in water or organic solvents, or else being soluble therein. The reaction is accelerated in the presence of a catalyst.

The lower alkylated celluloses are obtained by heating together 1 part cotton with 10 parts ethylene oxide for 10 hrs. at 100°. The reaction is then stopped, excess of reactant distilled off, the cellulose washed with water and dried. The yield is over 100%. The ether possesses an extraordinarily high reactivity, may be readily acetylated[2], nitrated or alkylated or otherwise treated. Depending upon the proportion of ethylene oxide to cellulose, a wide range of products may be produced as judged by their properties, especially solubility and viscosity.

1. (E. Hubert) D. R. P. 363192; abst. J. S. C. I. 1923, **42**, 348-A; Chem. Zentr. 1923, II, 276; Chem. Tech. Uebers, 1923, **47**, 6; Faser. 1923, **5**, 44.

2. F. Bayer & Co., 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. Zentr. 1905, II, 527; Wag. Jahr. 1905, **51**, II, 190; Jahr. Chem. 1905-8, II, 984; Chem. Ztg. 1905, **20**, 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.

If 1 part regenerated cellulose is heated with 10 parts ethylene oxide for 30-60 hrs. at 100°, the excess distilled off and the product washed with alcohol and dried, a water-soluble glycolcellulose is obtained in 130% yield. If heated with ethylene oxide beyond the period of water solubility, higher glycol ethers are formed which are insoluble in water. By the addition of catalyzers, reaction can be so accelerated that it may take place at ordinary temperatures. For example, if 1 part cellulose is treated with 10 parts ethylene oxide and 10 parts dimethylaniline and the mass allowed to stand in a closed vessel, the cotton increases 5-15% in weight in 2-4 days. By heating, a yield as high as 200% may be obtained, but still retaining the cellulose structure.

In an improvement on the above process[1], homologues of ethylene oxide are described as desirable alkylating agents, as ethylene sulfide, ethyleneimide, propylene oxide, trimethylene oxide, methylphenylethylene oxide and diphenylethylene oxide. Also fumacylglycidic acid and its esters. As an example, 100 parts dried potato, rice, corn or other starch are treated with an excess of ethylene oxide for 6 hrs. at 90-110° with stirring. The cellulose assumes a gummy form of high elasticity. The mass is extracted with alcohol and precipitated from the reaction mixture. When dextrin is similarly treated, a glycoldextrin results.

H. Peters[2] heats cellulose for some time with dichlorhydrin or epichlorhydrin in the presence of palmitic acid, and then adds a solution of formic acid to react thereon while the mixture is hot. Thus, 10 gms. cellulose are heated 4 hrs. in 80 gms. dichlorhydrin or epichlorhydrin and 0.5 gms. palmitic acid at 120°. After the mass has cooled, the hydrin is thoroughly pressed out and the mass dried. The cellulose is then placed in a bath of 10 gms. methylated

1. (O. Leuchs and E. Hubert) D. R. P. 368413 Addn. to D. R. P. 363192; abst. J. S. C. I. 1923, **42**, 620-A; Chem. Zentr. 1923, II, 755; Chem. Tech. Uebers, 1923, **47**, 77.

2. U. S. P. 1008557; abst. C. A. 1912, **6**, 293; J. S. C. I. 1911, **30**, 1447; Mon. Sci. 1912, **77**, 163. F. P. 432747; abst. J. S. C. I. 1912, **31**, 124; Mon. Sci. 1913, **79**, 130; Chem. Ztg. 1912, **36**, 209.

spirit. While this process was primarily designed as a pretreatment method of cellulose for esterification purposes, there is no doubt but that etherification of the cellulose takes place.

Commercial methods for the preparation of the glycolcelluloses and analogous ethers may be classified under the following five headings as follows:

1. *Methods of H. Dreyfus.* Cellulose is treated with substitution products of glycols as ethylene chloride, propylene chloride, ethylene chlorhydrin, propylene chlorhydrin, glyceryl mono- and di-chlorhydrin or epichlorhydrin, one or more of the hydroxyl hydrogens of the cellulose combining with one or more halogen atoms of the substitution product, forming corresponding cellulose ethers. Cellulose or conversion products as alkalicellulose, preferably of minimum depolymerization, may be treated with the halogen substitution product. Little or no water is employed in the reaction, the total amount of water present or added in the etherification, disregarding water formed in the etherifying reaction itself, is preferably between 50-150% of the weight of the cellulose used.

The process may be carried out as follows: Cellulose is impregnated with 50% NaOH solution so that 4 molecular equivalents of NaOH are contained in it relative to 1 molecule of cellulose. The mass is kneaded 0.5 hr. with 2-3 mols. ethylene chlorhydrin while cooling at about 0°, and the reaction product treated with a further 6 mols. powdered NaOH, the mass then kneaded 0.5 hr. with a further 3-5 mols. ethylene chlorhydrin. The cellulose ether is then precipitated, washed and dried[1].

Or[2], cellulose is caused to react with an aliphatic etherifying agent as ethylene chlorbromide, epichlorhydrin, 2.2′-

1. U. S. P. 1502379; abst. C. A. 1925, **19**, 176; J. S. C. I. 1924, **43**, 743. E. P. 277721; abst. C. A. 1928, **22**, 2663; J. S. C. I. 1927, **46**, 872-B; Plastics, 1928, **4**, 509; Chem. Zentr. 1928, I, 445. Belg. P. 339733.

2. E. P. 346806; abst. C. A. 1932, **26**, 2052; J. S. C. I. 1931, **50**, 626-B. Can. P. 311408. F. P. 39246, 39247 Addn. to F. P. 704871; abst. C. A. 1932, **26**, 2316.

dichlor-1-bromethane, 1-chlor-2-iodoethane, 2-chlor-1-brompropane or 3-chlor-1-brompropane. When a reagent containing an alkylene oxide group is used, the etherification is effected in the absence of alkali, but when the etherifying agent contains halogen, bases such as 40-50% NaOH should be present. The ethers produced may be treated with ammonia or organic amines to produce cellulose aminoethers which have a pronounced affinity for acid dyes.

Cellulose which has had a portion of the hydroxyls esterified as a cellulose acetate[1], dissolves directly in ethylene glycol, diethylene glycol, propylene glycol, trimethylene glycol and 1.2- and 1.3-butylene glycol at elevated temperatures to form transparent solutions which yield desirable films and filaments upon evaporation of solvent. For instance, when cellulose acetate is treated with ethylene glycol and the temperature gradually elevated to 180° with glycol, or to 210° if glycerol is used, the former gradually passes into solution, the viscosity depending upon the proportion of cellulose acetate used and the time and temperature of heating. Pigments may be added to the mass before treatment[2] to produce opaque films or low luster filaments.

2. *Processes of L. Lilienfeld.* In the production of oxy- and hydroxy-alkylcellulose by the disclosures of Lilienfeld by acting upon cellulose in the presence of an alkali with a monohalohydrin of a poly-alcohol, the essential feature is that the strength of aqueous alkali used is not greater than 25-30%. The cellulose ethers thus prepared[3] are soluble in aqueous alkalis, but insoluble in water, alcohol, acetone, glacial acetic acid, benzene, chloroform or ether, and are precipitable from their solutions in alkalis by acids, salts, alcohol or acetone. These cellulose ethers, in general, are distinguished for their inertness, stability towards alka-

1. F. P. 713857; abst. C. A. 1932, **26**, 1784.
2. F. P. 694119, 698093, 702174; abst. C. A. 1931, **25**, 4125.
3. U. S. P. 1722927; abst. J. S. C. I. 1929, **48**, 774-B. E. P. 231807; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 913-B; Ann. Rep. S. C. I. 1925, **10**, 149; 1926, **11**, 618. Aust. P. 108139. Cf. U. S. P. 1502379, 1722928. E. P. 164374, 166767. D. R. P. 363192.

lis, durability, and transparency and flexibility of films made therefrom. The process is indicated from the following details:

100 parts cellulose are soaked in 1000-2000 parts 18% NaOH solution at 15-20° until uniformly impregnated, allowed to stand in a tightly closed vessel at ordinary temperature for 3-24 hrs., then pressed to 3.5 times the weight of the original cellulose and comminuted in a shredder. It is then stirred or kneaded with 30-60 parts *a*-monochlorhydrin (chlorpropylene glycol), care being exercised that an intimate mixture is obtained. The mass is afterwards stirred for an hour or two and samples periodically withdrawn for testing purposes. After a few hours the mass becomes soluble in 5-10% NaOH solution but practically insoluble in water, retaining the original structure of the alkalicellulose before dissolving. The cellulose ether may be used directly in a 4-8% sodium hydroxide solution, or the reactants first washed out and then dissolved in dilute alkali.

A woven textile may be superficially etherified by the formation thereon and therein of glycolcellulose or hydroxyalkylcellulose[1], by treating the woven or spun fabric first with a solution of alkali, then acting upon the textile with a halohydrin as *a*-monochlorhydrin or ethylene chlorhydrin. The cloth is impregnated first with a 12-40% NaOH solution, then with a halohydrin as above indicated. This method is said to be especially applicable for the formation of differential effects by printing with the halohydrin in a viscous solution as with British gum, the goods being afterwards steamed or otherwise treated depending upon the depth of effect desired.

Cellulose may also be treated with one or more olefine halides as ethylene mono- or tri-chloride and acetylene dichloride in the presence of an alkali or other basic substance, cellulose ethers being formed. With protracted

1. E. P. 231804; abst. C. A. 1925, **19**, 3600; J. S. C. I. 1925, **44**, 801-B; Ann. Rep. S. C. I. 1925, **10**, 184; Chem. Zentr. 1926, I, 506.

etherification, a solubility is obtained in the usual range of organic cellulose ether solvents[1].

3. *Manufacture According to I. G. Farbenindustrie.* Ethers of cellulose, starch and other carbohydrates may be made by the reaction thereon of alkylene oxides in the vapor state under reduced atmospheric pressure[2], as indicated in the following examples:

a. 10 kilos sulfite cellulose are imbibed at 20° with 18% NaOH solution, pressed to 28 kilos, allowed to stand 48 hrs. at 20°, then introduced into a rotating nickel autoclave. The temperature is regulated to 20°, after which 6 k. ethylene oxide in gaseous form is uniformly admitted during 6 hrs. under a pressure of 50 mm. At the close of the reaction, the product is treated with methyl alcohol and dried at 40°. Yield 15.6 k. The product is soluble in water and is not coagulated by aqueous sodium sulfate solution of 2/*N* strength.

b. 10 k. cellulose precipitated from cellulose xanthate (regenerated cellulose) are placed in an autoclave, 4 k. propylene oxide admitted uniformly during 15-20 hrs., at 80-100°. The cellulose ether obtained is insoluble in water, but dissolvable in dilute alkali solutions.

The depolymerization or degradation of carbohydrates of high molecular weight may be accomplished without the use of alkali[3] by treatment with ethylene glycol or monochlorhydrin, the carbohydrate being simply boiled with the depolymerizing agent under reflux until the required degree of degradation has been reached. An important advantage in the use of monochlorhydrin as the depolymerizing agent is that it completely dissolves normal or unmodified cellulose or starch, products being obtained which are soluble

1. F. P. 719338; abst. C. A. 1932, **26**, 3376.
2. F. P. 700880; abst. C. A. 1931, **25**, 3833. Can. P. 309503. See F. P. 694696; abst. C. A. 1931, **25**, 2017. F. P. 697156; abst. Chem. Zentr. 1931, II, 2951.
3. U. S. P. 1714565; abst. C. A. 1929, **23**, 3543; J. S. C. I. 1929, **48**, 936-B; Chem. Zentr. 1929, II, 1747. E. P. 290377; abst. C. A. 1929, **23**, 981; J. S. C. I. 1928, **47**, 515-B; Chem. Zentr. 1928, II, 1818.

in alcohol and water, which no longer exert a reducing action, and which on hydrolysis with acids yield sugars. The products are light colored oils having a sweet taste and a bitter aftertaste, and are insoluble in ether. The following three examples are illustrative:

a. 500 parts ethylene glycol are heated to boiling and 100 parts starch dissolved therein with stirring. After heating to boiling for 2.5 hrs. the reaction mixture ceases to give a color with iodine. The glycol is distilled off at 88° at 8 mm. vacuum. The remaining residue is easily soluble in alcohol and has the appearance of a clear syrup.

b. 500 parts glycol are heated to boiling with 100 parts starch. After the addition of 5 parts monochlorhydrin and continued boiling for about 5 min., the iodine reaction becomes negative. Total duration of heating, 30 min. The product is an oily liquid easily soluble in water or alcohol, insoluble in ether. It does not reduce Fehling's solution.

c. 100 parts monochlorhydrin are heated to about 180° and 10 parts cotton introduced. After 1-1.5 hrs. heating, 85% of the cellulose has dissolved and is soluble in water and alcohol.

Hydroxyalkylcelluloses are also formed by the action of ethylene oxide or its homologues on cellulose in the presence of aqueous ammonia or hydroxyalkoxyamines as catalysts[1].

The reaction between cellulose or alkalicellulose may be carried out by causing gaseous alkylene oxides to react under reduced pressure[2], or a mixture of the gaseous alkylene oxide with an indifferent gas. The cellulose ethers formed are insoluble in alcohol, acetone, acetic acid and methylene chloride, but dissolving in warm or cold water to a colloidal solution, particularly when certain hydrogen ion concentrations are maintained. Excess of NaOH adhering may be removed by alcohol, hot water or water con-

1. F. P. 708538; abst. C. A. 1932, **26**, 3667.
2. E. P. 359618; abst. J. S. C. I. 1932, **51**, 224-B.

taining salt. They are loose, fibrous, colorless, resembling the parent material. On addition of hot or cold water there is an immediate pronounced swelling, dissolving upon the addition of a few drops of NaOH solution to a clear and ropy solution, which is coagulated by the addition of acetone or higher aliphatic alcohols.

Depending upon the working conditions, temperature, duration of action, concentration of the alkylene oxide, concentration of NaOH solution used or of the alkaline swelling agent employed, the products have wide variations in water solubility, viscosity and other characteristics. The hydroxylcelluloses may be soluble in 3-4% HCl, in water, or in 4% NaOH solution. They are prepared as indicated herewith:

1. 10 parts sulfite cellulose are soaked at 20° with 18% NaOH solution, squeezed to 28 parts and disintegrated. After ripening 48 hrs. at 20°, the product is introduced into a revolving autoclave which is then evacuated. After adjusting the temperature to 20°, 6 parts gaseous ethylene oxide are introduced in the course of 6 hrs., while maintaining a pressure of 50 cm. mercury, the temperature of the reaction being kept at 20° by cooling. After the reaction is complete, air is allowed to enter the apparatus, the product is freed from alkali by means of methyl alcohol and is then vacuum dried at 40°. The product is soluble in water of P_H value = 9 and is not coagulated by 9% sodium sulfate solution.

2. 10 kilos linters are soaked at 0° in a vacuum in 28% NaOH solution, squeezed to 24 k. and freed from alkali by washing with water at 40°. After drying at 40° *in vacuo* the product is introduced into a revolving nickel-plated autoclave, and 4 k. gaseous ethylene oxide under 0.5 atms. pressure introduced. The cellulose ether obtained is insoluble in water of P_H value = 5, but is soluble in water of 11 P_H value to ropy, clear, fiberless and highly viscous solution.

4. *Procedure of Societe pour L'Industrie Chimique a Basle.* Hydroxyalkylcelluloses and esters derived therefrom (as acetylcellulose-chlorhydrin-ether) may be obtained from cellulose as linters, or a cellulose derivative as acetylcellulose[1]. The invention is clarified by the following examples:

a. 100 gms. epichlorhydrin are gradually mixed while cooling, with 3 gms. concentrated sulfuric acid. The solution of chlorhydrin-sulfuric acid ester in epichlorhydrin thus obtained is heated with 10 gms. alkalicellulose for 35 hrs. at 130-140°. When the reaction is concluded the cotton or yarn is pressed and carefully washed. It is pure white and contains a cellulose ether having a replacement halogen atom.

b. In a suitable stirring apparatus 1 k. epichlorhydrin is mixed with 25 gms. boric acid, and there are added at the boiling point of the epichlorhydrin and during 50 hrs., 100 gms. partially acetylated cellulose in the form of yarn. When the reaction is complete the yarn is washed with benzene, then alcohol and finally with water. The product has similar properties to those of the product of (a).

c. 20 gms. partially acetated cotton yarn are impregnated with a 10% aqueous boric acid solution at 60-70°, well pressed and dried. The yarn is then treated for 50 hrs. with epichlorhydrin vapor at 120-130°. Same properties as in (b).

d. 100 gms. acetone-soluble cellulose acetate, 5 gms. boric acid and 500 gms. epichlorhydrin are heated 24 hrs. in a closed vessel at 130-135° while stirring. The viscous, liquid reaction mass thus obtained is extracted with petroleum ether to recover excess epichlorhydrin, and the residue washed with water. The glycolcellulose acetate thus obtained is a colorless mass, soluble in acetone, and may be worked up similar to cellulose acetate.

Nitrogen may be introduced into the cellulose ether molecule above by proceeding as follows, the products

1. E. P. 360742. F. P. 709122.

formed having an affinity both for cotton dyestuffs and acid wool colors.

e. The yarn as described in (a), (b), (c) or (d) is heated with 10 times its weight of pyridine for 8 hrs. on the waterbath. The pyridine is then expressed and the yarn washed. The product is particularly dyed with acid dyestuffs. Dimethylaniline may replace pyridine.

f. 100 gms. acetylcellulose-chlorhydrin ether are heated 16-20 hrs. at 60-70° with a 2% solution of trimethylamine in toluene.

A somewhat similar process has been described by H. Suida[1], who treats cellulose with an alkylene oxide in the presence of concentrated aqueous ammonia, or with an aqueous solution of a hydroxyalkylamine as a catalyst. A. Geake and M. Nierenstein[2] find that amino acids, their hydrochlorides or esters are not methylated by the action of diazomethane in ethyl ether solution, being recovered unchanged, while carbethoxyglycocoll gives the methyl ether.

5. *Imperial Chemical Industries Process* is particularly directed to the production of cellulose ethers which are soluble in water, and prepared by the action of ethylene chlorhydrin on alkalicellulose. The alkalicellulose is first allowed to mature between 10-35° for 60-96 hrs. and then etherified by admixture with powdered NaOH and ethylene chlorhydrin for about 8 hrs. at 100°. The production of glycolcellulose is indicated in the two examples herewith:

a. 100 parts cellulose are mercerized for any period up to 24 hrs., but preferably for 1 hr. with 18-25% NaOH solution, the mass pressed to 200-400 parts, shredded, and matured 2 days at 15-35°. The alkalicellulose is then thoroughly mixed with 100-150 parts powdered NaOH and 150-200 parts ethylene chlorhydrin, and then heated to 80-100° for 8 hrs. A further 50-100 parts powdered caustic soda

1. Aust. P. 125234; F. P. 708538; abst. C. A. 1932, **26**, 1439.
2. Zts. physiol. Chem. 1914, **92**, 149; abst. C. A. 1914, **8**, 3563; J. C. S. 1914, **106**, i, 1146.

and 150-200 parts ethylene chlorhydrin are again added, and the mixture heated a further 8 hrs. after which 50-100 parts ethylene chlorhydrin are added and heating continued 8-10 hrs. longer. The reaction product is a yellow, sticky mass which may be made into a viscous solution with water, and dialyzed until free from alkali and chloride. The glycolcellulose is then precipitated by acetone, filtered, washed with acetone then with ether. It is a white fibrous material readily soluble in water to a very viscous solution.

b. 100 parts cotton are transformed into alkalicellulose as above, and after maturing, mixed with 80 parts powdered NaOH and 200 parts ethylene chlorhydrin, and the whole heated 5-7 hrs. in a steam heated reaction kettle with stirring at about 100°. 30 parts NaOH and 80 parts chlorhydrin are then added and heating continued 5 hrs. longer. The cellulose glycol ether obtained is a brownish, sticky mass. It is malaxated with alcohol for 10-30 min. then filtered. After several such treatments it is washed with ether, when it is obtained in a white fibrous condition, the sodium chloride being free by washing with aqueous alcohol. Glycolcellulose as produced by this process is insoluble in benzene, ether, acetone and chloroform. With water the glycol ether gives clear, viscous solutions[1].

Hydroxypropylcellulose. A. Schorger[2] has described a comprehensive process for producing hydroxyalkylcelluloses as hydroxypropylcellulose and hydroxybutylcellulose, by etherifying cellulose or alkalicellulose with ethylene oxide, propylene oxide, butylene oxide or amylene oxide, or the chlorhydrins corresponding to them. It was found that the higher the number of carbon atoms in the reactive etherifying compound, the more difficult is it to effect the reaction, both increased time and heat being necessary. These hydroxycellulose ethers are almost instantaneously producible at room temperature by reacting upon moist

1. E. P. 343873; abst. J. S. C. I. 1931, **50**, 480; Brit. Plastics, 1931, **3**, #28, 63.
2. U. S. P. 1863208.

alkalicellulose with ethylene oxide or homologue in gaseous form. A vigorous exothermic reaction is initiated, especially when the alkalicellulose contains the amount of moisture normally left after squeezing at the close of the mercerization treatment. No excess of oxide is required, as the reaction is practically quantitative. If insufficient oxide is added so that some of the reaction products remain insoluble in an aqueous caustic soda solution at room temperature, it is necessary but to freeze the product in the caustic solution to obtain practically complete apparent solubility.

Whereas the hydroxyalphylcelluloses heretofore described by the action on cellulose of chlorhydrins contain at least one replaceable hydroxyl hydrogen atom per cellulose unit, the cellulose ethers producible under the Schorger process contain less than one hydroxyl hydrogen atom, yet are soluble in 10% NaOH solution, but insoluble or but slightly soluble in a corresponding strength of KOH solution. It is considered that a dicellulosehydroxyalkyl ether is produced (13.6% ethyleneoxide content) of the formula (ethyl ether) of $C_6H_{10}O_5$-$C_5H_7O_4$.CH_2OCH_2.CH_2OH. When less than 15% ethylene oxide is used, the alkalicellulose from cotton linters and ethylene oxide should be kept at about 0°, and must be carefully controlled so that only a small residue insoluble in dilute caustic soda solution remains. It is believed that under the reaction condition, the union of cellulose and ethylene oxide is effected by the substitution of ethylene oxide radical for the hydrogen atom of hydroxyl groups (preferably primary) of a cellulose unit, or two or more linked cellulose units, whereby one valence of the oxygen atom is replaced by an hydroxyl hydrogen atom of the cellulose molecule to form an hydroxyl group attached to the ethylene radical. In the accompanying Fig. 5 (page 1392) Fig. *1* illustrates the apparent solubility of a series of cellulose ethers in caustic soda solution, Fig. *2* the increased solubilities over those in Fig. *1* produced by freezing, Fig.

3 the apparent solubilities in caustic potash solution, and Fig. 4, the effect of freezing to increase solubility.

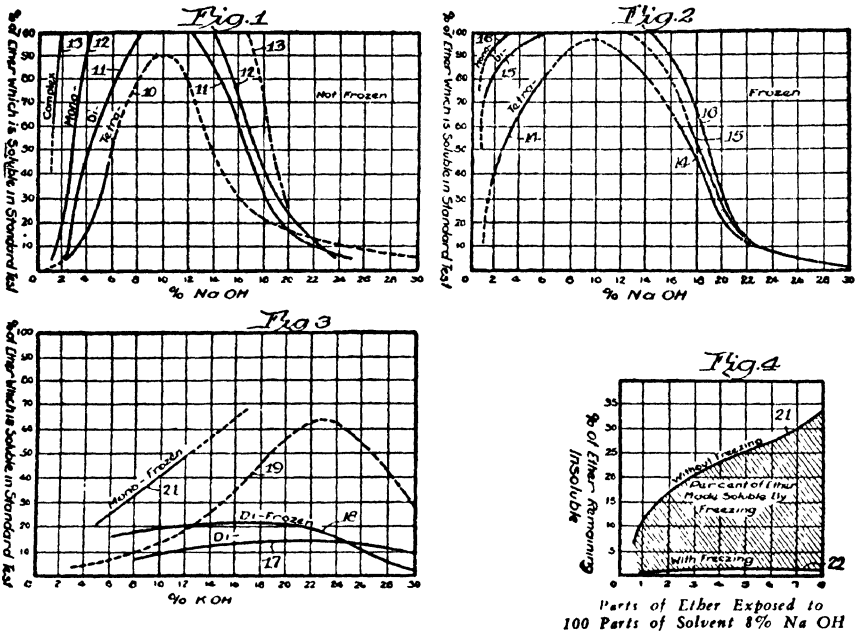


Fig. 5. Solubility Cellulose Ethers in NaOH.

The general scope of the process is indicated by the following methods of manipulation:

I. *Water-insoluble Cellulose-ethylene Oxide of 20% Ethylene Oxide.* 100 parts linters are thoroughly stirred into 1500 parts 30% NaOH solution, and after stirring a few minutes, the mass is squeezed to about a 30% cellulose, and is then shredded. The alkalicellulose is aged 24 hrs. at 20°, then placed in an evacuated pressure chamber with stirrers and cooled. While the alkalicellulose is being stirred, 20 lb. gaseous ethylene oxide are admitted at a rate which does not allow the reacting mass to rise above 100°. For best results temperature is kept below 45°. The resulting product is still fluffy and retains the physical megascopic form and structure of the linters. The product may be processed in either of the following two ways:

a. Dilute hydrochloric or sulfuric acid 5-10% strength is used to neutralize excess alkali. If the fibrous compound is stirred into the acid vigorously, local formation of gel spots may be prevented and the resulting products retain a fluffy, fibrous form. After neutralization, the product consists of the cellulose-ethylene oxide compound, hydroxyethylcellulose. After washing with water to remove sodium salts and drying, the cellulose ether remains as a fluffy fibrous mass, which is indefinitely stable. Soluble in dilute caustic soda solution.

b. The purified product from (a) above is stirred into water to a cellulose concentration of 5.5-8% (based on original cellulose weight). There should be sufficient NaOH present to show 2-2.5% free NaOH. The cellulose compound forms a clear, viscous solution, practically without residue. The solution is then passed through dies or formed into suitable shapes for films or masses, passed directly into an acid coagulating bath, and the gel washed with water and dried.

II. *Cellulose Ether of 7% Ethylene Oxide Using Refrigeration.* Sheets of high alpha-cellulose wood pulp are immersed in 30% NaOH solution as in the foregoing example, shredded, and placed in a closed reaction chamber with 7 parts gaseous ethylene oxide. After complete reaction, the mass is removed from the reaction chamber, dissolved in 6% NaOH solution, some undissolved residue being present. Enough water is added to the mass to bring the alkalinity to 4.75%, and the entire mass frozen to —20°. The mass is allowed to melt, NaOH added to produce a 6% caustic soda solution, a clear, viscous liquid resulting.

III. *Cellulose Ether of 12% Ethylene Oxide.* This product is said to be suitable for films of highest transparency, and is obtained by proceeding as in II, except that 12 parts ethylene oxide are employed, and a high grade wood pulp is used such as suitable for viscose rayon production. After refrigeration the product may be dissolved in a weaker solution of caustic soda needed to dissolve the

compound containing 7% ethylene oxide in II. A 4-5% NaOH solution is sufficient.

IV. *Water Soluble Cellulose Ethers from Wood Pulp and Ethylene Oxide.* The alkalicellulose is made as described in II. After excess caustic soda solution is removed from the wood pulp, it is allowed to stand in limited contact with the air for 24 hrs. or more, as by placing the alkalicellulose in a can with loosely fitting cover. The alkalicellulose is then etherified with a large amount of ethylene oxide, 75-95% based on original cellulose weight. The resulting compound is soluble in water and when neutralized by a mineral acid, coagulation does not take place. If acetic acid has been used as neutralizant, the sodium acetate formed may be removed by extraction with alcohol in which the cellulose ether is insoluble.

V. *Etherification with Ethylene Oxide in Solvents.* Alkalicellulose of I or II are treated with a 20% solution of ethylene oxide in benzene. The wet alkalicellulose is submerged in the benzene for 48 hrs. at about 4°, after which excess of benzene and ethylene oxide are removed. The resulting cellulose ether is soluble in weak alkali solutions, the etherification proceeding much slower in the liquid phase than in the vapor.

VI. *Cellulose Etherification with Liquid Ethylene Oxide.* Alkalicellulose as in I is immersed in liquid ethylene oxide for 24 hrs. at 4°, then removed, and excess of oxide removed by warming. The temperature may be increased to diminish the time required by using a pressure vessel.

VII. *Hydroxypropylcellulose of 12.4% Propylene Oxide.* Alkalicellulose of I is introduced into the reaction chamber, the latter evacuated, after which the requisite amount of propylene oxide vapor is introduced, about 12.4 parts propylene oxide being used. As propylene oxide boils at 35° it is desirable to carry on the reaction at this temperature. After the propylene oxide has been completely absorbed, the cellulose ether is recovered as previously described.

VIII. *Hydroxyalkylated Starch and Ethylene Oxide.* 100 parts ordinary corn starch containing 10% moisture are mixed with 200 parts 20% NaOH solution and thoroughly mixed until the reaction is completed. The alkalistarch is then introduced into the reaction chamber and treated with 15-17 parts ethylene oxide with stirring. A water-soluble translucent starch ether is formed, doughy and sticky. The excess NaOH may be dialyzed from the water soluble starch ether, excess alkali being neutralized with acetic acid, and the sodium acetate removed by alcohol extraction.

IX. *Hydroxyethylcellulose Using Ethylene Chlorhydrin.* Wet alkalicellulose of I is introduced into a pressure chamber with stirrer and false bottom. Into the chamber underneath the false bottom equal parts of 20% NaOH solution and ethylene chlorhydrin (sp. gr. 1.15) are introduced, enough of the two solutions being used to generate about 20 parts ethylene oxide. The bottom of the reaction chamber is then warmed to more quickly generate the ethylene oxide, which, after complete evolution and action upon the cellulose, the hydroxyethylcellulose is removed and purified.

X. *Making Dihydroxypropylcellulose.* Alkalicellulose made with 40% NaOH solution in fluffy shredded form is treated with 22.5 parts anhydrous glyceryl monochlorhydrin and the etherification carried out as explained above. This amount of glyceryl monochlorhydrin is equivalent to about 9% ethylene oxide. The resulting cellulose ether is very similar in properties to hydroxyethylcellulose.

XI. *Production of Hydroxyethylcellulose Benzoate.* 100 parts wood pulp containing 8.5% moisture are steeped in 30% NaOH solution at 18° for 45 min. The mass is squeezed to 350 parts, shredded and aged 21 hrs. at 19°. The alkalicellulose is then churned in a closed container 2.5 hrs. with 12 parts ethylene oxide. The ether is further agitated with 15 parts benzoyl chloride for 30 min. at room temperature in the presence of an excess of benzene. The resulting cellulose ether-ester is centrifuged to remove ben-

zene, dissolved in 4.75% NaOH, frozen and thawed. A 7.5% solution of the resulting compound is made up in 7.5% NaOH solution for use in film and filament manufacture. The process may be reversed in that the alkalicellulose may be first benzoylated and the cellulose benzoate then etherified with ethylene oxide with no appreciable difference in the final product.

Ethoxyethylcellulose. The disclosure of H. Dreyfus[1] involves the employment of glycol haloid esters, or ethers of polyhydric alcohols containing one or more hydroxy groups in interaction with cellulose to produce hydroxyalkyl ethers of cellulose in such a manner as to reduce the capacity for swelling or dissolving in water. This is brought about as shown in the example following:

98 parts of tri(hydroxyethyl)cellulose are impregnated with 100 parts 50% NaOH solution, allowed to stand 1-2 hrs., kneaded with 400-600 parts benzene, and during the mixing 200-240 parts calcium oxide are added gradually during 1-2 hrs., and while cooling. The actual etherification may then be conducted with the desired ethylating or other etherifying agent, as by means of 150-200 parts ethyl sulfate. When the reaction is complete the ethoxyethylcellulose is separated and washed with water in which it is insoluble. By etherifying with methyl sulfate, an ethoxymethylcellulose results.

Halogen containing cellulose ethers are prepared by treating cellulose or alkalicellulose with reagents containing an etherifying atom, and in addition at least one halogen atom. It is preferable to employ bodies containing different halogen atoms as ethylene chlorbromide, 2.2-dichlor-1-bromethane, 1-chlor-2-iodoethane, 2-chlor-1-brompropane or 3-chlor-1-brompropane[2]. Bodies containing the same halogen atom are in general more difficult to bring to reaction

1. E. P. 327157; abst. C. A. 1930, **24**, 5157; J. S. C. I. 1930, **49**, 610-B.

2. E. P. 277721; abst. C. A. 1928, **22**, 2663; J. S. C. I. 1927, **46**, 872-B; Plastics, 1928, **4**, 509; Chem. Zentr. 1928, I, 445. (As described in E. P. 327157.)

with cellulose to produce halogen-containing cellulose ethers. For example, ethylene dichloride when brought into reaction with cellulose in the presence of alkali usually gives products which do not contain chlorine. Ethylene bromide, on the other hand, can be brought to reaction with cellulose to form a bromethylcellulose, particularly in the presence of catalysts. The method of forming these haloalkylcelluloses is exemplified in the following two examples:

1. 162 parts linters are impregnated with 300 parts 50% NaOH solution, kneaded for 1-2 hrs., and 170 parts powdered NaOH then worked in. 400 parts ethylene chlorbromide are then added gradually, and the mass kneaded 2-4 hrs. at 20-40°. There is then further added 160 parts NaOH and 400 parts chlorbromide and the reaction allowed to proceed 2-4 hrs. longer. An additional caustic and chlorbromide is finally added and the temperature allowed to rise to 60°. The cellulose ether formed is washed with alcohol and dried[1].

2. Wood pulp is pretreated with alkali and then with formic or acetic acids[2] in liquid or vapor form[3], washed and dried. It is then allowed to steep over night in excess of epichlorhydrin. The steeped mass is then gently refluxed with 6-10 times its weight of epichlorhydrin for 4-8 hrs., or until a gain in weight corresponding to the cellulose ether desired is obtained. The cellulose may increase in weight 100-170%. The higher etherification products are soluble in chloroform-alcohol.

Mixed cellulose ethers result upon reaction of a simple or substituted alkyl halide and ethylene oxide or homologue upon alkalicellulose in the presence of a diluent and a catalyst, benzyloxyethylcellulose resulting from benzyl chloride, ethylene oxide and alkalicellulose and propyloxyethylcellulose from propyl chloride[4].

1. E. P. 346806; abst. J. S. C. I. 1931, **50**, 626-B. Can. P. 311408.
2. E. P. 249173 (as described in E. P. 346806). Can. P. 267551; abst. C. A. 1927, **21**, 1713. Ital. P. 232704.
3. E. P. 263938 (as described in E. P. 346806); abst. J. S. C. I. 1927, **46**, 247-B. F. P. 656654, described in E. P. 346806.
4. I. G. Farbenindustrie, F. P. 686598; abst. C. A. 1931, **25**, 592.

Chlorhydroxypropylcellulose obtained from cellulose or its derivatives and epichlorhydrin[1] may be converted by tertiary amines into nitrogenous cellulose compounds as propyloxyethylaminocellulose, having affinity for acid and direct dyes. Hydroxyalkylaminocelluloses as hydroxyethylaminocellulose or carboxyalkylcellulose esters (as ethylaminocellulose acetate) may be formed by aminating the corresponding hydroxyalkylcellulose or alkylcellulose ester with thionyl chloride, ammonia or amines[2]. Oxyalkylcellulose and hydroxyalkylcellulose[3] are especially indicated for coatings, sizes, finishes and cements.

H. Suida[4] prepares oxyalkylcelluloses through the use of ordinary concentrated ammonia in about the same amounts as the pyridine or dimethylaniline customarily employed, claiming that the water introduced with the ammonia acts to stabilize the ethylene oxide and obviate the possibility of explosions taking place. As an example, 12 parts bleached cotton linters are treated with 1.2 parts by weight of 23% aqueous ammonia and 60 parts ethylene oxide in an autoclave for 4 hrs. at 100°, the excess ethylene oxide then distilled off and the reaction product washed with water and dried. The product corresponds to a cellulose monoxyalkylether (monoxyalkylcellulose) and may readily be acetylated to a primary acetate. In place of ethylene oxide, propylene oxide or butylene oxide may be used, but the temperature and time of reaction must be correspondingly raised or lengthened.

In another method[5] cellulose or starch is treated at about atmospheric pressure and temperature with alkylene oxides in the presence of aqueous alkalis, the products ob-

1. Soc. Chim. Ind. Basle, E. P. 360742; abst. J. S. C. I. 1932, **51**, 256-B.
2. H. Dreyfus, E. P. 344480; abst. J. S. C. I. 1931, **50**, 626-B; Silk J. 1931, **8**, #86, 53. F. P. 704280; abst. C. A. 1931, **25**, 4705.
3. L. Lilienfeld, E. P. 231808; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 913-B; Chem. Zentr. 1926, I, 274. U. S. P. 1722928; abst. C. A. 1929, **23**, 4572.
4. Aust. P. 125234.
5. I. G. Farbenind. A. G., D. R. P. 550428; abst. C. A. 1932, **26**, 4174.

tained being soluble in water and in organic solvents. Instead of conversion of cellulose in an alkaline medium, acid may be used[1]. Thus, wood pulp may be digested in glacial acetic acid and sulfuric acid and then treated with a solution of ethylene oxide in benzene. The reaction product is filtered and directly acetylated with glacial acetic acid and acetic anhydride to give oxyethylcellulose acetate, soluble in acetone.

Tri(hydroxyethyl)cellulose. H. Dreyfus has described the etherification of hydroxyalkylcelluloses[2], the following example indicating the ethylation of tri(hydroxyethyl)cellulose, of which 98 parts are mixed with 100 parts 50% NaOH solution for 1-2 hrs., then mixed with 400-600 parts benzene, and during this operation, there is introduced gradually during 1-2 hrs. 200-240 parts of calcium oxide with cooling. The etherification is then carried on with the addition of ethyl sulfate, 150-200 parts of which are added gradually. After the reaction is terminated, the product is precipitated and washed to neutrality. It is insoluble in water[3].

Cellulose Xanthate-Chlorhydrin may be applied to reaction products of viscose and the chlorhydrins, and according to their mode of formation, chemical behavior and analytical results, the cellulose compounds in their free state are probably O-oxyalkylcellulose xanthic acids (dithiocarbonic-O-oxyalkylcellulose esters), and in the form of their salts, oxyalkylcellulose xanthates. In its simplest types, the reaction leading to the formation of these compounds represents the monocellulose ether of ethylene glycol and an *a*-monocellulose ether of glycerol. With the sodium alcoholate of monocellulose ether of ethylene glycol and carbon bisulfide, there results a xanthate of monocellulose-

1. I. G. Farbenindustrie, A. G., D. R. P. 542867, of April 9, 1930; abst. C. A. 1932, **26**, 4174. In this connection refer to O. Ernst, K. Sponsel, G. Balle and I. G. Farbenindustrie, D. R. P. 548456, Jan. 22, 1930, for the treatment of cellulose, starch and other carbohydrates with alkylene oxides as ethylene oxide, in the presence of aqueous alkalis.
2. F. P. 629099; Addn. 37753; abst. C. A. 1931, **25**, 4705.
3. H. Dreyfus, Can. P. 315360. E. P. 346793.

ethyleneglycol ether. With the sodium alcoholate of α-monocellulose ether of glycerol, there is formed the xanthate of α-monocellulose glyceryl ether.

The process may be carried out either by the action of a halohydrin upon alkalicellulose and the reaction mass washed and treated with NaOH solution and carbon bisulfide; or a halohydrin and carbon bisulfide are added simultaneously to alkalicellulose; or alkalicellulose is acted upon with a halohydrin and the product of reaction (an oxyalkylcellulose ether) isolated from the reaction mixture by dissolving in dilute alkali and afterwards precipitating with weak acid. The oxyalkylcellulose is then dissolved in NaOH solution and submitted to CS_2 in vapor form[1].

The general method of formation is indicated in the following concrete example: 10 parts wood pulp (9-10% moisture) or 10 parts linters (7-8% moisture) are steeped in 200 parts 18% NaOH solution at 15° for 3 hrs., pressed to 34 parts, shredded 3 hrs. at 12-13°, whereupon 1 part α-monochlorhydrin is gradually added and the mass kneaded 3 hrs. at 20°. The mass is then aged in a closed container at 20° for 21 hrs. A sample removed at that time is soluble in 10% NaOH solution and is precipitable by the addition of excess of acid thereto. The product is then washed free from alkali, pressed to about 3-4 times the weight of the parent cellulose, and then mixed with water and NaOH until the equivalent of 200 parts 18% NaOH is obtained. After remaining 3 hrs. at room temperature, it is pressed to 34-40 parts, again comminuted and 6 parts carbon bisulfide immediately added and kept in a closed vessel 10 hrs. at 19°. Excess CS_2 is removed by blowing and the xanthated mass dissolved to yield 5-7% dry residue of the washed and pressed oxyalkylcellulose xanthate and 8% NaOH.

The solution is practically free from undissolved particles and is precipitable with strong salt solutions as am-

1. L. Lilienfeld, U. S. P. 1858097. E. P. 335994 (Division of 335906); abst. Silk J. 1931, **7**, #80, 52. E. P. 335993 (Division of E. P. 335906); abst. Silk J. 1931, **7**, #80, 54.

monium or sodium chloride, alcohol or acids. The precipitate obtained with methyl or ethyl alcohols and stirring, when alcohol washed and dried at room temperature under reduced pressure, is almost colorless, readily soluble in alkali solutions, but precipitated by dilute acids. Analysis shows 1.79%-1.93% C_3H_7O, depending upon the analytical method used. The patent specification gives 27 additional examples.

Instead of the chlorhydrins, other halogen derivatives may be used as pinacone chlorhydrin (tetramethylethylene chlorhydrin), mannite chlorhydrin, erythrite chlorhydrin, pentaerythrite chlorhydrin, dulcitan monochlorhydrin, trimethyleneglycol chlorhydrin, divinylethyleneglycol chlorhydrin, phenylpropanol chlorhydrin, naphthylpropanol chlorhydrin, 4-methoxynaphthylpropanol chlorhydrin, glyceryl α-dihalohydrin and epichlorhydrin, with a corresponding variation in composition and properties of the cellulose ethers produced. The permutations of the process are almost unlimited and the field scarcely touched as to its technical possibilities.

Instead of proceeding as above outlined[1], viscose may be prepared in the manner customary for rayon utilization, and this incorporated with α-dichlorhydrin at 10-15°, the mass kneaded 2 hrs. at 16-20°, then spun into filaments or deposited in endless lengths as films. Or to a viscose solution aged to the point optimum for spinning purposes[2], ethylene chloride may be added under mixing, and this solution forced through spinneret orifices for filament formation. The ethylene chloride may also be added to the freshly prepared viscose (before ageing or ripening)[3].

It appears possible to produce artificial filaments and films having a high degree of tenacity in the wet or dry state and a high degree of extensibility (which are the two important requisites for an acceptable rayon), by mixing viscose with a halogen derivative or a divalent or polyva-

1. L. Lilienfeld, E. P. 362437.
2. *Ibid.* E. P. 357154.
3. *Ibid.* E. P. 341843, 357121, 357192. Mentioned in E. P. 357154.

lent alcohol or anhydride of such derivative (as epichlorhydrin), spinning in the usual manner and coagulating in the usual viscose acid setting bath. It is claimed possible without difficulty to produce artificial silk by this means of dry strength greater than 5 gms. per denier, wet strength up to 3 gms. per denier and an extensibility up to 15% or more. If this is so, the invention constitutes a notable advancement in the synthetic filament art. This is not to be confounded with the method of Lilienfeld whereby viscose filaments are treated with highly concentrated mineral acid as sulfuric in order to augment the tensile strength.

In its commercial aspects, the process is described as being carried out as follows:

100 parts wood pulp or cotton linters pulp are introduced into 2000 parts 18% NaOH solution at 15° for 3 hrs., pressed to 300 parts for wood pulp or 340 parts for linters, shredded 2.5-3 hrs. at 11-15°, then 40 (for wood pulp) or 60 (for linters) parts carbon bisulfide are added and allowed to act 8 hrs. at 18-20°. This is a radical departure from the usual viscose manufacturing procedure in that the alkalicellulose is not aged, and the xanthation (carbon bisulfide reaction on alkalicellulose) is usually not over 2 hrs. After xanthation, excess of carbon bisulfide is removed, and the xanthate dissolved in NaOH to contain 6.5% cellulose and 5% NaOH. When solution is complete 12.5 parts α-chlorhydrin (1.3-dichlorpropanol-(2)) are added to the viscose and well stirred in, and the solution left for 72 hrs. at 22.24°. There is now added a quantity of caustic soda solution equivalent to an alkalinity of 8%. The spinning solution is now thrice filtered through cotton, and after it has attained a total age (from the beginning of xanthation probably) of 96-100 hrs. is spun into filament form[1].

In an improvement upon this method[2], the halogen derivative of the di- or poly-valent alcohol is replaced by a

1. L. Lilienfeld, E. P. 335906; abst. Silk J. 1931, **7**, #80, 52.
2. *Ibid.* E. P. 357526, Addn. to E. P. 335906.

halogen olefine as *sym*-dichlorethylene (acetylene dichloride). Instead of dichlorethylene, trichlorethylene, vinyl chloride, tetrachlorethylene, allyl chloride or *b*-epidichlorhydrin may be employed, the orginal patent giving specific examples based upon the utilization of each of these in the process.

O-Oxyalkylcellulose Xanthate. When alkalicellulose is acted upon with a halogen derivative of a di- or poly-valent alcohol, and the product then xanthated in the usual manner, a xanthic derivative of the corresponding hydroxyalkylcellulose results. This method is not universal in that certain derivatives as *a*-dichlorhydrin, react with alkalicellulose to form a product, which in most cases, can be but imperfectly xanthated or not at all.

CHAPTER VII

MANUFACTURE OF ALKYLCELLULOSE

Preparation of the alkylcelluloses at the present time is primarily confined to production of the methyl and ethyl ethers, and to those ethers of comparatively high methylation and ethylation, which are the ethers of maximum technical usefulness, on account of the sensitivity of the lower methylated and ethylated celluloses to the action of water, both hot and cold. While the lower alkylated members have but a limited use by virtue of their water solubility or capacity of swelling in aqueous solutions for cements, agglutinants, sizes and as substitutes for gums, soluble starches and dextrinized carbohydrates, it is a field where price competition restricts their application.

In detailing the methods of manufacture which have been proposed and which have resulted in patent issuance, in many cases, due to the variable factors of time, initial cellulose purity, moisture present in the cellulose operated upon, ratio of water formed in the etherification reaction in respect to the alkali and/or etherifiant present, temperature of reaction, and the composition of the alkalicellulose employed as gauged by its initial composition and the period and temperature of ripening, have resulted in a multiplicity of solubility constants being obtained, which is difficult, and in many cases impossible, to reduce to a systematic generalization.

There are two systems available of outlining the methods and variations in manufacture of these ethers. One is to attempt to correlate all the processes into a composite method of procedure, but this appears impracticable on account of the large number of unexpectedly obtainable results recorded, especially in regard to solubility constants, and also to the fact that in the aggregation of meth-

ods which have been proposed and refinements advocated, a single method of manufacture embracing all the relatively minor improvements brought forward, would result in the detailing of a single method too involved for easy comprehension.

The second apparent method of presentation is to take the various processes which have been brought forward from time to time, critically analyze them as to procedure and results attained, clarify the methods of procedure by incorporating specific examples of operation, and correlate insofar as appears feasible, the strong and weak points of the process of one patentee over another, bearing in mind the specific uses to which the finished product is intended to be put. That is the method used herein, and it is believed will result in presenting a more accurate picture of the technical advancement of the art, especially as the processes evolved by an individual investigator, insofar as practicable, have been taken up chronologically, in order to accentuate advancements made.

Cellulose Treatment Prior to Etherification. For some time the desirability has been recognized of submitting cellulose, especially cotton, to a prior treatment in order to give to the fiber a larger surface, increase the porosity, augment the reactivity and increase the uniformity of the final product, but it is only recently that attention has been focussed on the feasibility of subjecting cellulose to treatment prior to etherification with the same ideas in view. The major portion of the older methods of cellulose pretreatment were evolved with the purpose of subsequent acetylation, but once the cellulose has been purified and placed in a specially receptive "mood," it usually is immaterial whether the final step in treatment be one of esterification or etherification. The primary object is to combine purification, usually bleaching, diminish the ash to the minimum, and leave the cellulose in a condition optimum for etherifying with the least possible degradation.

The processes which have been advanced fall under the following headings: (1) treatment with inorganic acids, (2) organic acids or (3) alkalis; with (4) oxidants or (5) solvent extraction; (6) by mechanical subdivision, (7) steam treatment, (8) exclusion of air, or (9) employment of an especially reactive product as the hydrated cellulose obtained by the acidification of a viscose solution.

This subject, it appears, is becoming of increasing importance in connection with the manufacture of cellulose ethers, for at the present time the stumbling block to commercial exploitation and economic competition with the acetylated celluloses is the bulk (and hence the cost) of etherifying component required, and any step that can be applied to the cellulose which will diminish the amount of etherifiant required is of paramount importance. These proposed treatment steps are supplementary to the transformation of the cellulose into alkalicellulose as a prerequisite to alkylation or aralkylation.

(1) *Cellulose Treatment with Inorganic Acids.* It has been known for some time in the cellulose ester art, that by treatment of normally purified cellulose with inorganic acids so dilute that no acylation takes place, after the mineral components are removed, the cellulose is rendered physically more porous, and becomes chemically more reactive. Treatment of the cellulose with halogen acids, usually 2-5% HCl, or a mixture of halogen acid with glacial acetic acid[1], or highly concentrated HCl for a brief period[2], or a halogen as chlorine in vapor form[3], or HCl followed by sulfurous acid[4], softens and opens up the cellulose fibers, removing pentosans, certain glucose-like bodies and diminishing the mineral constituents. Especially is hydrofluoric acid indicated[5] primarily on account of its direct solvent action

1. E. P. 312098.
2. U. S. P. 1679966.
3. Ruth-Aldo Co., Can. P. 301734.
4. A. Classen, Ital. P. 254138.
5. British Celanese, Ltd., E. P. 308348; abst. C. A. 1930, **24**, 239; J. S. C. I. 1930, **49**, 610-B; Chem. Zentr. 1929, II, 813; Silk J. 1929, **6**, #62, 70; Brit. Plastics, 1930, **2**, 135. See H. Dreyfus, E. P. 249173, 263938; abst. J. S. C. I. 1926, **45**, 436-B; 1927, **46**, 247-B.

upon silica and silicates in the cellulose. As an example, 100 parts cotton linters are moistened with 200 parts 5% aqueous HF, and the acid allowed to remain in contact with the cellulose for some time to dissolve any mechanically held or chemically combined silicon compound. At room temperature 7-10 days are required. The cotton is then washed free from acid, boiled with alkali, partially bleached, washed and dried. After the linters have been dried, they may be subjected to hot acetic acid which does not exert an esterifying action, but renders the cellulose much more susceptible to chemical reagents upon removal of acetic acid, and according to the patentee, the purified and "clarified" cellulose is especially indicated for methyl-, ethyl- and benzyl-cellulose formation.

When cellulose purified in the usual manner is dried by means of impregnation with liquid SO_2 at low temperature, the sulfur dioxide exerts a powerful solvent effect upon hemicellulose, pentosans and inorganic components, and may be afterwards extracted by lowering the pressure[1]. Cellulose thus treated when in the form of cotton linters, will sink in cold water within 0.5 min. Sulfuric acid of 60° Be[2]. at ordinary temperature, or 0.5-1.5% strength for 2 hrs. at 77° when brought in contact with either wood or cotton cellulose is said to leave the cellulose in an unusually permeable condition whereby it will etherify more readily and with great uniformity, so that the finished product is comparatively free from non-alkylated fibers[3], and less haze appears in films made therefrom.

The cellulose fiber may also be "opened up" by treatment with nitric acid up to 20% HNO_3 at temperature not above 50°, no nitration taking place[4], or impregnated with

1. G. Neumann, F. P. 693014; abst. C. A. 1931, **25**, 1670; Chem. Zentr. 1931, I, 2288.
2. L. Lilienfeld, Aust. P. 63524.
3. P. Seel, U. S. P. 1503604; abst. C. A. 1924, **18**, 2963; J. S. C. I. 1924, **43**, 784-B; Chem. Zentr. 1924, II, 2100.
4. H. Heimann, I. Petersen, A. Bayerl and H. Seefried, Can. P. 284973; abst. C. A. 1929, **23**, 979. I. G. Farbenindustrie, E. P. 274892, 276025; abst. C. A. 1928, **22**, 2273, 2464.

dilute nitric acid, followed by neutralization and boiling with 2% NaOH solution at ordinary pressure for 30-60 min.[1]. Certain halogenides of sulfurous acid as thionyl chloride[2], zinc chloride or calcium thiocyanate[3] have also been recommended, primarily in connection with esterification operations.

(2) *Cellulose Pretreatment with Organic Acids.* When cellulose is treated in the cold or at an elevated temperature with formic acid of concentration so that little or no formylation takes place[4], or formic acid admixed either with sulfuric acid[5], sulfuryl chloride, phosphorous oxychloride[6] or zinc chloride[7], the cellulose softens, intumesces, sometimes becomes partially translucent, and after removal of all acid, is in a form receptive to either esterification or etherification. Instead of formic acid may be used acetic acid, either alone at room temperature for several hours[8], or in the vapor phase[9], or heated with small amounts of sulfuric[10] or phosphoric acids[11], or hot acetic acid with sodium acetate[12], or the acetic acid may be used in conjunction with the chlorides of antimony, arsenic or phosphorus[13] or of tin[14], a supersensitivity to chemical reaction taking place. Glacial acetic acid at 0.3-0.5 atms.

1. H. Heimann, I. Petersen, K. Bitterfeld, A. Bayerl and H. Seefried, U. S. P. 1840198. H. Heimann, I. Petersen and A. Bayerl, D. R. P. 546314 Addn. to D. R. P. 503450; abst. C. A. 1932, **26**, 3376.
2. C. Ebert and T. Becker, U. S. P. 1701229.
3. E. P. 298087. H. Dreyfus (U. S. P. 1869307) pretreats cellulose with formic acid in the absence of a condensing agent, which renders it ultra-susceptible to further chemical treatment.
4. U. S. P. 1697907, 1711111, 1722914. E. P. 263938, 263939, 264937, 288657, 305601, 308322, 372095.
5. U. S. P. 1671513. F. P. 621376. 6. E. P. 287540.
7. U. S. P. 1671513. E. P. 287540.
8. U. S. P. 1543310, 1668944, 1668945, 1687059, 1692622, 1711111. E. P. 263939, 264937, 293757, 308322, 312095. F. P. 639119.
9. U. S. P. 1668484. Ruth-Aldo Co., Can. P. 301932.
10. U. S. P. 1652573. E. P. 269530. 11. U. S. P. 1683347.
12. H. Dreyfus, U. S. P. 1731299; abst. C. A. 1930, **24**, 238; J. S. C. I. 1929, **48**, 976-B; Cellulose, 1930, **1**, 34. E. P. 207562; abst. J. S. C. I. 1924, **43**, 129-B. F. P. 675354 and Addn. 36935; abst. C. A. 1930, **24**, 2880; 1931, **25**, 1081.
13. *Ibid.* E. P. 311790; abst. C. A. 1930, **24**, 961; J. S. C. I. 1929, **48**, 594-B; Silk J. 1929, **6**, 64.
14. E. P. 312095, 312098.

pressure above normal[1], acetic anhydride[2], and acetic acid under vacuum[3] have also been advocated, as furnishing a "reactive" cellulose not degraded.

The use of oxybenzenesulfonic acid or sodium oxybenzenesulfonate[4], or treatment of cellulose with chlormethyl alcohol, chlormethyl ether, acetyl chloride or propionyl chloride[5] is said to be unusually efficient, and especially applicable to the production of ethylcellulose. For example, 100 parts air dried cotton linters are allowed to stand 12 hrs. in 500 parts trichlorethylene containing 10 parts acetyl chloride, or 2% carbonyl chloride or 1% chlormethyl ether, for 12 hrs. at 20°. The linters are then hydro-extracted, washed until neutral and dried. Application of acetic acid vapor in the presence of a small amount of iodine trichloride[6], or the use of sufficiently concentrated hot acetic acid so that on cooling the acetic acid crystallizes out and disrupts the cellulose[7], are other variants.

(3) *Cellulose Pretreatment with Alkaline Solutions.* These methods are primarily aimed at purification of the cellulose without use of a concentration sufficiently high to induce a mercerizing effect. H. Dreyfus[8] describes treatment of the cellulose with alkali hydroxide up to 3%, or if a greater concentration is used, the solution must be cooled to prevent mercerization. The A. Pollard and J. Whincop method is similar[9]. Caustic alkali with a phenol or cresol is claimed as an excellent detergent for increas-

1. E. Hubert, A. Roest-Grande and E. Correns, U. S. P. 1752596; abst. J. S. C. I. 1930, **49**, 900-B.
2. H. Dreyfus, F. P. 675354; abst. C. A. 1930, **24**, 2880.
3. C. Dreyfus and G. Schneider, U. S. P. 1783184; abst. Plastics, 1931, **7**, 233; C. A. 1931, **25**, 414; Cellulose, 1930, **1**, 294.
4. O. Strecker, D. R. P. 505401 Addn. to D. R. P. 486533.
5. British Acetate Silk Corp., Ltd., F. Stoyle, G. Edwards and A. Lipscomb, E. P. 340555; abst. C. A. 1931, **25**, 5030; J. S. C. I. 1931, **50**, 343-B; Silk J. 1931, **7**, #83, 52.
6. E. P. 303134.
7. J. Bulmer, 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. See J. de la Roza, Australian P. 14598.
8. U. S. P. 1711110.
9. E. P. 315902.

ing the porosity and reactivity of cellulose[1]. Pretreatment with dilute alkali as basic purifying material followed by extraction with acetic acid is the essence of another H. Dreyfus patent[2], while F. Ohl[3] has detailed a method, particularly applicable to sulfite cellulose, whereby the acid treatment is prior to the alkaline digestion. Another variant is acetic acid and chlorine[4].

It has been observed[5] that the addition compounds which alkylating agents form with tertiary bases or solutions of the bases in suitable solvents have the property of dissolving cellulose with the formation of viscous solutions, the cellulose being readily separable by means of precipitating agents, such cellulose being in a very reactive form, and, therefore, especially suitable as base material for etherification purposes or for esterification, in particular reacting readily with acid anhydrides and acid chlorides. The process may be carried out by melting 200 parts anhydrous benzylpyridinium chloride in a stirring vessel, heating to 110-115° and stirring in 10 parts cellulose, the temperature being maintained until the cellulose completely dissolves with the formation of a viscous liquid. Or, 100 parts benzylpyridinium chloride are mixed at 110-115° with 20 parts pyridine, and to the homogeneous solution are added 6 parts cellulose. While continually stirring, the mixture is kept at 115°, whereby the cellulose dissolves with formation of a viscous liquid, and from which it may be precipitated.

(4) *Treatment of Cellulose with Oxidants.* In order to porosify and bleach simultaneously, treatment of cellu-

1. L. De Wolf, U. S. P. 1726142.
2. E. P. 249173. See also Ital. P. 242635, 255928. E. P. 6463, 14101, 1915; 100009, 101555, 207562.
3. Kunst. 1930, **20**, 217; abst. Chem. Zentr. 1931, I, 2700; J. S. C. I. 1931, **50**, 1134-B.
4. H. Barthelemy, F. P. 660393; abst. C. A. 1930, **24**, 238.
5. Society Chemical Industry, Basle, E. P. 359249.

lose with chromic acid[1], potassium permanganate[2], alkaline hydrogen dioxide[3], sodium peroxide or perborate[4], or alkali peroxide and a soap[5] are some of the methods which have been brought forward. Sodium peroxide, especially, has a very pronounced swelling and bleaching effect, and leaves the cellulose in a soft and receptive state for either etherification or esterification, especially if the cellulose so treated is mercerized without an intervening drying operation. Aluminum, manganese, copper, zinc, ammonium, magnesium, calcium, barium, lead, methylamine, quinoline or pyridine perchlorates[6] form the basis of cellulose treatment in another process, by combining a bleaching and solvent action upon the non-alphacellulosic bodies.

(5) *Treatment of Cellulose with Steam.* Hydrolysis of the cellulose by treatment with steam at 140-145°, alternately in conjunction with 1-2% acetic acid[7], or steam in the presence of a small proportion of ammonia or pyridine[8], combines both a hydrolytic and emulsifying action upon fatty and resinous impurities, especially where a small amount of saponifying material is present.

(6) *Solvent Purification of Cellulose.* Unitary or compound solvent extraction of cellulose, while it leaves the latter in the normal condition without any depolymerization or degradation, is limited to the removal of fats, waxes, resins and similar materials, otherwise the treatment does not affect the porosity of the cellulose, and pure solvents do not appreciably remove dried protoplasmic material in the interstices of the individual cell. The usual method of

1. R. VanDyke, C. Staud and H. Gray, J. A. C. S. 1931, **53**, 2725; abst. C. A. 1931, **25**, 4398; I. E. C. Analyt. Ed. 1931, **3**, 269; J. S. C. I. 1931, **50**, 1041-A.
2. H. Hibbert and J. Parsons, U. S. P. 1768253; abst. C. A. 1930, **24**, 4391.
3. H. Specht, U. S. P. 1379699.
4. H. Barthelemy, F. P. 662265.
5. Ruth-Aldo Co., Inc., Can. P. 301935.
6. C. Malm, U. S. P. 1645915.
7. L. Clement and C. Riviere, E. P. 343712; abst. C. A. 1931, **25**, 5556. Soc. Clement et Riviere, F. P. 38582 Addn. to F. P. 700478; abst. C. A. 1931, **25**, 3832; 1932, **26**, 1118.
8. I. G. Farbenindustrie, E. P. 293757.

procedure is to swell the cellulose by a hot water treatment, then replace the water by a miscible cellulose non-solvent, diacetin being stated as especially useful where the cellulose is intended for benzylation or acylation[1]. Glycerol or glycol have also been brought forward for the same purpose. In the benzylation of cellulose where the reaction takes place in an alkaline medium, the glycerol or analogous solvent is left in the cellulose and carried through the etherification step.

E. Mezey[2] prepares a highly voluminous cellulose by heating commercial cellulose for 3-4 hrs. at 3-5 atms. pressure with a dihydric aliphatic alcohol or derivative thereof, a small quantity of alkali as borax or soap being present. Thus, washed sulfite cellulose may be heated as above with ethyleneglycol monoethyl ether 2 and ammonia 0.5%, the product washed, then bleached. Dichlorethyl ether, ethyleneglycol monomethyl ether and ethyleneglycol monomethyl (or ethyl) acetate are also recommended.

(7) *Physical Comminution of Cellulose.* In order to present a greater surface area for chemical attack, H. Plauson by attrition reduces the size of the cellulose particles to the "colloidal condition" before etherification, his definition being that the *macroscopic* condition results when the particles exceed 0.001 mm. diameter, the *molecular* condition when the diameter is less than 0.01 of this, and the *colloid* condition when in between. By means of a colloid mill described[3] and patented[4] by him, the cellulose particles are dispersed to ultra-microscopic size after the usual purification, and etherified in this condition. A particle size of 0.8 micron is recommended.

1. F. Klein, E. P. 313538; abst. C. A. 1930, **24**, 1216; J. S. C. I. 1931, **50**, 108-B.
2. D. R. P. 514466; abst. C. A. 1931, **25**, 1670.
3. H. Plauson, Zts. ang. Chem. 1921, **34**, 469, 473-A; abst. C. A. 1922, **16**, 450.
4. H. Plauson, E. P. 183908; abst. C. A. 1923, **17**, 209; J. S. C. I. 1922, **41**, 748-A; Ann. Rep. S. C. I. 1922, **7**, 139; Chem. Zentr. 1922, IV, 1086. E. P. 184533; abst. C. A. 1923, **17**, 210; J. S. C. I. 1922, **41**, 806-A; Ann. Rep. S. C. I. 1922, **7**, 122; Chem. Zentr. 1922, IV, 1182; Faser. 1923, **5**, 59.

In the etherification of cellulose according to the E. I. du Pont formula[1], which does not require the formation of alkalicellulose and incorporation of powdered NaOH therewith, the cellulose is finely ground in a Hollander, then added to a slurry of alkali in an inert or non-etherifiable liquid, intimately mixing, then proceeding with the etherification step, methyl or ethyl chlorides being used in an autoclave in the presence of benzene. By obviating grinding the cellulose with solid alkali it is claimed impairment of the ultimate quality of the cellulose is thereby avoided, and an unusual uniformity in ether production maintained.

(8) *Conditioning Cellulose in Absence of Air.* In the patented process of carbohydrate etherification of O. Ernst and K. Sponsel[2], "uniform, ropy and supple" solutions of cellulose ethers are obtained by excluding the air prior to and during the preparation of alkalicellulose, probably to obviate the formation of oxycellulose from atmospheric oxygen. The operation is performed in a vacuum and (very peculiarly) in an atmosphere of carbon dioxide, which is detrimental in alkalicellulose formation owing to its absorption by the NaOH to form the corresponding carbonate. The invention is exemplified by drying in a vacuum chamber air-moist cellulose board while passing CO_2 through the chamber at 60° until all air has been displaced. The chamber is then filled with alkali solution of high percentage and the board allowed to swell for some time. After the material has been squeezed, the alkalicellulose is ready for immediate etherification. Nothing is said as to the advisability of using an inert gas as nitrogen to displace the air.

In the C. Dreyfus method of procedure[3], the cellulose is introduced into an airtight chamber which is then evacuated, and glacial acetic acid heated approximately to its boiling point, admitted in amount incompletely sufficient to

1. E. P. 311697; abst. C. A. 1930, **24**, 960; J. S. C. I. 1930, **49**, 985-B.
2. U. S. P. 1858731. E. P. 293757; abst. C. A. 1929, **23**, 1750.
3. Can. P. 287774.

satisfy the vacuum, the cellulose being acted upon by the acid for about an hour.

(9) *Hydrated Cellulose from Viscose.* In the preparation of viscose films as Cellophane there is a waste of approximately one inch on each edge of the roll, which after glycerol salvaging, is practically of no technical use. A. Pellerin[1] takes waste viscose filaments or other scrap from the viscose industry, washes out impurities, desulfurizes, bleaches, and etherifies in the usual manner.

Somewhat similar is the idea of L. Lilienfeld[2] who uses viscose waste, denitrated nitrocellulose and the discards from cuprammonium rayon filament production. The "raw" material is preferably cut into small portions, dried, and directly etherified. Or[3], crude viscose (usually viscose which is too young or has been over-ripened) and soluble in alkali, is dissolved in 50% NaOH and ethyl sulfate or other etherifiant directly added to produce the corresponding etherified cellulose[4]. H. Dreyfus uses viscose waste for esterification purposes[5].

Superficial Etherification of Cellulose. The superficial or incomplete esterification of cellulose has been known for some time through the disclosures of G. Miles[6] and of Chemische Fabrik vorm. Sandoz[7], but the partial etherification of cellulosic bodies, especially in the woven textile form was first published by L. Lilienfeld[8], who embodied his results in patent form.

1. U. S. P. 1128624; abst. C. A. 1915, **9**, 1114; Mon. Sci. 1915, **82**, 45; J. Soc. Dyers, 1915, **31**, 127; J. S. C. I. 1915, **34**, 349.
2. E. P. 318088; abst. C. A. 1930, **24**, 2291; J. S. C. I. 1929, **48**, 1011-B. See E. P. 269531. Aust. P. 112620, 112623. Ital. P. 194918, 199196. Swiss P. 97634. F. P. 523931.
3. L. Lilienfeld, D. R. P. 470142; abst. C. A. 1929, **23**, 2293; Chem. Zentr. 1929, I, 1528.
4. E. Rinman, India P. 6151. See Elektro-Osmose, A. G., Swed. P. 49078. Benardini, Ital. P. 243811.
5. H. Dreyfus, E. P. 312095.
6. E. P. 11164, 1902. See p. 340, n. 2.
7. E. P. 323500. See p. 857, n. 3.
8. E. P. 234847; abst. J. S. C. I. 1925, **44**, 668-B; Chem. Zentr. 1925, II, 1824; Ann. Rep. S. C. I. 1925, **10**, 143. See p. 85, n. 2.

A silky gloss, brilliance, and elastic feel may be imparted to woven and spun material of vegetable origin, as linen, flax, hemp, ramie, jute or cotton, by treatment in the presence of alkalis with an inorganic ester of a monohydric alcohol, and stretching. The reagents may be applied simultaneously or in either sequence, and the fiber treated at any stage from the crude state, or after bleaching, mercerizing, hydrolyzing or gelatinizing (as with a strong mineral acid). As alkalis, the hydroxides are preferred, although alkali sulfides may be employed. As esters, dialkyl sulfates, alkyl halides or aralkyl halides are suitable, and alcohol may be added to the alkali to assist in the penetration of the fiber, and the esters may be used alone or in conjunction with solvents (benzene, alcohol) and thickening agents (starch, dextrin, British gum, albumen).

Patterns may be produced by first printing the material with a reserve paste containing albumens, gums, alum or ammonium sulfate, or the etherifying agent or alkali may be printed on the goods, thickening agents being used. The details of the process are apparent from the following two methods:

1. The woven or spun material is first treated with a solution of NaOH of 12-40% strength at up to 50° either by impregnation under stretching, or by printing in a paste form, the quantity of alkali used being 2-10 times the weight of the textile. If the alkali solution is not too weak, the process of mercerization may be carried out at room temperature. The textile is then etherified at those places where alkali has reacted, by application thereto of an alkyl ether as ethyl sulfate where the cellulose is to be transformed into ethylcellulose, a solvent as benzene or alcohol being added if desired. After the etherifying agent has contacted with the cellulose the desired time, depending upon the degree of superficiality of etherification desired, the textile is washed free from reactants and dried, preferably still under tension.

2. The order of treatment in Ex. 1 is reversed, that is, the textile is first treated with the etherifying agent, then with the alkali solution. Since the etherifiants have no action on the cellulose in absence of alkali, treatment with alkali solution may follow at leisure. By appropriate selection of working conditions, the degree of luster and "feel" may be modified within wide limits. The silky luster is improved by one or more repetitions of the process.

Cellulose Alkyl Ether Manufacture. There are two general methods for the production of ethers from aliphatic alcohols. The first comprises the action of an alkyl halide on an alcoholate as sodium alcoholate, a typical equation being:

$$C_2H_5ONa + C_2H_5X = NaX + C_2H_5OC_2H_5$$

in which X may represent any halogen.

The second method consists in the action of an ester, as esters of inorganic acids, upon an alcohol, ethyl alcohol and ethyl hydrogen sulfate yielding diethyl ether (ordinary ether) according to the reaction:

$$C_2H_5OH + C_2H_5OSO_2OH = H_2SO_4 + C_2H_5OC_2H_5.$$

Diethyl sulfate (ethyl sulfate) acts similarly. Analogous reaction to those two just cited may be carried out with cellulose, expressing cellulose in its simplest terms, $C_6H_{10}O_5$, a mono-cellulose ether being formed:

$$C_6H_9O_4.ONa + C_2H_5I = C_6H_9O_4.OC_2H_5 + NaI$$

That is, one mol. alkalicellulose (sodium cellulose) plus 1 mol. ethyl iodide gives 1 mol. mono-ethylcellulose and 1 mol. sodium iodide.

$$2C_6H_9O_4.OH + (C_2H_5)_2SO_4 = 2C_6H_9O_4.OC_2H_5 + H_2SO_4$$

Two mols. cellulose plus 1 mol. ethyl sulfate gives 2 mols. mono-ethylcellulose and 1 mol. sulfuric acid. While these reactions show the substitution of one hydroxyl hydrogen atom in cellulose or alkalicellulose, similar replacement may take place with two or three hydroxyl hydrogen atoms in cellulose in an analogous manner. An important point to be borne in mind is that in the usual cellulose etherification

process, at all stages of the reaction period there must be sufficient alkali present to neutralize the acid liberated by virtue of the chemical reaction, and still maintain an alkalinity in the reacting mass.

In order that the above reactions may be carried out to a commercially profitable yield, it is obvious that the cellulose used be in a readily susceptive form, as by first transforming the cellulose into an alkali alcoholate (alkali-cellulose) or operating upon cellulose in solution, or in an alkali-soluble modification. The two technical processes employed substitute the halogen iodine by chlorine on account of its relative cheapness, methyl chloride and ethyl chloride being used, and inasmuch as both are normally gases, the alkylation must be performed under pressure greater than atmospheric. In the second method, wherein methyl sulfate or ethyl sulfate is used, as either of these boils above 100°, pressure apparatus is not necessary, the etherifications being made in open containers.

Irrespective of the process for manufacture employed, the cellulose ethers obtained are never homogeneous products, but a mixture of several alkylated celluloses of various degree of etherification, i.e. of varying alkoxyl content. By laborious purification, ethers giving analytical figures for trimethylcellulose and triethylcellulose have been obtained, these indicating the maximum of etherification.

I. *Processes of L. Lilienfeld.* In the number and diversification of methods for the production of cellulose ethers, both alkyl and aralkyl, the methods of L. Lilienfeld appear to cover the field more exhaustively than those of other inventors in this field. Due to extensive descriptive overlapping from one patent to another, it is difficult to always draw a clear line of demarcation between the specified and claimed methods. They are grouped under the following fourteen numbered headings as follows:

1. *Original Lilienfeld Process.* This has been examined in detail in pages 10-22 in the development of the

historical advancement of the cellulose ethers. The original patent which issued in 1912[1] was followed by specific processes for the manufacture of cellulose ether films[2] in 1913, filaments[3] in 1914, and the substitution for cellulose, of other carbohydrates as starch, dextrin, amylose and inulin[4] into ethers of technical usefulness. The production of these latter are considered in Chapter VIII under alkylated starches.

2. *Manufacture from Unripened Alkalicellulose.* In order to eliminate some of the time-consuming operations connected with the ageing of alkalicellulose preparatory to etherification[5], it is claimed that expression of excess caustic from the alkalicellulose and the ripening of the comminuted product could be obviated, and the mercerized cellulose directly after its formation, alkylated in the usual manner. No alkylcellulose is produced at the present time using unripened alkalicellulose, insofar as aware, it being pretty definitely established that the proper ageing of the

1. U. S. P. 1188376; abst. Kunst. 1916, **6**, 282. E. P. 6035, 1913.

2. U. S. P. 1217027, 1917; abst. C. A. 1917, **11**, 1545; J. S. C. I. 1917, **36**, 383. 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. 73001; abst. Kunst. 1917, **7**, 222. Aust. P. 62809, 1913; abst. Chem. Ztg. 1913, **37**, 1499. Hung. P. Appl. L-3294; abst. Chem. Ztg. 1913, **37**, 11. Ital. P. 173413, 183582.

3. U. S. P. 1217028; abst. J. S. C. I. 1917, **36**, 383.

4. U. S. P. 1350820; abst. C. A. 1920, **14**, 3251; J. S. C. I. 1920, **39**, 654-A; Paper, 1921, **17**, No. 20, 19. E. P. 3370, 1914; abst. J. S. C. I. 1916, **35**, 534; Kunst. 1918, **8**, 42; J. Soc. Dyers, 1916, **32**, 181. F. P. 468162; 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; abst. C. A. 1923, **17**, 1803; Chem. Ztg. 1920, **44**, 877; Chem. Zentr. 1921, **92**, IV, 41; J. C. S. 1921, **119**, 650. Ital. P. 140506; abst. Chem. Ztg. 1914, **38**, 1027. D. R. P. 360415; abst. Chem. Tech. Rep. 1922, **46**, 366; Chem. Zentr. 1923, **94**, II, 264. Aust. P. Appl. 2182, 1920; abst. Chem. Ztg. 1922, **46**, 687. Nor. P. 27507; abst. C. A. 1917, **11**, 1748. Can. P. 248226; abst. C. A. 1925, **19**, 3491.

5. U. S. P. 1441989; abst. C. A. 1923, **17**, 1141; J. S. C. I. 1923, **42**, 180-A; Chem. Zentr. 1923, II, 1122. E. P. 163016; abst. C. A. 1921, **15**, 3207; J. S. C. I. 1922, **41**, 10-A; Chem. Zentr. 1921, IV, 586. Can. P. 248228; abst. C. A. 1925, **19**, 3491; Chem. Zentr. 1927, I, 1251.

alkalicellulose is one of the most delicate and important steps in carbohydrate etherification.

3. *Conversion of Lower Cellulose Ethers to Those of Higher Ether Content.* The lower alkylated celluloses in general, due to their solubility or swelling propensity in water, are of diminished technical value in respect to those of higher ether substitution, therefore their field of utility is correspondingly restricted as compared to the cellulose ethers of higher stages of alkylation. Conversely, the aralkyl ethers as benzylcellulose, which are poor in aralkyl groups, while insoluble in water, are also practically insoluble in the important industrial organic solvents. Increase in the number of alkyl groups substituted, opens up with the methylcelluloses and ethylcelluloses an extraordinary increase in the series of organic solvents in which they may be dissolved, swollen or plasticized, and also causes their solubility or capacity to swell in water to disappear. In the case of the benzylcelluloses, augmentation of benzylation procures an excellent degree of solubility in organic solvents. The rise in alkyl content of an alkylcellulose may be effected as follows:

240 parts of alkali-soluble cellulose solution containing 20 parts by weight of cellulose and an equal weight of NaOH, are gently heated and gradually mixed with 36-72 parts ethyl sulfate, the addition of alkylating agent requiring preferably 1-2 hrs. The temperature is allowed to rise from 30-50° during this period, the mass assuming the consistency of a salve-like paste, containing ethylcellulose soluble in cold water, which may be recognized by the fact that a sample withdrawn will be found non-precipitable with sulfuric acid but soluble in glacial acetic acid. The reaction mixture is then cooled, filtered if necessary, and gently heated to remove the water therefrom, being continuously stirred, the temperature maintained being under 100°. In vacuum evaporation the temperature may be reduced to 30-40°.

Expulsion of water is continued until the reaction mixture has reached a weight of 40-140 parts—according to the degree of water removal desired and the amount of etherifiant used—these figures corresponding to ratios of 5:1 and 6.83:1 of actual cellulose in the material being operated upon. The resultant friable mass is dry to the touch and is rubbed down and disintegrated to a fine uniform powder, and after cooling, 7-15 parts powdered NaOH or equivalent amount of KOH added, the temperature of the mass being meanwhile kept down. The resultant mixture, which is in powdered form, is then incorporated with 30-80 parts ethyl sulfate, the reaction proceeding at 50-100° for 1-3 hrs. Any alcohol or ether formed as a byproduct during the reaction is then distilled off, the mass neutralized, washed to eliminate the salts formed, and dried at a low temperature[1].

4. *Alkylation by Minimum of 15 Parts 30-50% NaOH to 1 Part Cellulose.* It is claimed that carbohydrate ethers, especially those of cellulose[2], having the fullest technical utility and particularly of the maximum water-resisting characteristics, are obtained when at least 15 parts of a 30-50% solution of alkali to 1 part of carbohydrate are employed, the process being that normally used in alkylcellulose formation.

5. *Treatment with Solid Alkali Prior to Alkylation.* The employment of large quantities of alkali and alkylating agent may be minimized to a considerable degree, so it is

1. U. S. P. 1483738; abst. C. A. 1924, **18**, 1198; J. S. C. I. 1924, **43**, 291-B. E. P. 149320; abst. C. A. 1921, **15**, 436; Chem. Met. Eng. 1920, **23**, 1269; Paper, 1921, **28**, 33; J. S. C. I. 1922, **41**, 53-A; Ann. Rep. S. C. I. 1921, **6**, 133, 138. F. P. 523931; abst. Chem. Zentr. 1921, IV, 1140. D. R. P. 475214; abst. C. A. 1929, **23**, 3232; Chem. Zentr. 1929, II, 237.

2. U. S. P. 1488355; abst. C. A. 1924, **18**, 1750; J. S. C. I. 1924, **43**, 374-B; Chem. Zentr. 1924, II, 1645. E. P. 163017; abst. C. A. 1921, **15**, 3207; J. S. C. I. 1922, **41**, 10-A; Chem. Zentr. 1921, IV, 586. F. P. 534778; abst. Caout. et Gutta. 1922, **19**, 11425; Chem. Zentr. 1922, IV, 248. D. R. P. 488030; abst. C. A. 1930, **24**, 2291. Aust. P. 93928 addn. to 78217. E. P. 203346; abst. C. A. 1924, **18**, 587; J. S. C. I. 1924, **43**, 11-B; Ann. Rep. S. C. I. 1924, **9**, 153; Chem. Zentr. 1924, I, 383.

claimed[1], by the use of solid NaOH either alone or in presence of water or alkali solutions prior to etherification. For carrying out the process, the carbohydrates or materials containing them, preferably in a finely comminuted condition, and kneaded or otherwise mixed with pulverulent NaOH, either alone or with an insufficient amount of water so that alkali remains partially undissolved. The method is shown in the following example:

1.5-4 parts powdered NaOH are mixed with 1 part by weight of finely divided cellulose until a uniform mass results. Either at once or after standing, the mass is then etherified in the usual manner. Or, to 0.5-3 parts water or a 40-50% NaOH solution, 1-4 parts powdered NaOH are added and the whole thoroughly intermingled. Then 1 part finely divided cellulose is most thoroughly incorporated mechanically with cooling or at not above room temperature, and the product then alkylated, aralkylated or arylated.

6. *Treatment with Solid NaOH and Alkylation.* In order to hasten the process of carbohydrate etherification[2], it is recommended to treat the cellulose with up to 75% powdered NaOH in the presence of an alkylating agent, an example being to heat 200 parts by weight of sulfite cellulose under cooling in a kneading machine with 100 parts powdered NaOH until a uniform-appearing product results, and then at once or after 2-3 days standing, placing in an autoclave with stirring arrangement with 160 parts ethyl chloride, brought to 100-110° and maintained at this temperature with stirring for 6-12 hrs.

7. *Water-Insoluble Alkylcellulose by Regulation of Alkali-Water.* An improvement in cellulose ether produc-

1. U. S. P. 1858018; abst. C. A. 1932, **26**, 3919. D. R. P. 488780, 499129; abst. C. A. 1930, **24**, 4157. E. P. 163018; abst. C. A. 1921, **15**, 3207; Chem. Met. Eng. 1921, **25**, 340; Chem. Zentr. 1921, IV, 586. Can. P. 222377; abst. C. A. 1922, **16**, 4087; D. R. P. 475884; abst. C. A. 1929, **23**, 3807; Chem. Zentr. 1929, II, 237. Dan. P. 30677. Norw. P. 36952. Cf. L. Lilienfeld, India P. 11141. Ital. P. 199098, 199099, 199100. Aust. P. 91246, 97634.

2. D. R. P. 521453 Addn. to D. R. P. 496978; abst. C. A. 1931, **25**, 4401.

tion[1] is said to take place when maintaining a proportion of water to caustic alkali between $\frac{a^2 - a + 2}{4}$ and $\frac{1.5\,a^2 - 1.5\,a + 3,}{4}$ in which a is the amount of alkali to be employed to each part by weight of the cellulosic body[2].

8. *Alkylation of Dry Alkalicellulose.* In order to attenuate the amount of NaOH required together with alkylating agent for the formation of ethers of maximum alkylation, it is recommended to reduce the moisture in the reacting system to the minimum by the employment of alkalicellulose in a substantially dry condition[3], it being conceded that in so doing, cellulose ethers are formable of

1. E. P. 200815; abst. C. A. 1924, **18**, 328; J. S. C. I. 1924, **43**, 938-B; Chem. Zentr. 1923, IV, 808; Faserstoffe, 1924, **6**, 21. Aust. P. 101665.

2. The question of relative proportions of water and alkali and the preponderance of one over the other in cellulose etherification is of paramount importance. A lack of unanimity of opinion between L. Lilienfeld and H. Dreyfus has arisen on this point and Interference Actions Nos. 2773 and 2775 (U. S. Offic. Pat. Gaz. 1931, **413**, 1102) was decided by Judge P. Graham June 5, 1931, in reference to Dreyfus, U. S. P. 1451330, and Lilienfeld, Serial No. 695854, filed Feb. 28, 1924, the subject matter being set out in six counts as follows:

1. Process for the manufacture of cellulose derivatives, being aralkyl ethers of cellulose, comprising treatment of a cellulosic body with an aralkylating agent in the presence of a base.

2. Process for the manufacture of cellulosic derivatives, being aralkyl ethers of cellulose, comprising treatment of a cellulosic body not soluble in alkali, with an aralkylating agent in presence of alkali.

3. As new products aralkylethers of cellulose being cellulosic derivatives wherein hydroxyl hydrogen of the cellulose is substituted by aralkyl.

4. As new products, aralkyl ethers of cellulose, wherein the hydroxyl hydrogens of the cellulosic body are partially substituted by aralkyl.

5. As new products, benzyl ethers of cellulose.

6. As new products, benzyl ethers of cellulose, wherein the hydroxyl hydrogens of the cellulosic body are partially substituted by benzyl.

Examiner of Interferences awarded priority of invention of subject matter of counts 1, 2, 4 and 6 to Dreyfus, and the remaining counts to Lilienfeld. The Board of Appeals awarded priority of subject matter of count 2 to Dreyfus and of the remaining counts to Lilienfeld. Judge Graham affirmed the decision of the Board of Appeals.

3. U. S. P. 1683682; abst. C. A. 1928, **22**, 4246. E. P. 200816; abst. C. A. 1924, **18**, 328.

maximum alkyl content and hence of most desirable solubility in a maximum range of organic solvents. The invention is predicated on the statement that it is possible to dry alkalicelluloses of any water content, provided the drying is carried out at below 20°, preferably about 10°. As a preferred method of manipulation, 10 parts cellulose are impregnated with 100 parts 20% NaOH solution, and after standing 24-72 hrs., pressed until the weight has decreased to 60 parts (an unusually high ratio between cellulose and alkali). The pressed residue is then disintegrated and after standing 1-3 days is placed on a vacuum shelf drier at —15° to —10° until the moisture content is reduced to 10-25%. The dried alkalicellulose is then placed in an autoclave with stirrer and 20 parts ethyl chloride added, the mixture being heated to 90-100° for 10-24 hrs. The mass is kept in motion during the entire etherification period.

The resulting ethylcellulose is a powdery, flocculent substance, soluble in a number of organic liquids as benzene-alcohol, chloroform, alcohol, chloroform-alcohol, glacial acetic acid, amyl acetate and nitromethane, dissolving to clear, transparent solutions, which evaporate to water-resistant films.

9. *Alkylcelluloses Water-Soluble at 16° Made Insoluble.* By adjustment of the percentage of alkali prior to etherification, and the ratio of water to alkalicellulose, it is possible to transform ethylcellulose soluble in water at about 16°, into technically more useful ethers insoluble in water at this temperature. The initial material is an ethylcellulose of water-solubility as above, but which may swell or become soluble or is soluble in colder water, particularly below 10°, by so calculating the content of the reaction mixure in alkali, that the quantity of alkali amounts to not less than one-tenth, and not more than one-fourth of the quantity of water present in the reaction mixture. If (for instance) a reaction mixture contains 2-5 parts of water to 1 part (calculated as the dry substance) of an ethylcellulose

soluble in water at 16°, then according to the invention the NaOH content of the reaction mixture should be 0.3-1 part. If the reaction mixture contains 5-10 parts water to 1 part ethylcellulose soluble in water at 16°, then not less than 0.75 and not more than 2.5 parts NaOH are to be contained therein. If the reaction mixture contains 10-20 parts water to 1 part ethylcellulose, then the reaction mixture is to contain not less than 2 and not more than 5 parts NaOH.

In executing the process an ethylcellulose soluble in water at 16° is taken, isolated, and treated with water and alkali within the quantitative limits above stated, then ethylated in the usual manner. Or, in a modification of the process, the crude reaction mixture containing ethylcellulose soluble in water at 16°, has sufficient NaOH added thereto in solid or liquid form to give a proportion of water to alkali within the above stated quantitative limits. In either instance, after the adjustment has been made, ethyl sulfate or ethyl halide is added and the mixture heated to 40-150° for 24 hrs. If ethyl sulfate is used, the ethylation is carried out at 40-60°, if ethyl chloride be employed, the temperature required will be 70-150°. The isolation of the ethylcellulose is accomplished by placing the reaction mixture, either diluted with water or not, or prior or subsequent to neutralization, on a filter, washing with water, and drying[1].

10. *Preparing Alkylcellulose Soluble in Alkali, Insoluble in Water.* Cellulose ethers insoluble in water but soluble in alkali solutions from which they are precipitable by

1. U. S. P. 1505043; abst. C. A. 1924, **18**, 3272; J. S. C. I. 1924, **43**, 784-B. E. P. 181395; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1923, **42**, 1126-A; Chem. Zentr. 1922, IV, 963. Aust. P. 101021. Can. P. 248229; abst. C. A. 1925, **19**, 3491. Can. P. 248230, 252955. See U. S. P. 1488355, E. P. 200834. F. P. 552771; abst. Chem. Ztg. 1923, **47**, 474. E. P. 181393; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1924, **43**, 51; Ann. Rep. S. C. I. 1924, **9**, 153; Caout. et Gutta. 1923, **20**, 11687; Faserstoffe, 1924, **6**, 20; Chem. Zentr. 1924, II, 963. Can. P. 220831; abst. C. A. 1922, **16**, 2989; Faserstoffe, 1922, **4**, 143. See U. S. P. 1505044. D. R. P. 488781; abst. C. A. 1930, **24**, 2290.

acids are formed[1] when cellulose is warmed or heated in the presence of alkylating agents with such quantities of caustic alkalis as are not sufficient in themselves at the same temperatures and in the same periods of reaction to convert the cellulose wholly into alkali-soluble conversion products. The cellulose ethers so produced are stable, soluble in dilute alkali solutions from which they are precipitated by acids. In general, they congeal when spread out in thin layers and treated with acids, acid salts or alcohols to form coherent products which may be washed and dried to produce technically useful products. The majority of these products, however, are soluble in concentrated acids as HCl, and on addition of water, alcohol, glacial acetic acid or acetone, are wholly or partially precipitable from such fresh solutions.

These cellulose derivatives are differentiable from the typical cellulose ethers in dissolving in alkalis, and are soluble neither in water alone nor in the customary organic solvents such as benzene, alcohol, alcohol-benzene, acetone or chloroform. The solubility in aqueous alkalis further differentiates them from cellulose ethers stated to be formed from alkalicellulose and methyl sulfate by the W. Denham and H. Woodhouse method[2]. As an initial material, any form of cellulose may be used, it being warmed in the presence of alkylating agents with such quantities of NaOH as are insufficient in themselves under the conditions of reaction to transform the cellulose into alkali-soluble conversion products. The alkalicellulose after comminution is then etherified at as low a temperature as expedient (around 40-100°) for 2-12 hrs.

1. U. S. P. 1589606; abst. J.S.C.I. 1926, **45**, 661-B; E. P. 177810; abst. C. A. 1922, **16**, 3206; J. S. C. I. 1924, **43**, 11-B; Ann. Rep. S. C. I. 1924, **9**, 153; Chem. Zentr. 1922, IV, 682; Faser. 1924, **6**, 20. F. P. 549525; abst. Chim. et Ind. 1923, **10**, 1130. Can. P. 248231 E. P. 318088; abst. C. A. 1930, **24**, 2291; J. S. C. I. 1929, **48**, 1011-B. See E. P. 269531. See Aust. P. 112620, 112623. Ital. P. 194918, 199196. Swiss P. 97634. F. P. 523931. D. R. P. 496978; abst. C. A. 1930, **24**, 3646. F. P. 715661; abst. C. A. 1932, **26**, 2052.

2. J. C. S. 1913, **103**, 1735, 1861; Proc. Chem. Soc. 1913, 251, 261.

11. *Insolubilizing Water-Soluble Alkylcellulose by Tannin.* The rather astonishing observation has been made[1] that alkylcelluloses which are soluble or swell in water, when treated with many of the albumen-precipitating agents, and particularly with tanning agents including natural tannin and tannin substitutes, are capable of forming technically useful compounds insoluble in water, and which swell but slightly or not at all therein. When alkylcelluloses are treated with such albumen precipitants as trichloracetic acid, phosphotungstic acid, phosphomolybdic acid, chrome alum, potash alum, aluminum sulfate, and especially with tannins, insoluble compounds result, either forming water-insoluble products, or those but slightly affected by water. They, however, dissolve in glacial acetic acid, benzene-alcohol, chloroform, or chloroform-alcohol.

For example, to a 5% solution of methyl- or ethyl-cellulose, a 10-30% solution of tannin is slowly added with stirring until precipitation ceases. Excess of tannin is not harmful. The fibrous, flocculent precipitate is filtered and washed, then either dried or dissolved in an organic solvent as glacial acetic acid, and used in this condition. Formaldehyde may replace the tannin. Or, an alcoholic solution of ethylcellulose becoming stretchable or dissolving in cold water, is treated with an alcoholic solution of tannin, and the clear solution either precipitated by water or used directly for film or filament formation.

Synthetic tannins are especially applicable for de-solubilizing alkylcellulose, such as condensation products obtained by treating oxynaphthalene sulfonic acid with phosphorous oxychloride[2]; condensation products obtained by

1. E. P. 234847; abst. J. S. C. I. 1925, **44**, 668-B; Ann. Rep. S. C. I. 1925, **10**, 143; Chem. Zentr. 1925, II, 1824. Aust. P. 107831. U. S. P. 1505044; abst. C. A. 1924, **18**, 3279; J. S. C. I. 1924, **43**, 784-B; Kunst. 1925, **15**, 101. E. P. 181392; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1923, **42**, 1126-A; Chem. Zentr. 1922, IV, 851; Caout. et Gutta. 1923, **20**, 11687. F. P. 552770; abst. Chem. Ztg. 1923, **47**, 474; Chim. et Ind. 1923, **10**, 944. Can. P. 249775. See also E. P. 181393. Aust. P. 94837.

2. Deutsche Koloniale Gerb und Farbstoff Ges., D. R. P. 293693, Addn. to D. R. P. 293042; abst. C. A. 1917, **11**, 2581; J. S. C. I. 1916, **35**, 1072.

treating *a*- or *b*-naphthol with sulfuric acid or by treating *a*- or *b*-naphthol sulfonic acids with condensing agents[1]; or condensation products of aminonaphthalenesulfonic acids with formaldehyde[2]; or condensates of amino-oxynaphthalenesulfonic acids with formaldehyde[3]; or phenols treated with neutral sulfites and formaldehyde[4], to which sulfuric acid may have been added[5]; or treating benzene- or naphthalene-oxysulfonic acids with formaldehyde[6]; naphthalenesulfonic acids plus formaldehyde[7]; or cresolsulfonic acids heated with condensation agents[8]; or dioxydiarylethanes plus formaldehyde[9]; or naphthalene-formaldehyde condensates[10]; or phenolsulfonic acid condensates[11].

12. *Alkylating Alkali-Soluble Cellulose.* The reluctance of normal or unmodified cellulose to react, especially in esterification and etherification processes, may be obviated to a large degree, it is claimed, by the treatment of alkalis, heat and alkylating agents into derivatives which dissolve in aqueous alkalis, and which may be precipitated therefrom by the addition of acids. These types of cellulose derivatives, in the isolated condition, or the reaction masses containing them and formed in their production, are excellent starting materials for the production of cellulose ethers of maximum desirable qualities, it being then neces-

1. Deutsche Koloniale Gerb und Farbstoff Ges., D. R. P. 293042; abst. C. A. 1917, **11**, 1520; Wag. Jahr. 1916, II, 40.
2. *Ibid.* D. R. P. 293640; abst. C. A. 1917, **11**, 2581; Chem. Ztg. Rep. 1916, **40**, 332.
3. D. R. P. 331523.
4. Roehm & Haas, D. R. P. 265855; abst. C. A. 1914, **8**, 443; Chem. Zentr. 1913, II, 1635.
5. E. Stiasny, D. R. P. 262558; abst. C. A. 1913, **7**, 3554; Chem. Zentr. 1913, II, 634.
6. Badische Aniline und Soda Fabrik, D. R. P. 291457; abst. C. A. 1917, **11**, 2742; Chem. Zentr. 1916, I, 865.
7. *Ibid.* D. R. P. 292531; abst. C. A. 1917, **11**, 1532; Chem. Ztg. Rep. 1916, **40**, 272. E. P. 7137, 1913; abst. C. A. 1914, **8**, 2780.
8. *Ibid.* D. R. P. 265415; abst. C. A. 1914, **8**, 443; Chem. Zentr. 1913, II, 1530.
9. Gesellschaft fuer Chem. Ind. Basle, D. R. P. 285772; abst. C. A. 1916, **10**, 1609; Chem. Zentr. 1915, II, 511.
10. Badische Aniline und Soda Fabrik, D. R. P. 207743; abst. C. A. 1909, **3**, 2058; Chem. Zentr. 1909, I, 1208.
11. *Ibid.* D. R. P. 260379; abst. C. A. 1913, **7**, 3198; Chem. Zentr. 1913, II, 106.

sary to use only those amounts of etherifiants stoichiometrically required or in slight excess. It is possible thus to carry out the reaction at considerably reduced temperatures than normal and to shorten the time of reaction. Furthermore, the small volume of the mass in reaction permits an increase in the output efficiency of the alkylating apparatus.

In executing the process the cellulose is first converted into the intermediate incompletely etherified product soluble in alkali and precipitable therefrom by acids, by heating any form of cellulose with such quantity of alkali as is insufficient in itself for converting the cellulose into alkali-soluble compounds. Such products dissolve in 5-10% NaOH solutions to viscous liquids, insoluble in pure water. This is then incompletely alkylated at 30-100° for 2-12 hrs. with the usual alkylants into low alkyl ethers. If the degree of alkylation is very low, the alkylcelluloses are soluble in cold water and insoluble in hot water, and are not substantially soluble in dilute alkali solutions at any given temperature than in pure water at the same temperature. After this intermediate ether has been formed, either the entire reaction mixture is etherified or else the alkali-soluble initial product may be isolated from the reaction mixture and etherified in a more or less purified condition[1].

13. *Cellulose Pretreatment with NaOH and Carbon Bisulfide.* This process is based on the observation that cellulose ethers having desirable properties are obtainable from cellulose which has been treated before etherification,

1. U. S. P. 1589607; abst. C. A. 1926, **20**, 3084; J. S. C. I. 1926, **45**, 661-B. E. P. 177809; abst. C. A. 1922, **16**, 3545; J. S. C. I. 1924, **43**, 11-B; Chem. Zentr. 1922, IV, 682; Faserstoffe, 1924, **6**, 10; Caout. et Gutta. 1922, **19**, 11497. D. R. P. 488446; abst. C. A. 1930, **24**, 2599. F. P. 549568; abst. Chim. et Ind. 1923, **10**, 1131. Can. P. 248232; abst. C. A. 1925, **19**, 3163; Aust. P. 83400. See also E. P. 177810; abst. C. A. 1922, **16**, 3206. E. P. 203347; abst. C. A. 1924, **18**, 587; J. S. C. I. 1924, **43**, 11-B; Ann. Rep. S. C. I. 1924, **9**, 153; Chem. Zentr. 1924, I, 525. F. P. 700535; abst. C. A. 1931, **25**, 3833. Cites E. P. 231807. Addn. 35752 to F. P. 664416; 676756, 679149, 700534, 700545. D. R. P. 527254, Addn. to 467003. D. R. P. 470142; abst. C. A. 1929, **23**, 2293; Chem. Zentr. 1929, I, 1528. This patent was applied for March 16, 1912, and issued Jan. 9, 1929.

with an alkali and carbon bisulfide under such conditions that the product of the reaction is at least partially water-soluble[1]. It is claimed that cellulose esters and ethers made from this initial product have a higher viscosity and greater stability. Alkalicellulose is treated with a quantity of CS_2 insufficient to convert the major portion of the alkalicellulose into viscose soluble in water (10-15 parts CS_2 are used per 300 parts alkalicellulose), the operation of partial xanthation occupying 0.5-0.75 hr. For etherification purposes, the product of CS_2 action, after removal of excess bisulfide, may be directly etherified in the usual manner.

14. *Multi-Stage Cellulose Alkylation.* It is claimed that it is possible to produce technically usable cellulose ethers of a high degree of etherification[2], and in a multi-stage process with small amounts of alkylating agents and alkalis, if cellulose materials are used which have a content of less than 2 molecular proportions of alkali to 1 molecular proportion of cellulose, and at the same time a water content of less than 0.5 parts by weight to 1 part by weight of air dry cellulose, or even with no water at all. These materials are treated with etherifying agents and the resulting intermediate product further etherified in the usual manner.

For example, the following method may be used: Cellulose is first treated with etherifying agent in the presence of less than 1.5 mol. alkali to 1 mol. cellulose (less than 3 of NaOH to 8 of cellulose), the water content being less than 0.1 part to one of air-dry cellulose. The resulting partially etherified cellulose, when the amount of water is not too small is partially soluble in aqueous alkalis, but if the water content is very small, they are at least partially soluble in cold water and in acetic and hydrochloric acids. These "intermediate" cellulose ethers are then fur-

1. E. P. 318088; abst. C. A. 1930, **24**, 2291; J. S. C. I. 1929, **48**, 1011-B. Aust. P. 118598.
2. E. P. 200834; abst. C. A. 1924, **18**, 469; J. S. C. I. 1925, **44**, 202-B; Chem. Zentr. 1923, IV, 809. U. S. P. 1683831; abst. C. A. 1928, **22**, 4246; J. S. C. I. 1928, **47**, 811-B.

ther etherified into products of substantially maximum ether groups, possessing the desirable properties of the fully etherified celluloses, especially as to satisfactory solubility in a wide range of organic solvents.

The intermediate cellulose ether is soluble 86-90% in 8% caustic soda, 0.4-0.5% in glacial acetic acid, 1-2% in 60% acetic acid, and 99.2-100% in concentrated HCl. Further etherification is effected by kneading the reaction mixture with 60-100 parts solid NaOH, adding 100-160 parts ethyl chloride and again heating for 6-24 hrs. at 90-150° in an autoclave. Ethylcellulose is then obtained from the product by acidification and thorough washing with water[1].

II. *Methods of Dreyfus and Celanese Co.* The first disclosure of H. Dreyfus for the manufacture of alkylcellulose is contained in his French Patent applied for in 1912, as detailed in the Historical Section of the Cellulose Ethers, pages 22-24. The inventions in this field may be grouped under the following general headings:

1. *Alkalizing in Presence of Volatile Solvents.* In order to keep the amount of water present in the reactions to the minimum and also to economize as much as possible on NaOH employed, the cellulose is first finely disintegrated to an impalpable powder to increase the reactive surface, and then ground with powdered NaOH, either in the entirely dry form or in the presence of a small amount of water, and to increase penetrativeness of alkali upon cellulose, a volatile solvent or diluent is added which also keeps down the temperature of reaction, and reduces the oxidizing influence of alkali upon cellulose in the finely divided condition of the latter in which it is ultra-susceptible to chemical influences. The cellulose is therefore suspended in benzene, carbon tetrachloride, ligroin, toluene or xylene, but it has been found that alkalicellulose containing volatile solvents as above requires a much longer time to age to the

1. W. Dyes, Kunstseide, 1928, **10**, 401; abst. C. A. 1929, **23**, 701. C. Claessen, Chem. Ztg. 1928, **52**, 189; abst. Rayon J. and Cellulose Fibers, 1928, **3**, No. 4, 24, 39; C. A. 1929, **23**, 520.

point optimum for etherification. Such volatile solvents do not interfere with the alkylation step[1].

2. *Restriction of Water in Alkylation.* Realizing the importance of restricting the quantity of water employed in both the alkalizing and alkylating steps, the cellulose is combined with alkali while the latter is in the solid form or in as concentrated aqueous solution as possible, followed by the etherification step so adjusted that the water introduced during or before the etherification, but disregarding the water formed in the reaction, in total amount of water employed, is restricted to 50% relative to the weight of the cellulose or conversion products. This is concretely synopsized in the following example: 120 parts of cellulose are impregnated with 25-36 parts of water, well mixed with 1.5-2 mols. (93-124 parts) sodium oxide, or an equivalent of potassium oxide, calcium oxide, magnesium oxide, barium oxide, calcium hydride, magnesium hydride, metallic calcium, barium or sodium, or sodamide or sodium ethylate powder. Meanwhile the mixture is strongly cooled with brine. The sodium oxide combines with the water to form 3-4 molecules NaOH, and at the same time takes about 1.5-2 mols. water (25-36 parts) out of the cellulose, thus leaving the cellulose practically anhydrous, while the NaOH formed becomes united with the cellulose. After kneading the mixture 1-2 hrs. ethyl sulfate is incorporated, using 3-4 mols. Temperature during etherification is kept below 80° and preferably below 55°. The actual etherification is completed within 4 hrs[2].

1. H. Dreyfus, U. S. P. 1501207; abst. C. A. 1924, **18**, 2809; J. S. C. I. 1924, **43**, 743-B. E. P. 176420; abst. J. S. C. I. 1922, **41**, 324-A; Chim. et Ind. 1923, **9**, 769; Caout. et Guttap. 1922, **19**, 11496; Chem. Zentr. 1922, IV, 182; Faserstoffe, 1923, **5**, 71. F. P. 462274; abst. J. S. C. I. 1914, **33**, 248; C. A. 1914, **8**, 3859; Chem. Ztg. Rep. 1914, **38**, 349; Rev. Chim. Ind. 1914, **25**, 81.

2. H. Dreyfus, U. S. P. 1542541; abst. C. A. 1925, **19**, 2411; J. S. C. I. 1925, **44**, 587-B. E. P. 164375; abst. C. A. 1922, **16**, 495; J. S. C. I. 1921, **40**, 540-A; Ann. Rep. S. C. I. 1921, **6**, 138; Chim. et Ind. 1922, **8**, 654; Chem. Tech. Uebers. 1921, **45**, 327. E. P. 187639; abst. C. A. 1923, **17**, 1141; J. S. C. I. 1923, **42**, 10-A; Chem. Met. Eng. 1923, **28**, 511; Chem. Zentr. 1923, II, 643; Ann. Rep. S. C. I. 1923, **8**, 150; Chim. et Ind. 1923, **10**, 542. F. P. 530891; abst. Chem.

3. *Cellulose Etherification with Phosphoric Acid.* In order to further control the reaction, the etherification is carried on with the use of orthophosphoric acid, either alone or with admixture of metaphosphoric acid, to which control materials, catalyzers, contact bodies or condensing agents may be added, small quantities of sulfuric acid being helpful in promoting the reaction. The process is preferably carried on at as low a temperature as possible, depending upon the reactants. With sulfuric acid, care must be exercised to maintain low temperature limits. For instance, benzylcellulose may be prepared by the direct action upon cellulose of benzyl alcohol and phosphoric acid. The scope of the process embraces the production of ethers when any portion of the hydrogen of the OH groups of cellulose or its conversion products has been replaced by a radical as benzyl, but instead of using the corresponding alcohol (benzyl alcohol), it may be wholly or partially replaced by benzyl chloride or by mono- or di-benzyl sulfate.

The cellulose to be treated may be subjected to a pretreatment operation before etherification in order to promote the reaction, as by treatment with a mixture of glacial acetic acid containing 2-3% sulfuric acid for a period sufficiently long to bring the cellulose to the degree of reactivity desired; or pretreatment with 70-85% orthophosphoric acid with or without the addition of alcohol in the presence of a relatively small amount of sulfuric acid may be used[1].

4. *Alkylation Without Prior Alkalicellulose Formation.* Ethers are directly preparable from normal cellulose in a quite simple and expeditious manner by treating the cellulose with an etherifiant at room temperature for several hours, and to prevent tendering of the cellulose by the

Zentr. 1922, II, 899-R. F. P. Addn. 24082 to F. P. 530891. F. P. 549880. Can. P. 237709; abst. C. A. 1924, **18**, 1051. Australia P. 6250, Addn. to 2543. Belg. P. 290613. See H. Dreyfus, Can. P. 236956. E. P. 164374; abst. C. A. 1922, **16**, 493; J. S. C. I. 1921, **40**, 540-A; Ann. Rep. Soc. Chem. Ind. 1921, **6**, 138; Chem. Tech. Uebers. 1921, **45**, 327; Chim. et Ind. 1922, **8**, 654. F. P. 522613. Belg. P. 290449.

1. C. Dreyfus, E. P. 269531; Chem. Zentr. 1927, II, 655. F. P. 632616; abst. C. A. 1928, **22**, 3528. Can. P. 286918.

action of the etherifying material, a small amount of sodium or potassium hydroxide or carbonate is added. It is preferable not to allow the reaction temperature to rise above 60° until the reaction is completed, which requires 5-24 hrs. Thus, 5 k. cotton linters are treated with 60 liters ethyl sulfate and 2 k. sodium carbonate, the mixture being permitted to stand over night at about 45°, after which it is cooled and 25 liters 50% NaOH solution added. The mixture is placed in a water-jacket vessel and the temperature maintained at 40° for 12 hrs., an ethylcellulose being produced almost completely soluble in benzene and alcohol. Or, 10 gms. cotton are treated with 70 cc. ethyl sulfate and 2 gms. sodium carbonate over night, then 20 cc. 50% aqueous NaOH solution added together with 5 gms. 20-mesh NaOH. The mixture is maintained at about 45° for 5 hrs. and then washed. There is obtained 10 gms. ethylcellulose of which 25% dissolves in benzene, the remainder, except for a trace, being soluble in ethyl alcohol[1].

5. *Alkylcellulose Production in One-Step Etherification.* This method of manufacture comprises treating alkalicellulose containing free alkali with the full amount of the etherifying agent required to produce cellulose ethers containing no cold water soluble portions. As a starting material there is used an alkalicellulose formed by impregnating cellulose with a large excess of 18% NaOH solution for 1 day, and then pressing to a weight of 240 parts per 100 of original cellulose. Employing 18% NaOH solution, this requires a very high pressure, and the alkalicellulose formed is almost dry to the feel, 20 parts of this alkalicellulose (containing 1 molecular proportion of cellulose) is treated with 54 parts ethyl sulfate (7 mols.). To this mixture solid NaOH is added in increments during the etherification, the total amount of NaOH employed being 14 parts

1. G. Miles, U. S. P. 1841335; abst. C. A. 1932, **26**, 1781; Plastics, 1932, 8, #5, 219. Brit. Celanese, Ltd., E. P. 315278; abst. C. A. 1930, **24**, 1740; J. S. C. I. 1930, **49**, 1022-B; Silk J. 1929, **6**, #66, 68; Br. Plastics, 1930, **2**, 322. C. Dreyfus, F. P. 677927; abst. C. A. 1930, **24**, 3368.

by weight (8 mols.). Ethylation proceeds for 9 hrs. at 40-45°, at the end of which time the alkali content has dropped from 19.3% to 3.1%, no further decrease in alkali content taking place on further heating at 50°. The ethylcellulose after washing contains no cold water soluble cellulose ethers, and dissolves in benzene[1].

6. *Etherifying Cellulose Esters.* Esters of cellulose as the formate, acetate, propionate, butyrate and benzoate may be converted into cellulose ethers[2] by the action of reducing agents as hydrogen or carbon oxides in the presence of a catalyst (nickel, nickel oxide, copper, copper oxide, platinum, palladium, cobalt or iron, by the application of reducing agents as sodium amalgam, aluminum amalgam, zinc-copper couple, hydriodic acid, phosphorous iodide or a mixture of iodine and phosphorus. The reduction is preferably conducted with anhydrous materials. The ester is dissolved or suspended in an appropriate solvent or solvent mixture as ether, benzene or toluene, and the reducing agent applied.

Cellulose esters may also be transformed into cellulose ethers[3] by treatment with hydroxy-compounds as alcohols or phenols in the presence of organic bases containing the OH-group as dialkyl-anilines or -naphthylamines, pyridine, quinoline, dimethyl-*n*-hexylamine and *iso*amyldiethylamine, and in the presence of sodium or potassium methylate, ethylate or benzylate.

III. *Processes of I. G. Farbenindustrie.* The methods of alkylcellulose production, as disclosed by the scientists of this organization, may be summarized in the following seven separate processes, numbered consecutively from one to seven:

1. In order to facilitate the soaking step in the prepa-

1. G. Miles, U. S. P. 1864546. Can. P. 325061, 325062.
2. H. Dreyfus, F. P. 713699; abst. C. A. 1932, **26**, 1781. See F. P. 679284.
3. *Ibid.* F. P. 713700.

ration of alkalicellulose[1], air is excluded during the mercerizing, whereby it is claimed more valuable and uniform cellulose ethers are obtainable. The invention makes use of a gas or vapor capable of reacting with and being absorbed by the alkali solution, the cellulose being subjected to a current of the gas or vapor passed through the mercerizing vessel while a vacuum is maintained therein. When the air has been eliminated as indicated by analysis of the effluent gas, NaOH solution is introduced and more completely fills the pores than if added to the cellulose before exhaustion of air and replacement by other gas. Suitable gases are carbon monoxide, carbon dioxide, acetaldehyde, formaldehyde, formic acid or acetic acid. The following are illustrative examples:

(a) Air-dried sulfite cellulose pulp (92% alphacellulose) is dried under vacuum while CO_2 is passed through at 60° until the cellulose is freed from air. The chamber is then filled with "strong" caustic soda solution and the pulp allowed to swell therein for some time. After it has been squeezed, the alkalicellulose is ready for etherification.

(b) Wood pulp as above is treated for a few hours with a current of acetaldehyde vapor while maintaining a vacuum, and is then soaked in caustic soda solution. After the mass has been allowed to swell, then squeezed, and the pulp wound together with wire netting into a roll in which adjacent layers of pulp are separated by wire netting, and then methylated in a current of methyl chloride at 70°. The methylcellulose obtained is highly viscous, and suitable for agglutinating purposes.

2. Particular advantages are claimed to result when the alkylant is used in vapor form, and the alkalicellulose in a semi-moist state, the proportion of alkali to carbohydrate being represented by 20 mols. of the former to 1

1. E. P. 293316; abst. C. A. 1929, **23**, 1750; J. S. C. I. 1929, **48**, 1011-B; Chem. Zentr. 1928, II, 1840. E. P. 293757; abst. J. S. C. I. 1929, **48**, 1011-B; Chem. Zentr. 1928, II, 2060. D. R. P. 492246; abst. C. A. 1930, **24**, 2469. F. P. 656861; abst. C. A. 1929, **23**, 4342. O. Ernst and K. Sponsel, U. S. P. 1858731; abst. C. A. 1932, **26**, 3919.

mol. of the latter[1]. The salient points in the process are indicated in the following illustrations:

(a) 60 k. cotton are soaked in 900 k. 35% NaOH solution for 24 hrs., squeezed to 180 k., allowed to age 120 hrs., then ethyl chloride is conducted over the mass in an autoclave for 17 hrs. at 125-130° while stirring. The light-yellow fibrous product thus produced dissolves partially in cold water and partially in alcohol-benzene. It is then again soaked with 900 k. NaOH solution of 35%, the mixture allowed to stand 24 hrs., and treated with ethyl chloride as above. Yield 40 k. or 67% of a light yellow product of 43% ethoxyl. Considering the moderate temperature of etherification (130°) and the comparatively high percentage of ethoxyl, the yield appears unduly low.

(b) 25 k. wood pulp are soaked in 50% NaOH solution 2 hrs. at 30°, squeezed to 60 k., disintegrated, and placed in a 700 liter reaction vessel with pump for circulating gas of variable efficiency up to 36 cu. m. per hr., a cooler with receiver and a heating device. The reacting vessel is well insulated thermally. After the air has been expelled from the apparatus by means of methyl chloride gas, the alkalicellulose is carefully warmed by the circulating methyl chloride, a temperature of 70° being maintained. There is no formation of gaseous products as methyl ether. The mass, which still shows an alkaline reaction, is washed and dried. It contains 34-38% methoxyl, and dissolves in water at 5° to a clear, viscous solution, which yields transparent firm film. Soluble also in glacial acetic acid, formic acid, alcohol-benzene and alcohol-chloroform; insoluble in methyl acetate, butyl acetate or acetone.

1. E. P. 302191; abst. C. A. 1929, **23**, 4342; J. S. C. I. 1929, **48**, 167-B. F. P. 640174; abst. C. A. 1929, **23**, 846; Chem. Zentr. 1928, II, 1616. Can. P. 283917. I. G. Farbenindustrie, O. Ernst, G. Balle and K. Sponsel, D. R. P. 525650, Addn. to D. R. P. 522575; abst. C. A. 1931, **25**, 4705; Nitrocellulose, 1931, **2**, #6, 104. K. Sponsel, G. Balle and O. Ernst, D. R. P. 533462, Addn. to D. R. P. 522575; abst. C. A. 1932, **26**, 3376. O. Ernst and K. Sponsel, D. R. P. 522575; abst. C. A. 1931, **25**, 3832. F. Guhring and I. G. Farbenindustrie, Can. P. 317262. See E. P. 275660.

(c) 50 k. sulfite cellulose are soaked at 60° for 2 hrs. in 70% NaOH, squeezed to 125-130 k. and disintegrated. After introducing into an autoclave and expulsion of air therefrom, the reaction was conducted as in (a) but at 110-115°, the formed ethylcellulose being fibrous. Ethoxyl 44%. Soluble in but a few solvents, as glacial acetic acid, formic acid, alcohol-benzene, alcohol-chloroform; does not dissolve or swell in water, acetone, benzene, methyl acetate or butyl alcohol.

(d) 100 k. unbleached wood pulp (90% α-cellulose, copper number less than 2) are steeped 2 hrs. at 60° in NaOH solution, sp. gr. 1.63 at 60°, squeezed to 250 k., disintegrated and then exposed for 12 hrs. at 100-105° under 5 atms. pressure to ethyl chloride gas, which is pumped through the agitated mass. The product is precipitated, washed and bleached. The ethylcellulose obtained is soluble in alcohol-benzene 1:1 to a clear solution, but insoluble in alcohol, benzene, water, methyl acetate, acetone or other individual solvent.

3. The etherification operation is carried out in such a manner that a vessel containing NaOH is placed within the alkylating vessel to absorb the water given off in the reaction, the sodium hydroxide upon absorption of water liquefies and drops down into the etherifying mass, thus maintaining the alkali concentration automatically and continually[1]. The alkalicellulose and ethyl chloride are heated in the customary manner in a stirring autoclave, in the upper part of which a perforated vessel is placed, which is charged with solid caustic soda. At the commencement of heating the autoclave, the ethyl chloride first reacts with the alkalicellulose, while simultaneously water is abstracted from the reaction mixture owing to the presence of dry NaOH in the vessel placed above. The NaOH gradually

1. O. Leuchs and E. Doerr, U. S. P. 1694127; abst. C. A. 1929, **23**, 981; Plastics, 1929, **5**, 454; J. S. C. I. 1929, **48**, 353-B; Chem. Zentr. 1929, I, 1635. E. P. 306857; abst. C. A. 1929, **23**, 5317; J. S. C. I. 1929, **48**, 353-B. D. R. P. 505797; abst. C. A. 1931, **25**, 592. See E. P. 286789, 288143.

passes into solution incident to absorption of water, and then drops down into the alkylating mixture, thus replacing the caustic soda which enters into the etherification reaction. In this manner NaOH is automatically introduced to the alkalicellulose. The quantity of alkali placed in the vessel above is so adjusted that the alkali passes completely into solution. Or an arrangement may be made so that a second vessel filled with calcium chloride may be used as drying agent, in which event, more NaOH is required for the actual etherification, if an ether of maximum alkyl is desired to be produced.

4. Whereas it is usually necessary to produce cellulose ethers in at least a two stage process[1] in which the first operation is the formation of alkalicellulose which is then transformed into etherized cellulose by another and separate procedure, if the cellulose be previously disintegrated it may be simultaneously admixed with alkali and alkylating agent into a kneading apparatus provided with stirring equipment, and heated for several hours at 80-150° until etherification takes place. At the conclusion of the reaction, the etherifying agent and the volatile secondary products formed are distilled off or extracted, and the cellulose ether precipitated and purified. Depending upon the amount of alkali or water present in the reaction mixture, one or more hydrogen hydroxyls in cellulose may be replaced by alkyl in a single operation, as indicated quantitatively in the following examples:

(a) 10 parts disintegrated cellulose, 100 parts 50% NaOH, 60 parts ethyl chloride are introduced into a horizontal autoclave provided with a stirring apparatus and heated 6 hrs. at 120-140°. The volatile portion of reaction (ethyl chloride, ether, alcohol) is distilled off and the ethylcellulose washed and dried. Contains 45-46% ethoxyl, and is soluble in benzene-alcohol 8:2.

1. E. Huber, U. S. P. 1805365; abst. C. A. 1931, **25**, 3832. E. P. 346426; abst. C. A. 1932, **26**, 2052; J. S. C. I. 1931, **50**, 671-B; Silk J. 1931, **8**, #88, 54. See Belg. P. 358020. Ital. P. 260707, 260746.

(b) 10 parts beaten sulfite wood pulp, 40 parts 50% NaOH, 60 parts ethyl chloride are heated together 5-6 hrs. at 110° in a pressure kneading vessel with agitation arrangement, the volatile secondary products removed, and the ethylcellulose washed and dried. 42% ethoxyl, and soluble in benzene-alcohol 1:1.

(c) 10 parts cotton linters, 10 parts 50% NaOH, 7.5 parts powdered NaOH, 60 parts ethyl chloride are heated at 110° 5-6 hrs. in a horizontal autoclave provided with stirring apparatus. The ethyl chloride is vaporized and the ethylcellulose washed and dried. 42-43% ethoxyl, and soluble in benzene-alcohol 1:1.

5. A process has been described for alkylcellulose manufacture in which the alkalicellulose in the form of the pulp-board as marketed is etherified with gaseous agents, which have a sufficient intensity of penetration on coherent alkalicellulose to ensure proper degree of alkylation. To improve the permeability of the alkalized boards, it is advantageous to isolate the individual boards by interstices as by the interposition of wire nettings between the layers. The process is carried out as follows[1]:

(a) *Methylcellulose.* A roll of cellulose weighing 100 k. is continually steeped at 55° in 60% NaOH solution, squeezed on a rolling frame to 250 k., and wound up on a winding trestle together with a wire netting cloth. The roll thus obtained is placed in a pressure vessel wherein the methylating operation is to be performed, and methylated 8 hrs. at 70° under 5 atms. pressure by means of methyl chloride gas. The product is washed with hot water and dried at 95°. The cellulose ether dissolves in alcohol-benzene 1:1 to a clear and viscous solution, likewise in ice water.

(b) *Ethylcellulose.* Cellulose pulp-boards are steeped in 70% NaOH solution, which is preferably done in the

1. O. Ernst, K. Sponsel and G. Balle, U. S. P. 1863745. D. R. P. 536993; abst. C. A. 1932, **26**, 1438. E. P. 275660; abst. C. A. 1928, **22**, 2464; J. S. C. I. 1929, **48**, 50-B; Plastics, 1928, **4**, 508; Chem. Zentr. 1927, II, 2583. F. P. 639150; abst. C. A. 1929, **23**, 703.

heat and in a vacuum, the material squeezed to 2:5 times the original weight of the cellulose. After interposing wire nettings between the layers and placing them in a bomb, the material is ethylated at 100° under 5 atms. pressure for 12 hrs. with ethyl chloride. The ethylcellulose dissolves to a clear and viscous solution in mixtures of solvents, and in alcohol, benzene, acetic acid and acetates.

6. In addition to the difficulty of ensuring uniformity in mixing the components of the etherizing mixture as is absolutely necessary for accordant quality, and the entering of the two undesired side reactions, namely the action of the metallic hydroxides liberated from the metallic compound of the cellulose by the dissociating action of the water upon the alkylating agent whereby a large proportion of the alkylating agent is withdrawn from the reaction; and the degrading action of the free metallic oxides upon the cellulose whereby mostly water-soluble products are formed, the alkylation of which results in ethers of diminished technical usefulness, it is claimed the addition of water-soluble neutral salts, preferably in such amounts that the reaction mixture continually forms a powdery dry mass, insures a uniform etherification with a minimum of cellulose degradation[1]. As a result of the saturation of the water contained in the reaction mixture with salts, dissociation of the cellulose-metallic compounds is repressed, formation of undesirable by-products minimized, and the degrading action of free metallic oxides or hydroxides on the cellulose substantially prevented. Besides this, there is said to result because of the continuous motion of the reaction mixture containing salts, a grinding action of the sharp cornered salt crystals on the cellulose, a point described by E. Teupel in XI using sodium chloride, and by D. Bradner in VIII, employing potassium chloride. The process is carried out by preparing an alkalicellulose containing 2

1. G. Balle, D. R. P. 494917; abst. C. A. 1930, **24**, 3646. E. P. 326865; abst. C. A. 1930, **24**, 4931. See D. R. P. 592062; abst. C. A. 1930, **24**, 2599. F. P. 669256; abst. C. A. 1930, **24**, 1740. E. P. 305946; abst. C. A. 1929, **23**, 5040. Belg. P. 354784.

mols. NaOH per mol. $C_6H_{10}O_5$, corresponding to a 40% dipping lye, and thus adding 44% cellulose, 22% NaOH, and 33% water. This is mixed with about 3 times its weight of sodium sulfate, calcium chloride or magnesium chloride, and upon this mixture 2-4 mols. ethyl sulfate are allowed to react at 60-80°; another 2 mols. NaOH are then introduced, either in solid powdered form or in 50% solution and 2-4 mols. ethyl sulfate are allowed to react upon the dry mixture. In place of ethyl sulfate, a corresponding amount of sodium ethylsulfate or chlorethylethylsulfuric acid may be used, only the etherification is carried on under pressure.

7. To facilitate etherification[1], it has been proposed to moisten cellulose with water or steam, treat with organic solvents as dimethylaniline, then mercerize with NaOH and finally etherify as with ethyl chloride, or to conduct the etherification under reduced pressure or by passing a stream of nitrogen or carbon dioxide through the reaction chamber[2].

IV. *Imperial Chemical Industries Alkylation Processes.* An alkali concentration of but 18-20% NaOH is used with cellulose for alkalicellulose formation[3], which is matured at 20-30° and then treated with a mixture of 50 parts caustic soda per 100 parts cellulose with methyl chloride or ethyl chloride as the alkylating agent. The methylcellulose or ethylcellulose formed is soluble in ethylenechlorhydrin, alcohol, benzene or alcohol-benzene. The scope of the process is indicated by the following three methods of procedure:

1. 100 parts cellulose in sheets are immersed in 18-20% NaOH solution at room temperature for an hour or more, pressed until the mass is reduced to 2-3 parts based on the original cellulose used, then shredded in a Werner Pfleiderer and allowed to ripen at —10-+50°, preferably

1. E. Huber, D. R. P. 526792; abst. C. A. 1931, **25**, 5030.
2. F. P. 717623; abst. C. A. 1932, **26**, 2862.
3. F. P. 696158; abst. C. A. 1931, **25**, 2847.

20-30°. For artificial filament manufacture, it is preferable to mature the alkalicellulose 12-24 hrs. at 20-25°, to obtain a solution of 10% in toluene-alcohol of a viscosity of about 2000 c.g.s. units. The properly matured alkalicellulose is placed in an autoclave with stirring arrangement with 50 parts powdered NaOH per 100 of original cellulose, an excess of methyl chloride or ethyl chloride introduced, and the mass heated to 90-110°. As the halogen alkyl becomes consumed, the pressure in the autoclave diminishes. Heating is continued for 4-24 hrs. To obtain the solubility desired in the etherified cellulose, a further quantity of NaOH and alkyl chloride may be added and heating continued. With methylcellulose, the ether is soluble in water, and is obtained as a white, granular mass. If ethylcellulose is produced, this is found soluble in alcohol-benzene, alcohol-toluene, or in benzene, alcohol or ethylenechlorhydrin.

2. 100 parts cellulose are immersed in 18-20% NaOH solution for 24 hrs., pressed to 200-400 parts, shredded in a Werner Pfleiderer disintegrator, matured 3 days at 25°, then treated in an autoclave with 75 parts finely pulverized NaOH and 300 parts ethyl chloride. Intimate mixing with a heat of 90-110° is carried on for 8 hrs. Another addition of the same quantity of NaOH and ethyl chloride is made, and heated for a further 8 hrs. After each heating period the excess of ethyl chloride is recovered. The cellulose ether is finally precipitated, washed with water to remove salts, neutralized and dried. It is easily soluble in alcohol, mixtures of benzene or toluene with alcohol, and in ethylenechlorhydrin. Ethylcellulose produced in this manner in a 10% strength in benzene-alcohol or toluene-alcohol 80:20 by volume, has a viscosity of 15-50 c.g.s. units, that is, it is exceedingly limpid.

3. 100 parts cellulose are immersed in 18-20% NaOH solution for 24 hrs., pressed to 200-400 parts, shredded, matured 3 days at 25°. Then the matured alkalicellulose is placed in a pressure reaction chamber together with 75

parts finely powdered NaOH and 300 parts ethyl chloride and heated to 90-100° for 8 hrs. A second and third addition of NaOH and ethyl chloride as above is added, with 8 hr. heating intervals between. The precipitated and purified ethylcellulose readily dissolves in mixtures of benzene or toluene with alcohol, and in benzene-toluene (80:20) and produces thermoplastic mixtures which are highly resistant to abrasion.

4. Alkalicellulose is produced as in (2). This is matured 3 days at 25° and placed with 50-100% NaOH based on original cellulose weight in an autoclave, in which an excess of methyl chloride is pumped in at 14 k. pressure per centimeter. After 8 hrs. heating another amount of NaOH and methyl chloride is introduced and the mass heated 8 hrs. additional. Dimethylcellulose is obtained.

V. *Eastman Kodak Processes.* In order to increase the ratio of NaOH in alkalicellulose without a drying operation after mercerization and ageing, J. Donohue[1] has proposed to squeeze out the excess alkali after alkalizing until the remainder carries the right amount of water for the etherifying action. This may be accomplished by adding a quantity of powdered alkali mixed into the mass of mercerized cellulose fibers shortly before the excess of solution is mechanically pressed out and removed. Thus, 32 gms. dried cellulose are soaked in 576 gms. 50% NaOH solution for 72 hrs. at 18°, 16 gms. powdered NaOH then mixed into the mass, and the latter then pressed down to 144 gms., the excess solution being thus pressed out. It is claimed this results in a very intimate mixture of cellulose with the right amounts of NaOH and water for subsequent use in the etherifying operation, although it must be obvious that the loss in alkali must be unduly high. This mixture is then charged into an autoclave with 120 gms. ethyl chloride, then heated 24 hrs. at 90-170°, the contents meanwhile being agitated.

1. U. S. P. 1415023; abst. C. A. 1922, **16**, 2406; J. S. C. I. 1922, **41**, 542-A; Chem. Zentr. 1922, IV, 600; Chem. Tech. Uebers. 1922, **46**, 282; Caout. et Guttap. 1923, **20**, 11930.

It has been found that the reaction may be successfully carried on in an autoclave lined with steel[1], and although the fresh surface of the steel causes contamination and the formation of dark colored cellulose ethers, where the steel lining is repeatedly subjected to the action of the alkylating components, it becomes immunized from the formation of a dark ferrous compound being formed on its surface. Or[2], the autoclave walls may be lined with nickel or a nickeliferous alloy as Monel metal. By so doing, so the patentee asserts, tendency to produce films with haze is obviated. Not that the haze is due to metallic salts formed by the action of ingredients upon the lining of the autoclave, but that certain metals have a specific beneficial action which improves the product—a novel and ingenious theory.

P. Seel[3] claims that cellulose ethers which yield better and stronger sheets and films are producible where the etherification step requires a longer time, especially in the heating up of the material. For example, there is placed in an oil-heated autoclave an intimate mixture of cellulose 100, water 250 and NaOH 200. To this there is directly added without ageing of the alkalicellulose or comminuting the same, 400 of ethyl chloride. The temperature is then gradually raised through heating the oil-bath until the desired reaction temperature has been reached. After the slow warming up or induction period is over, the reaction temperature is maintained during the residual period. The mass is initially heated up over a 12 hr. induction period at 90-170°, the residual period being the same.

It is alleged cellulose ethers of sufficiently satisfactory quality for the production of electrical insulating coatings[4] are obtainable when all the ingredients are added substantially separately to the reaction space and then agitating

1. P. Seel, U. S. P. 1437820; abst. C. A. 1923, **17**, 879; J. S. C. I. 1923, **42**, 91-A.
2. J. Donohue, U. S. P. 1489315; abst. C. A. 1924, **18**, 1908; J. S. C. I. 1924, **43**, 464-B; Chem. Zentr. 1924, II, 1992.
3. U. S. P. 1437821; abst. C. A. 1923, **17**, 879.
4. P. Seel, U. S. P. 1464158; abst. C. A. 1923, **17**, 3253.

and heating the reaction mass until the degree of etherification desired has been obtained. By "substantially separately" is to be construed as meaning that the very intimate preadmixture of alkali and cellulose has been obviated. For example, an autoclave is charged separately with cotton 100, water 250, solid NaOH 200 and ethyl chloride 400. The ingredients are then stirred at temperatures from 90-170° (considerable latitude) for about 24 hrs., or until the desired etherification has taken place.

P. Seel[1] claims, and very rightly, that the strength, flexibility and transparency of cellulose ether films depends to a large degree upon the manner and intimacy with which the alkali is admixed with the cellulose prior to etherification. This may be obviated by causing the mixture of cellulose and alkali to be subjected to rapidly repeated impacts, sufficiently violent and rapid to disintegrate the fibers and cause an intimate physical union. This may be done by charging them into a disintegrating mill in which a series of rapidly revolving arms repeatedly strike and throw the ingredients in different directions, the blades being so adjusted to give a series of violent blows as distinguished from mere attrition. In this manner, bundles of woody fibers or cotton filaments are crushed and torn apart, being fractured into minute pieces.

In order to simplify the process and economize in amount of alkali used per unit weight of cellulose etherified[2], the water and alkali are added separately to the cellulose in amounts approximating those required during the alkylation. For example, 100 parts of cellulose are moistened with 50 parts of water, and this intimately mixed with 200 parts dry NaOH, preferably as indicated in the paragraph above. This eliminates treatment of the cellulose with caustic solution and subsequent expression of excess alkali,

1. U. S. P. 1507210; abst. C. A. 1924, **18**, 3477; J. S. C. I. 1924, **43**, 904-B.

2. P. Seel, W. Webb and J. Donohue, U. S. P. 1813665; abst. C. A. 1931, **25**, 5288; J. S. C. I. 1932, **51**, 500-B; Plastics, 1932, **8**, #1, 43.

and permits the use of a low percentage of water in proportion to the cellulose present.

VI. *Societe Chimique des Usines du Rhone.* In large scale etherification operations, the apparatus of N. Grillet[1] may be employed. It comprises, as shown in Fig. 6, a cylindrical container *a* provided with peripheral rails *b b* resting on rollers *c c* and driven round by a toothed wheel *d* engaging a peripheral rack *e*. The container is cooled or heated by the sprayer *f*. A manhole *g* and a drainage aperture *h* are provided, also sampling pipes *k k*.

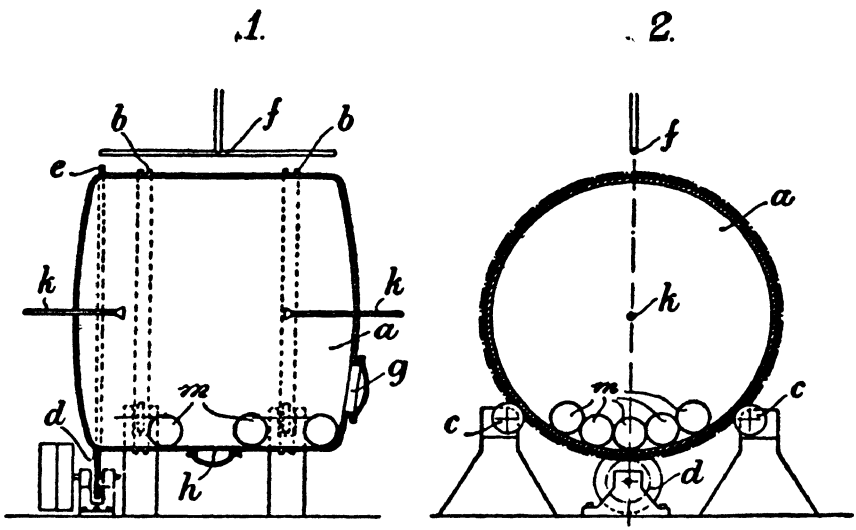


Fig. 6. Cellulose Ether Purification.

It is feasible to construct the apparatus to hold a charge of 1000 k. cellulose or more, whereby installation costs, power consumed and cost of supervision and manufacture are reduced. Large amounts of cellulose ethers perfectly homogeneous are thereby obtainable, allowing

1. U. S. P. 1566398; abst. C. A. 1926, **20**, 503; J. S. C. I. 1926, **45**, 152-B; Plastics, 1926, **2**, 134; Chem. Zentr. 1926, I, 2522. E. P. 231837; abst. C. A. 1925, **19**, 3593; Chem. Zentr. 1925, II, 2331; J. S. C. I. 1926, **45**, 483-B. F. P. 592423; abst. Chem. Zentr. 1925, II, 2331. D. R. P. 511793; abst. C. A. 1931, **25**, 1378. Swiss P. 113353, 124767.

large scale production of filaments and films of uniformity in composition and properties. It is also said to be possible to noticeably reduce the quantity of solvent employed to 2-3 times the weight of cellulose used. The apparatus may be cylindrical, with horizontal or oblique axis, rolling on its side upon rollers, or by means of gearings. By varying the speed of rotation and the number and weight of balls therein, a wide range of stirring is possible. The apparatus is externally cooled, as by dipping into a trough of cooled brine.

The diluent selected is preferably a solvent for the alkylcellulose being produced, so that the mass under treatment, thick at first, gradually becomes thinner as esterification proceeds and the cellulose ether formed passes into solution, the ratio of solvent to cellulose being 6:1. By constructing a spherical apparatus without the internal use of mixers or baffles, danger of but partially acted-upon cellulose adhering in corners is obviated.

VII. *Farbenfabriken vorm. F. Bayer & Co.* This process of O. Leuchs[1] is mainly of historical interest from the comparatively early date of application, Jan. 12, 1912, in Germany, and Aug. 8, 1917, in the United States. The process depends upon the now familiar action of halogen alkyls upon alkalicellulose, the cellulose ether obtained being insoluble in water, caustic alkalis and dilute acids, but dissolvable in alcohol, ether, chloroform, benzene, benzine, carbon tetrachloride, ethyl acetate and acetone. According to the method of preparation, products are obtained only partially soluble in benzene, the remainder merely swelling, but dissolving in another solvent as alcohol. In other words, the cellulose ether passes into solution in alcohol-benzene.

1. D. R. P. 322586; abst. Chem. Zentr. 1920, IV, 416. Although this invention was applied for in 1912, it quiesced in the German Patent Office archives until 1920, when it issued on July 1 under the name Farbenfabriken vorm. F. Bayer & Co. U. S. P. Appl. Serial No. 185198, filed Aug. 8, 1917; official letter Aug. 28, 1917; Lilienfeld, E. P. 12854, 1912, and 6035, 1913, cited against applicant. Nine claims. The invention was assigned to Farbenfabriken vorm. F. Bayer & Co. and came into the possession of Synthetic Patents Co.

The solutions in benzene and in dry ether deposit transparent films, which melt but do not ignite when melted.

The patent is exemplified by allowing cellulose to swell in NaOH solution (1:1) for 1-2 days or longer, excess of lye removed and the alkalicellulose formed then dried. The alkalicellulose thus obtained is heated with 3 parts ethyl chloride to 1 part cellulose under pressure, at 130° for 8 hrs., the ethyl chloride excess then distilled off, the residue (ethylcellulose) leached out with water for the removal of salts, and dried. The cellulose ether is then dissolved in alcohol, pressure filtered, precipitated by dilution with water, refiltered and dried. It is thus obtained as a white, amorphous powder. As a rule, one uses 2 mols. alkylating agent per mol. cellulose.

It seems peculiar with the relatively low proportion of ethyl chloride to cellulose, that ethylcelluloses are obtained of sufficient high ethylation to be insoluble in water, and yet dissolve in ether or benzine.

VIII. *Du Pont Alkylcellulose Processes.* It is known that the use of very high ratios of caustic alkali to water in cellulose etherification is necessary to obtain ethers which are completely soluble in the more common organic solvents and which are water-resistant. It is also recognized that strong caustic solutions at relatively high temperatures have a detrimental action upon the film-forming qualities of the cellulose nucleus, whereas cellulose ethers are relatively stable toward the action of strong alkali solutions. It is desirable therefore, to etherify the cellulose as quickly as possible to conserve to the maximum its desirable film-forming qualities.

D. Bradner[1] recommends replacing the sodium chloride used in etherifying by E. Teupel (see p. 1454) by means of potassium chloride, or salt other than the salt formed in the etherification, which is normally NaCl, having found, so he says, that the addition of potassium chloride to an

1. U. S. P. 1813726; abst. C. A. 1931, **25**, 5287; Plastics, 1932, **8**, #1, 43; J. S. C. I. 1932, **51**, 500-B. Can. P. 311489.

ethylation mixture containing cellulose, caustic soda, water and ethyl chloride is much more effective than sodium chloride in increasing the rate of ethylation, comparative yields showing without the use of any solid a yield of 116%, with sodium chloride 126%, and with potassium chloride 134%, assuming all the other ethylation factors remained constant.

A comparison of a standard ethylation (using a slurry of caustic soda and cellulose in benzene, water and ethyl chloride in a 25 gal. autoclave) with a similar ethylation to which potassium chloride was added, shows the following advantages gained by the use of a potassium salt:

1. Reduction in consumption of ethyl chloride by about 20%.
2. Decrease in time of ethylation by about 50%.
3. Films obtained appear to be as good as those obtained from standard products.

Potassium sulfate, potassium carbonate, or lithium, rubidium or caesium chlorides may replace potassium chloride. The recommended method of procedure is as follows:

10 lb. each cellulose, water and potassium chloride, 40 lb. NaOH, 50 lb. ethyl chloride and 87 lb. benzene are charged into an autoclave. Observe that E. Teupel uses no benzene or similar diluent. The mixture is agitated and heated 5 hrs. at 150°. Excess of ethyl chloride and benzene, with some alcohol and ether are removed from the reaction mixture by steam distillation, the ethylcellulose remaining as a fine granular mass which is washed to neutrality and dried. Yield 14 lb. or 140% against a 130% yield by E. Teupel.

F. Hahn[1] seeks to avoid grinding of the cellulose with alkali on the ground that the operation has been found injurious to the cellulose if the grinding is at all severe. He so conducts the etherification process as to avoid incorporation of soda solutions in cellulose, on the ground

1. U. S. P. 1819600; abst. C. A. 1931, **25**, 5769; Plastics, 1932, **8**, #2, 87; J. S. C. I. 1932, **51**, 500-B. E. P. 311697; abst. C. A. 1930, **24**, 960.

that excess water interferes with a proper alkylation. The invention is carried out by grinding the cellulose to a suitable degree of fineness. There is also prepared a slurry of caustic soda in benzene, into which is introduced the ground cellulose, the components thoroughly intermingled, placed in an autoclave and etherified with methyl chloride or ethyl chloride in the usual manner. By avoiding grinding of cellulose and alkali, impairment of the ultimate quality of the cellulose ether formed is obviated, and the film forming quality of the product suitably maintained.

IX. *Processes of A. Wacker Gesellschaft.* The invention of A. Ascherl and W. Gruber[1] concerns a process which makes it possible to fix the endpoint of the etherification reaction in a simple manner, and at the same time to prevent the formation of free acid. In the etherification of cellulose with alkyl sulfates, whereby pressure apparatus is not required on account of the high boiling point of the alkyl sulfate over the corresponding chloride, it is advisable to control the course and endpoint of the reaction by means of the periodic withdrawal of samples for testing purposes. On the other hand, it is of especial importance in alkylating with alkyl esters of inorganic acids, that the reaction be terminated at the right time, since prolongation of etherification develops free mineral acid, which acts to decompose the cellulose in the presence of the high temperature employed. Previously this was brought about by either the use of a large excess of alkali[2] which requires added consumption of alkylating agent, or else particular care must

1. D. R. P. 520384; abst. C. A. 1931, **25**, 2847. F. P. 703338; abst. C. A. 1931, **25**, 4401.

2. L. Lilienfeld, D. R. P. 488780; abst. C. A. 1930, **24**, 2291. D. R. P. 499129; abst. C. A. 1930, **24**, 4157. E. P. 200827; abst. C. A. 1924, **18**, 469; J. S. C. I. 1925, **44**, 67-B; Chem. Zentr. 1923, IV, 808. O. Leuchs and E. Dörr, U. S. P. 1694127; abst. C. A. 1929, **23**, 981; J. S. C. I. 1929, **47**, 353-B; Plastics, 1929, **5**, 454; Chem. Zentr. 1929, I, 1635.

be exercised with respect to regulation of temperature and pressure[1].

Fixation of endpoint and prevention of occurrence of free acid is ensured by conducting the alkylation in the presence of carbonates (see D. Bradner, p. 1448, who employs potassium carbonate), which fulfills a double purpose:

1. After the alkylation of the alkalicellulose is completed, carbon dioxide is evolved by the excess of alkylating agent, by means of which the endpoint may be established by taking gas samples.

2. The observation has been made that alkyl halogen reacts significantly lower with carbonates than with free alkalis, so that free acids, even when the end reaction is not sharply perceivable, do not occur in the presence of these salts.

The advantages claimed for this process are a lower consumption of alkali, and with it, of alkylating agent; special precautions in maintaining temperature and pressure are unnecessary; and the uncertainty of the endpoint is obviated by a precise fixing of the point analytically. Decomposition of the cellulose ether by the formation of free acid by overstepping the optimum reaction time is avoided by the presence of CO_2 and carbonates, the finished product being neutral, is readily washed free from reactants.

The carbonic acid salts, such as sodium, potassium, calcium and barium carbonates, may be added in the solid condition, a small amount being usually sufficient. As far as their solubility permits, they may also be added to the steeping lye, or first prepared by the treatment of alkalicellulose with definite amounts of CO_2. The taking of gas samples from the pressure reaction vessel is continuously possible without interruption of the etherification. The

1. I. G. Farbenindustrie, E. P. 305946; abst. C. A. 1930, **24**, 5040; J. S. C. I. 1930, **49**, 414-B; Chem. Zentr. 1929, II, 111. F. P. 669256; abst. C. A. 1930, **24**, 1740. D. R. P. 492062; abst. C. A. 1930, **24**, 2599.

CO_2 is detected by familiar methods, as by a barium hydroxide solution.

The alkylation of cellulose has heretofore been proposed in the presence of salts, either to shorten the reaction period[1], to minimize the amount of alkali required[2], or to keep the reaction mass in a loose condition[3]. Thus, 1 part sodium carbonate is mixed with 100-200 parts of alkalicellulose, and this is ethylated with an excess of ethyl chloride at 100-140°. After about 1 hr. gas samples are passed through baryta water at short intervals, and as soon as a copious precipitate of barium carbonate forms in the receiver, the ethyl chloride is distilled off. Heating 0.5-1 hr. beyond the endpoint is said not to be injurious to the ethylcellulose formed. Yield 120% on the weight of the cellulose.

It has been found[4] that in alkylating alkalicellulose by means of alkyl halide in presence of a certain proportion of water without addition of solid NaOH or of alkali solution, ethers are obtained which are insoluble in all the pure solvents as ethyl chloride, methyl alcohol, ethyl alcohol, acetone, dichlorethylene, methyl acetate or benzene, but are soluble in such mixed solvents as benzene-alcohol or dichlorethylene-alcohol. For this purpose, the quantity of water must not exceed six times the weight of the cellulose contained in the alkalicellulose and must be greater than twice the weight of the alkali contained in the alkalicellulose.

The cellulose ethers have in addition to the above solubility characteristics, certain other advantages, such as a

1. E. Teupel, D. R. P. 408342; abst. J. S. C. I. 1925, **44**, 397-B; Chem. Zentr. 1925, I, 1665.
2. *Ibid.* D. R. P. 435346, Addn. to D. R. P. 408342; abst. J. S. C. I. 1927, **46**, 388-B; Chem. Zentr. 1927, I, 207.
3. G. Balle, D. R. P. 494917; abst. C. A. 1930, **24**, 3646.
4. A. Wacker Gesellschaft fur Elektrochemische Industrie, E. P. 306125; abst. C. A. 1929, **23**, 5041; J. S. C. I. 1930, **49**, 900-B; Cellulose, 1930, **1**, #4, 126; Brit. Plastics, 1930, **2**, #17, 230; Silk J. 1929, **6**, #61, 72; Chem. Zentr. 1929, I, 3161. F. P. 667307; abst. C. A. 1930, **24**, 1216. A. Ascherl and W. Gruber, D. R. P. 541146; abst. C. A. 1932, **26**, 2052.

high tenacity and characteristic flexibility in plastic, film or filament form. The following example is illuminating:

70 parts cellulose are impregnated for 2-24 hrs. with 700-1000 parts NaOH solution 40%, pressed at 100 atms. to 100 parts by weight, and then heated with 400 parts water and any desired excess of ethyl chloride (but not less than 125 parts) 4-24 hrs. at 90-130°. The excess of ethyl chloride is then expelled, and the ether washed and dried.

The manufacture may with advantage be carried out in a specially constructed apparatus[1], being a rotating autoclave containing spheres or like pieces which break up and mix the materials on the principal of an ordinary ball mill. It is recommended to construct the apparatus of nickel.

X. *Procedure of G. Young.* The etherification of cellulose, starch or dextrin with methyl, ethyl, *n*-propyl, *iso*-propyl, butyl or amyl chlorides to form the respective methyl-, ethyl,- propyl-, butyl- or amyl-cellulose[2], is carried out in the Young process by mixing 2 parts cellulose with 2-3 parts NaOH and 1-1.5 parts water, the cellulose being soaked 30 min. in about 40% alkali, then gently pressed until "the excess of liquid" has been removed. Then 20 molecular weights of alkyl chloride to one C_6 cellulose are added, any excess being recovered at the close of etherification. With methyl chloride or ethyl chloride, etherification takes place with sufficient rapidity and completeness at 100°, at which no deterioration of the cellulose takes place. With the higher members of the series as propyl, butyl and amyl chlorides, which have a reaction velocity decreasing with increasing molecular weight, satisfactory results are obtainable only at temperature between

1. A. Wacker Ges., F. P. 677745; abst. C. A. 1930, **24**, 3368.
2. U. S. P. 1504178; abst. C. A. 1924, **18**, 3272; J. S. C. I. 1924, **43**, 743-B; Chem. Zentr. 1925, I, 2050. E. P. 184825; abst. C. A. 1923, **17**, 878; J. S. C. I. 1922, **41**, 854-A; 1924, **43**, 743-B; Chem. Zentr. 1923, II, 591; Kunst. 1923, **13**, 56; Chim. et Ind. 1923, **10**, 542. F. P. 555279; abst. Chem. Zentr. 1923, IV, 681.

100-130°, and time of heating 6-8 hrs. As the reaction is carried out above the boiling point of the alkyl chlorides, an autoclave is required, the alkylating liquid being admitted by pumping or by injection from a cylinder under pressure. The cellulose ethers so produced are stable to either hot or cold water, soluble in cuprammonium solutions, in glacial acetic acid, and melt with slight coloration at about 200°. The essence of the process appears to be that the ratio of water to alkali must not be materially greater than 1:5. By the use of mixed chlorides as methyl and ethyl chlorides, a methylethylcellulose results.

XI. *Teupel Processes for Alkylcellulose Production.* The Teupel process is carried out in such a way that the cellulose is saturated with 50% sodium hydroxide solution, allowed to swell for 2 days, then centrifuged or pressed out, *dried,* and heated with the calculated amount of halogen alkyl, the alkylcellulose obtained being again dissolved, filtered and re-precipitated in order to increase the clarity of solutions made therefrom[1]. In operating under the Teupel processes, it is not recommended to use diluents as benzene in order to provide a greater amount of liquid during the etherification, and obtain a lighter colored product, as no favorable action was noted, either by the use of benzene or of ether.

It is claimed that the alkylation may be carried out materially quicker, and technically more useful products obtained, when the salt (sodium chloride), which forms during the ether formation from the interaction of halogen alkyl and free alkali present, is present before the reaction is initiated. In this respect, see the use of potassium chloride for the same purpose (page 1448). It is suggested that the favorable results obtained are probably due, in great measure at least, to the fact that the salt crystals, aided by the salt formed in the reaction cause a sufficiently far-reaching mechanical disturbance to actually disintegrate

1. D. R. P. 408342; abst. J. S. C. I. 1925, **44**, 397-B; Chem. Zentr. 1925, I, 1665. U. S. P. 1877779.

the alkalicellulose by attrition, and thus hasten the process of cellulose ether formation. Other solid materials such as sand, or copper turnings are only not beneficial but injurious in that with sand, for instance, large amounts of colloidal silicic acid are formed which are detrimental. The salt may be incorporated by adding it to the NaOH used in alkalicellulose formation, or may be added to the formed alkalicellulose.

By operating in this manner a considerable shortening in the process is claimed, and a more complete etherification of the cellulose. Likewise, purification through re-solution and re-precipitation is usually unnecessary. The following is a specific example:

30 kilos cellulose are saturated with about 50% NaOH solution, pressed or centrifuged (the latter a difficult and unsatisfactory operation in our experience due to the gummy nature of the alkalicellulose), mixed with 30 k. NaCl, and the mass heated in an autoclave with stirring arrangement with 150-300 k. ethyl chloride for 1-2 hrs. at 130°. The excess of ethyl chloride is then distilled off and the ethylcellulose formed ground and washed until all salt has been removed. Yield 39 k. or 130% on the cellulose. Where the NaCl is added to the cellulose before its immersion in the lye, it completely remains in the cellulose. If a lower temperature of heating be employed, say 120°, the time should be increased to 4 hrs.

It has also been shown[1] that by the addition of salts, the concentration of the alkali solution may be materially reduced—from 50% to 25-40%. This also is a considerable reduction in the working time in addition to saving of caustic and alkyl halogen. The swelling of the cellulose in the alkali is less, and drying of the formed alkalicellulose unnecessary. By the use of 50% NaOH solution, 7 mol. NaOH are absorbed per 1 mol. cellulose. By use of 30% NaOH, however, only 3 mol. alkali are required, and of this,

1. D. R. P. 435346, Addn. to D. R. P. 408342; abst. J. S. C. I. 1927, **46**, 388-B; Chem. Zentr. 1927, I, 207.

2 mol. are necessary for carrying through the reaction. This would indicate the saving of about half in caustic soda required. At the same time it is possible to insure a substantially maximum alkylation by working with a large excess of alkyl halide and without fear of loss, because no more than 3 mol. of alkylating agent can be converted. The excess should serve as a solvent for the ethylcellulose formed, increasing the homogeneity of the cellulose ether obtained.

It is claimed it was found (which must have been unexpected) that with a more dilute alkali, a considerably higher molecular product is obtained, as evidenced by a considerably higher viscosity as compared to that of alkylcellulose resulting from working with more concentrated alkali solutions.

XII. *Other Alkylcellulose Manufacturing Processes.* According to A. Liebster[1] a highly pure cellulose ether may be prepared where the cellulose is preliminarily treated with alkali hydroxide in strength insufficient to form alkalicellulose, but sufficient to remove oxycellulose, hemicellulose, pentoses, mannan and xylan therefrom. If a properly purified linters is used as a source of cellulose, such a pre-treatment appears superflous, and if wood pulp be employed as the source of cellulose, the usual alkalicellulose method of formation, when excess of caustic soda is removed by means of the application of pressure until the weight remaining is about three times that of the original cellulose operated upon, especially when the sodium hydroxide solution is circulated during mercerization, seldom leaves over 1.5% hemicellulose and less than 1% other inferior cellulosic bodies (non-resistant cellulose) in the formed alkalicellulose.

It is claimed by Liebster in following out his method, that ethylcellulose prepared by this process is insoluble in and does not swell in pure alcohol, pure benzene, or in hot

1. E. P. 355563; abst. J. S. C. I. 1931, **50**, 1006-B. F. P. 705732; abst. Chem. Zentr. 1931, II, 2087.

or cold water, but does dissolve in acetone, carbon tetrachloride and glacial acetic acid and possesses an unusually high viscosity. The method is amplified in the following example:

Air-dried sulfite cellulose (wood pulp) is digested with tenfold quantity of NaOH solution, 20-25° Be. (14.3-18.5% NaOH at 15°) at ordinary temperature, and after 20-30 min., washed with luke warm water until neutral, the whole operation being repeated 4-5 times. The purified cellulose is then dried, and 50 parts digested with 100 parts NaOH solution of 50° Be., then mixed with 70-75 parts ethyl chloride previously cooled to 5°. This mixture is then heated under pressure to not exceeding 150° for 20 hrs. while stirring. After cooling, the reaction product is washed with hot water, acidified with dilute mineral acid (as 10% sulfuric), washed to neutrality and dried[1].

A. Liebster[2] has also described a process for the production of highly etherified cellulose in a single operation by mixing previously untreated cellulose simultaneously with a dry alkali hydroxide, an indifferent organic liquid, and an ester of an inorganic acid as etherifying agent. Thus, 100 gms. cellulose as wood pulp, are covered in an autoclave with 100-200 gms. petroleum, 180 gms. finely powdered NaOH, and 180-200 gms. ethyl chloride. The mixture is then heated with stirring to 150° or under for 10-15 hrs. After cooling, the autoclave contents are diluted with a low boiling hydrocarbon as benzine, pressed, washed with hot water to neutrality and drying. The ethylcellulose obtained is white and friable, readily soluble in benzene-alcohol 1:1 and glacial acetic acid, and forms transparent, flexible films.

Cellulose Ether Precipitation. Closely allied to the subject of "Purification" in the preceding topic, are certain mechanical arrangements which have been perfected for

1. See E. P. 229678, 249173, 278767, 288997.
2. E. P. 364463; abst. J. S. C. I. 1932, **51**, 256-B; Chem. Zentr. 1932, I, 3131.

the precipitation of the cellulose ethers, which do not naturally fall into the topic "Coagulation." According to K. Werner[1] separate streams of cellulose ester or ether solution 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 intimate admixture. The precipitating liquid (usually water) is drawn through a pipe by a centrifugal pump supplied with cellulose solution by a pipe preferably through a fine slit through which the solution is forced under pressure against the plane of rotation of the vanes. The solution is preferably at a temperature around 70°, and the precipitating liquid the same. The precipitated mass is discharged through a pipe into a vessel where it may be further treated. The precipitated material may be formed into a continuous, coherent web[2], and after squeezing between heavy rollers to remove the bulk or liquor, is washed with water in a series of vats working on the counter-current principle, the web being finally dried on steam heated cylinders.

In another method[3], cellulose ethers are precipitated from their solutions by aqueous or organic precipitating agents in previously determined and regulable form, by bringing the solution and precipitant or a precipitant-solvent mixture together under a definite angle in a continuous manner, whereby the amount, velocity of flow and viscosity of the mixing liquids can be regulated according to the kind and nature of the product being operated upon.

1 K. Werner, E. P. 338214; abst. J. S. C. I. 1931, **50**, 108-B. See E. P. 336349.

2. Verein. f. Chemische Industrie, E. P. 269543; abst. C. A. 1928, **22**, 1473; J. S. C. I. 1928, **47**, 228-B.

3. Lonza Elektrizitätswerke & Chemische Fabriken A. G., F. P. 714488; abst. C. A. 1932, **26**, 1782. The apparatus is shown in Fig. 7 in which the dissolved cellulose ester or ether is fed into the center of a centrifugal in such proportions of solvent to non-solvent and at a predetermined centrifugal speed so that the precipitated material may be obtained in a granular, long fibrous, or short fibrous condition at will, and in such a porous condition as to be washed and stabilized readily and with the minimum expenditure of time and purifying chemicals.

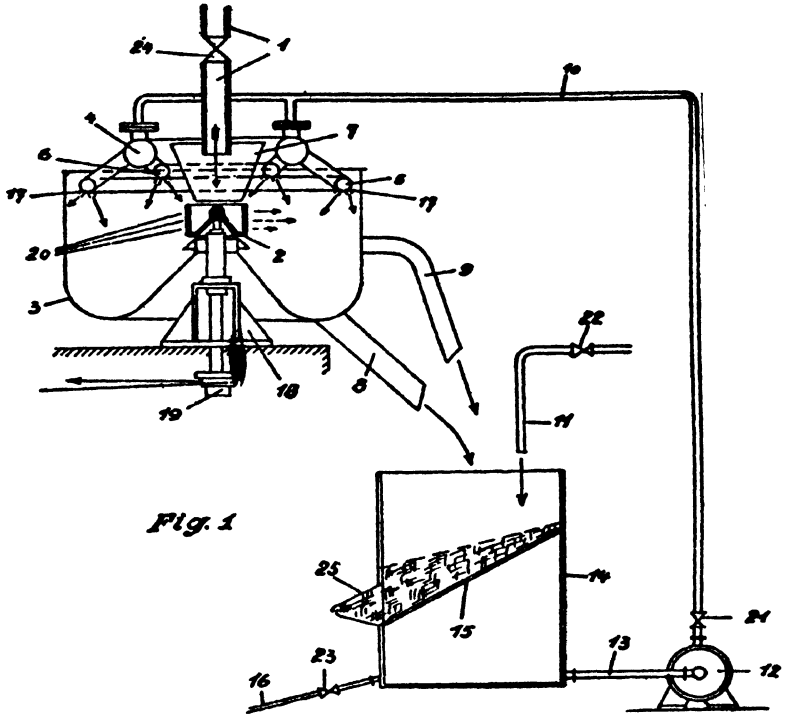


Fig. 1

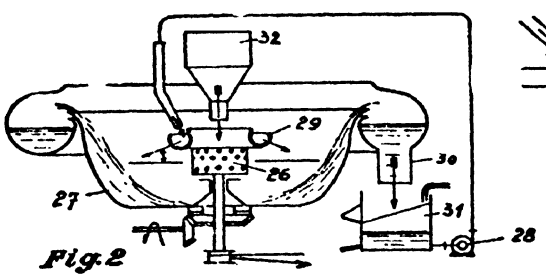


Fig. 2

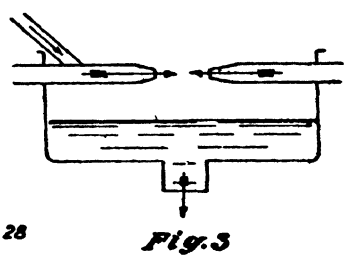


Fig. 3

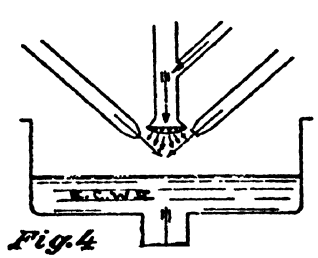


Fig. 4

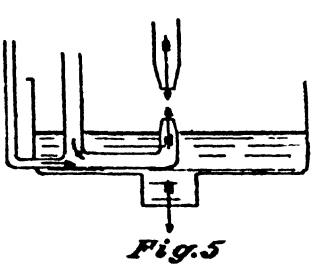


Fig. 5

Fig. 7. Continuous Manufacture of Cellulose Ethers.

The process of the I. G. Farbenind.[1] is the antithesis of the above, in that their method seeks to avoid coagulation and precipitation. The process is especially applicable to those cellulose ethers which are soluble in cold water but coagulated when heated to 70-90° with a separation out of the cellulose from the aqueous solution. This coagulating of cellulose ethers at higher temperatures may be avoided by adding small amounts of partially or completely water-miscible organic solvents containing hydroxyl. For instance, to a 10% solution of methylcellulose in water, 10% of alcohol is added. If such a solution is poured out on a glass plate, the drying can be carried out to a clear film at 80-90° without any coagulation taking place, whereas without the addition of alcohol, the cellulose ether precipitates out at 15-40°.

Other organic solvents containing hydroxyl may be used as methyl alcohol, propyl alcohol, glycol, glycerol, methylglycol ether, or acetol. The proportionate amounts of these compounds which it is advisable to add to produce the maximum effect, vary within wide limits depending upon the physical constants of the cellulose ether and the relative solvent or swelling action of the hydroxyl compound.

S. Sheppard and L. Eberlin[2] have described a process for the precipitation of cellulose compounds in solution which comprises disseminating air into a solution containing the ester or ether simultaneously with a liquid precipitant, the precipitate being obtained, it is said, in a very light and flocculent condition, very easy of purification.

Cellulose Ether Purification. The purification of the cellulose ethers, some of which processes involve solution and precipitation, is separate from the topic "Coagulation" in the section treating of Artificial Filaments, the latter topics having to do entirely with the mere solidification of the cellulose ether by withdrawal of solvent, either by an

1. D. R. P. 524509; abst. Nitrocel. 1931, **2**, 104.
2. U. S. P. 1844717.

evaporative process as in "dry" spinning, or by means of a precipitating bath in the "wet" spinning methods. The two topics are closely allied.

The three general methods of purifying crude cellulose ethers are classifiable under two general headings, treatment with an acid mixture for the purpose of purifying and decolorizing, and treatment with a mixture containing a solvent, with the object of separating some undesirable component (usually a lower alkylated ether).

(1) *Acid Treatment Purification of Cellulose Ethers.* The P. Seel process[1] depends upon treatment of the wetted and finely divided ether with nitric acid of about 5% strength for several hours, after which the acid is washed out by repeated cold washing. Calcium salts are more readily removed by a nitric acid treatment than by the use of sulfuric acid on account of the higher solubility in water of calcium nitrate over calcium sulfate. When the process is applied to ethers which are soluble in cold water as the lower etherified methyl and ethylcelluloses, but which are insoluble in warm or hot water, the dilute acid and subsequent washing baths are kept at such a temperature that harmful solution and consequent losses are minimized. Ethers purified in this manner are said to be clearer and free from a slight veiling or haziness, which is especially to be avoided in film formation, especially in laminated glass production.

Purification, clarification and decoloration are said to result where the ether is treated with relatively concentrated acid, the ether, after precipitation from solution following the acid treatment, being a white, voluminous powder, which upon re-dissolving gives practically colorless solutions. The process is indicated by the three following examples[2]:

(a) 15 cc. HCl of 8° Be. are poured into a liter of acetic solution containing 100 gms. crude ethylcellulose.

1. U. S. P. 1448091.
2. J. Altwegg and C. Maillard, U. S. P. 1599508; abst. Plastics, 1927, **3**, #2, 80; J. S. C. I. 1926, **45**, 1010-B; C. A. 1926, **20**, 3567.

After thoroughly mixing, the mass is allowed to stand 30 min. at ordinary temperature. The ethylcellulose is obtained by precipitation in a large quantity of water, under the form of a white mass which, washed and dried, is suitable for film and filament formation.

(b) 50 of ethylcellulose (ethoxyl 40%) are dissolved in alcohol 93°, 500, and sulfuric acid 35°, 15 parts are added with stirring. After standing 1 hr. at 20-25° the mixture is poured into water, filtered, and the purified ether washed to neutrality and dried.

(c) 15 cc. HCl of 8° Be. is brought in contact with methylcellulose as in (a) above.

By the use of sulfurous acid, combined purifying, bleaching and neutralizing is combined in a single operation[1], the mass resulting from etherification of cellulose, which contains sodium salts, excess of alkali, and sometimes amounts of unconsumed etherifying agent, being first washed with water and then with dilute sulfurous acid. Inasmuch as the sulfurous acid is volatile, there is no residue left in or on the cellulose ether. Treatment with sulfurous acid in the cold is advisable and a longer contact allowed, depending upon the degree of whitening required in the purified ether.

2. *Solvent Purification of Cellulose Ethers.* The majority of these processes, both for the purification of cellulose esters and cellulose ethers, are based upon the observation that (usually) the lower substituted members are inferior in desirable technical properties, and the solvent combination is based upon the extraction and removal of these undesirable components.

The method of H. Henecka and E. Dörr[2] involves solution and a partial extraction, e.g., from alcohol-soluble ethylcellulose, by extraction with aqueous alcohol, to which

1. R. Baybutt, U. S. P. 1510735; abst. J. S. C. I. 1925, **44**, 7-B; C. A. 1924, **18**, 3719.

2. D. R. P. 511019; abst. C. A. 1931, **25**, 1379. I. G. Farbenind. A. G., E. P. 321651; abst. C. A. 1930, **24**, 2882; J. S. C. I. 1930, **49**, 99-B; Cellulose, 1930, **1**, #7, 198.

a bleaching agent as hydrogen dioxide may be added. The process is exemplified in the following four examples:

I. 1500 gms. ethylcellulose (45-47% ethoxyl), just soluble in 67-70% ethyl alcohol, are covered with 6-10 parts of 50% alcohol, and stirred for up to 2 days. The residue is filtered, washed with 50% alcohol, then with water and dried. The improvement in quality is indicated by the increase in viscosity, which in three experiments went from 7 to 12, 11.5 to 13 and 21 to 29.

II. Ethylcellulose as in I is covered with 6-10 times the quantity of 55% alcohol, stirred for 2 days, and worked up as in I. By this more intense extraction, the viscosity of the last product (21 to 29) went from 21 to 40. The constituents of low viscosity can in part be recovered by acidifying the filtrate.

III. 1.5 kilos ethylcellulose as in I are covered with 6-10 times the quantity of a 2% aqueous NaOH in 50% alcohol, and strongly stirred for up to 2 days. The residue is then filtered, washed with neutral 50% alcohol, and then with water until neutral. Viscosity increase and lighter color also result in this method of treatment.

Basically similar is the process of the I. G. Farbenind.[1] who use as appropriate solvents for highly ethylated cellulose (47% ethoxyl), only those which operate as solvents upon heating, as benzene, ligroin, or such hydroaromatic substances as the solvents known under the names of "Bornylan" (mixture of natural hydroaromatic hydrocarbons boiling 135-150°) and "Sangajol" (mixture of natural hydroaromatic hydrocarbons boiling 150-200°). Pure benzene is suitable for ethylcellulose of 42% ethoxyl.

The following example is explanatory:

(a) 2 kilos ethylcellulose (46% ethoxyl) are dissolved at 100° in 40 k. ligroin b. pt. 110°, filtered hot, if necessary,

1. U. S. P. 1814208; abst. C. A. 1931, **25**, 5287. E. P. 288143, abst. C. A. 1929, **23**, 513; J. S. C. I. 1929, **48**, 714-B; Br. Plastics, 1929, I, #5, 191; Plastics, 1929, **5**, 335; Silk J. 1928, **5**, #49, 80; Chem. Zentr. 1928, II, 304.

through a filter press and then cooled to room temperature with thorough stirring. The ethylcellulose is precipitated as a white, flaky product, which is worked up while still wet, with ligroin into a plastic mass, or it can be dried *in vacuo*. In the latter case the ethylcellulose is obtained as a fine, flaky, very spongy white product, which dissolves smoothly in the customary solvents.

The cellulose ether may be dissolved[1], with water added in small portions until the higher ether-content members are precipitated, the water-soluble ethers remaining in the water. Depending upon the composition of the ether operated upon, the water may range in temperature from ice cold to nearly boiling.

The cellulose ether is dissolved, and the lower ethers removed by repeated extraction with an immiscible liquid, acetone being the original solvent and chloroform being the immiscible extractive[2]. J. Bregeat[3] has suggested the rather expensive absolute alcohol as extractive.

When cellulose ethers or esters are purified by cooking with water under pressure[4], there is a tendency for a portion of the charge to climb up the inside the pressure vessel and become decomposed. This disturbing phenomena may be obviated when the cellulose ether is cooked with water for a longer time at ordinary pressure with exclusion of air, or subjected to the action of a vacuum with heating, or at the ordinary temperature.

C. Bary[5] has suggested a method of purification applicable equally to the cellulose ethers and esters, in which

1. C. Dreyfus, F. P. 689134; abst. C. A. 1931, **25**, 1081.
2. British Celanese, Ltd., 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, 52.
3. J. Bregeat, E. P. 226142; abst. C. A. 1925, **19**, 1629; J. S. C. I. 1925, **44**, 706-B; Plastics, 1926, **2**, 134; Chem. Zentr. 1925, I, 2030; Kunst. 1925, **15**, 223; Schiess. & Spreng. 1925, **20**, 110; Ann. Rep. S. C. I. 1925, **10**, 147. F. P. 587486; abst. Plastics, 1926, **2**, 134; Kunst. 1925, **15**, 224.
4. Wolff & Co. and H. Schulz, D. R. P. 440844; abst. C. A. 1931, **25**, 1379; Chem. Zentr, 1927, I, 2028.
5. C. Bary, U. S. P. 1136462; abst. C. A. 1915, **9**, 1556; Mon. Sci. 1916, **82**, 56; Zts. ang. Chem. 1916, **29**, I, 243.

the cellulose derivative in dissolved condition is purified from objectionable constituents by sumitting them to dialysis, if there are dissolved crystalloids therein. In the method of Aceta, G. m. b. H.[1], waste of cellulose ethers is worked up by means of sulfur dioxide under pressure, the excess of SO_2 liquid being removed by filtration and distillation, and the cellulose derivative precipitated by water. After washing and drying, it is suitable for film or filament formation.

When the cellulose ethers are in the dissolved condition, they may be purified and decolorized by filtration through charcoal, or, as in the method of the Akt. Ges. fuer Anilin Fabrikation[2], who treat the solution with substances containing silicic acid in those forms having active absorbent surfaces, such as the Diatomite or Fullers Earth as obtained from Florida and other localities in the United States. The solution of cellulose ether is allowed to percolate by gravity, or forced through a layer of diatomaceous earth previously deprived of its moisture, which is excellent for removing the very fine suspensions (haze) found in some cellulose derivative solutions.

Fibrous Cellulose Ethers comprehends the etherification of cellulose in such a manner that the morphological structure of the original cellulose remains unchanged, i.e., the cellulose does not pass into solution during the esterizing treatment. The esterification, usually acetylation, of cellulose, notwithstanding the fact that the acetated celluloses in the dry state have little or no technical applications, has received considerable attention[3]. In the production of inorganic cellulose esters typified by the nitrocelluloses, the ester never passes into solution in the esterizing bath, for the very simple reason that nitrocellulose is insoluble in a mixture of nitric and sulfuric acids used for commercial nitrating purposes.

1. D. R. P. 536890; abst. C. A. 1932, **26**, 1119.
2. E. P. 245078.
3. See this work, pp. 339, 345, 350, 362, 363, 396, 400, 412, 443, 471, 472, 496, 558, 619, 631, 634, 658, 668, 713, 887, 949, 958, 1014.

In preparing fibrous alkylcellulose according to the directions laid down by H. Sessler[1], 10 gms. cotton cellulose are submitted to the action of a mercerizing solution of NaOH 20% strength, and the resultant product exposed in a vacuum of about 10 mm. pressure to a stream of methyl sulfate vapor, methyl sulfate boiling at about 70°. The distillation of the sulfate is continued 2.5 hrs. The product resulting from this process is a dimethylcellulose in which the "fibrous"[2] structure has been preserved, and which is said to dissolve uniformly in such organic solvents as ethylenechlorhydrin, methylene chloride, without insoluble residue.

Where the structure of the cellulose has been substantially maintained is logical evidence that the cellulose molecule has not been profoundly disintegrated, and a product is obtainable which forms clear solutions in a number of organic solvents and solvent combinations, in which the "haze" often noted after the filtration of cellulose ether and ester solutions, is practically non-existent. This is mainly explainable that under the usual etherifying processes, either a destruction of the fibrous form by grinding, dissolving or otherwise is often resorted to, and this is often accompanied by high temperature, extreme concentration of alkali used, even to grinding with powdered sodium hydroxide. No statement is made as to the viscosity of the cellulose ether formed, which, it would appear, must be unduly high.

The Society of Chemical Industry, Basle[3] produces cellulose compounds by treating alkalicellulose with a mixture of carbon bisulfide and alkyl halide or aralkyl halide, the finished product showing considerable increase in weight but retaining its fibrous structure, and having acquired an affinity for acid dyestuffs.

1. U. S. P. 1704304; abst. C. A. 1929, **23**, 2033; Chem. Zentr. 1929, I, 2938.
2. The patentee wishes it to be understood that the term "cellulose" is to be taken in the broad sense and to include also mercerized cellulose and conversion products and derivatives of cellulose.
3. E. P. 341237.

Laboratory Method for Ethylcellulose Manufacture. The following method can be recommended for the production of a few pounds of ethylcellulose of maximum desirable physical properties.

The cellulosic material is viscose, i.e. selected because of the care taken in alkalicellulose formation and ripening, and the uniformity of the product, viscose intended for artificial filament formation being the most desirable. The viscose is precipitated into regenerated cellulose by the "heat method" of precipitation, using a viscose solution ripened to the point optimum for spinning purposes. The usual viscose solution is about 7% original cellulose therein, and this is diluted with distilled water to a 5% cellulose content, after the viscose has been subjected to the last filtration. After stirring in the water for a few minutes, the solution is given a pressure filtration through a layer of canton flannel to remove any semi-dissolved particles and last traces of undissolved fibers. The diluted filtered solution is then placed in a jacketed kettle, preferably glass lined, and provided with efficient stirring device. The temperature of the viscose when introduced into the kettle is about 19°. By means of water circulation in the jacket, the temperature of the stirred mass in the kettle is raised by about 3° each 5 min. until 60° is reached, at which precipitation commences[1]. The temperature is then slowly raised at about the rate of 2° per 5 min. for a further 25 min., at which time precipitation is complete[2], the total heating period being 1.5 hrs. for best results.

1. It is essential that the precipitated mass be in a fluffy condition in order that it may be purified by washing readily.

2. Correctly pressed alkalicellulose (ratio 100-305) and correctly aged viscose (about 95 hrs. at 19° when 60 cotton to 40 wood pulp is used as initial cellulose and the air dry condition α-cellulose of the mixture is at least 95%) precipitates at 64-65°. Correctly aged but incorrectly pressed as to ratio of cellulose to alkali precipitates at 74-75°. Correctly pressed but incorrectly aged precipitates at 86-87°, and when the pressing and ageing are not correct, usually no precipitation takes place unless the solution is heated to the point of decomposition, when an alkali-insoluble viscoid results, unsuited for etherification. Another suitable raw material, when obtainable, is the cuttings from cellophane sheet manufacture of the non-water

The contents of the kettle are then pumped through a flannel filter cloth with absorbent cotton layer between with the fuzzy side in, and the thiocarbonates washed away first with warm water and then with cold, washing being continued until all traces of alkali have disappeared, and the washing continued (advantageously with the addition of a small amount of hydrogen dioxide in the wash water) until the precipitate is bleached to the desired degree of whiteness[1]. The water is then allowed to drain off and the mass squeezed or centrifuged until it weighs about 4.5 times the weight of the hydraulically pressed alkalicellulose it contained, that is, it is squeezed so that after adding the required amount of 50% NaOH solution, the mass will contain about 8% cellulose[2]. It is then dissolved in well-clarified 50% NaOH solution (using about twice the weight of the cellulose content), after which it is again filtered cold, and is then ready for use.

The solution is placed in a Werner & Pfleiderer or other similar mixer and the jacket filled with water at 15°. A connection at the top of the mixer is connected with a receptacle containing 15 lb. ethyl sulfate, the purity of which has been proven. This liquid is allowed to run in very slowly so that it requires 1.5 hrs. for the entire alkylant to be consumed[3]. As soon as the ethylant is admitted the water is turned off in the jacket and the latter drained, being replaced by live steam for not over 2 min., and then

resistant form (containing glycerol only and without the addition of plasticizers, paraffin and nitrocellulose), which have but to be comminuted and washed in warm water to remove the 12-13% glycerol thtrein.

1. The appearance of well washed regenerated viscose should be a pale, uniform green transparent gelatinous mass, free from an indication of lumpiness. If the precipitation has been properly conducted, the precipitate should wash very readily and be free from alkali in 1-1.5 hrs., which is not the case when precipitation is made at 75-76°, as described by Lilienfeld, E. P. 14339, 1914.

2. If squeezed further, it becomes insoluble in NaOH, and this cannot be remedied by the addition of water after the NaOH has once been added.

3. It is preferable for the Pfleiderer to be connected with a sprayer and the ethylating liquid to be forced into the mass by atomizing under pressure.

turned off. This is repeated each 10 min. and the temperature of the solution noted each time to record the effect of the preceding 2 min. of heat. The increase in heat each 10 min. should be 5°.

When all the ethyl sulfate has run in, the periodical heating is continued for a further period of 2 hrs., at which time, the temperature being 80-85°, the solution will suddenly thicken quickly and then almost immediately thin again, at the same time turning to a whitish color with the appearance of cream. Heating is then continued for a full 10 min. and the steam then turned off. The low ethylated cellulose thus formed is filtered through a double layer of cheese cloth to remove any lumps that may have formed, and is then ready for the next step.

The product is then placed in a pressure apparatus equipped with both heating and cooling means, automatic stirring device and distilling coils, brine turned into the jacket, the stirrers started and the solution cooled to 10°. 51 lb. powdered (at least 150 mesh) NaOH are then added and the whole stirred for 10 min. without rise in temperature above 15°. 3.5 lb. ethyl sulfate are then added and the whole stirred 10-15 min. The brine is then turned off and replaced by live steam. As the solution warms and rises to about 60° a small amount of distillate appears. At about 70° the reaction commences and may be recognized by the foam splashing on the sight glass. Heating is continued slowly until 104° is reached when the steam is turned off and brine turned on until the temperature has again fallen to 10°.

5 lb. more NaOH are then added, and after 10 min. of stirring, 3.5 lb. ethyl sulfate. The whole is again mixed and a temperature of 104° obtained in not less than 15 min. This operation is repeated until 50 lb. NaOH and 35 lb. ethyl sulfate have been added, equivalent to 10 completed reactions.

At the close of the last reaction the heat is maintained at 102-104° for 0.5 hr., after which the valve in the bottom

of the apparatus is opened and the mixture blown through a connecting pipe to a Sweetland or Kelly type filter press. When the precipitate in the filter press has been washed free from alkali, the water is blown out of the press by air pressure, the press then opened, the cakes scraped off, broken up into small pieces and placed in a crock. About 3 gal. 10% sulfuric acid are then added and the mass broken up into a homogeneous mush, this treatment being necessary to split off the unused -OH groups. After standing 2 hrs. at room temperature about 5 times the bulk of water is added and stirred mechanically for about an hour. The ethylcellulose is then allowed to settle, the supernatant liquid decanted, and this washing continued to neutrality. At the last decantation, the mush is placed in a plate filter press and the water forced out through a piece of No. 4 canvas duck by air pressure. The cake then contains 25-30% moisture, is powdered, placed on cloth trays and dried at not to exceed 100°.

The ethylcellulose obtained is a white, flocculent powder of 2.6-2.65 ethyl groups per C_6 cellulose, soluble in an almost unlimited range of solvents, a practical solvent being chloroform-denatured alcohol 60:40 by weight. A slight amount of triphenyl phosphate clears any tendency to milkiness that is liable to form when making films using volatile solvents. Yield about 98% calculated on the original cellulose. Total efficiency of process including recoveries, about 87% of theory.

CHAPTER VIII

STARCH ETHERS

Our knowledge of the ethers of starch, especially the earlier investigations, was primarily obtained incidental to attempts to elucidate the structural configuration of the starch aggregate. When a carbohydrate is treated with an alkylating agent, as methyl sulfate or chloride, one or more of the convertible hydroxyls is transformed into methoxyl groups, and these, in contradistinction to acetyl groups, survive the action of hydrolytic agents. A fully methylated starch (trimethyl starch) should yield either a single trimethylglucose, or alternately a mixture of methylated sugars, according as the hydroxyl groups of the parent compound are symmetrically distributed. It is also obvious, that if definite positions can be assigned to the methyl groups in the methylated sugars formed on hydrolysis, it then becomes possible to determine the relative positions of attachment of the glucose residues in the original starch molecule.

P. Karrer[1] in 1920, in studying the chemical structure of the polysaccharides, methylated starch in the usual manner, obtaining three preparations containing about 1, 1.5 and 2 methoxyl groups respectively per C_6 cellulose complex. The first was sparingly soluble in cold water, insoluble in alcohol and chloroform, and undoubtedly contained

1. Helv. Chim. Acta, 1920, **3**, 620; abst. C. A. 1921, **15**, 61; Chem. Zentr. 1920, III, 880. Paper, 1920, **27**, #11, 24, 34. K. Hess, Zts. Elektrochem. 1920, **26**, 232. Translated by C. West and published in Paper, 1920, **27**, #13, 13; 1920, **27**, #14, 22. H. Pringsheim (Zts. ang. Chem. 1922, **35**, 345) confirms the observations of P. Karrer on tetramethyl starch in respect to the mol. wt., which cannot be greater than 900-1200, since the molecular weight determination as Karrer himself has shown, gave a maximum value, and also from the observation (which has since been found erroneous) that starch combines with a maximum of two methyl groups. Diamylose is methylable only to the dimethyl stage. On the other hand, the third hydroxyl in octamethyltetramylose (see p. 101, n. 8), can be esterified by the acetyl group, just as triacetyl derivatives are known for all polyamyloses.

non-methylated starch. The second was sparingly soluble in water, somewhat soluble in alcohol but insoluble in chloroform, whereas the third preparation was soluble in all three. The products showed no reducing power towards Fehling's solution, and no decomposition of the starch molecule. With iodine, the non-methylated starch reacted blue, with preparation I, red violet, with II, brownish yellow, and with III, slightly yellow, thus indicating that with increasing solubility of the starch ether, there takes place a simultaneous destruction of the starch crystalloid, the large starch particles of colloid size having been divided and decreased in size, so that in the methylated starch we have the simple molecule.

His investigations were extended the year following[1], potato starch being alkylated with methyl iodide and silver oxide at 45-65°, the potato starch being prepared according to the method of G. Malfitano and A. Moschkoff[2], and the ash being reduced to less than 0.1% by repeated freezing out. When 10 gms. starch were methylated with 580 gms. methyl iodide and silver oxide used, a colorless amorphous powder was obtained, "inclined to be" soluble in cold water or phenol, completely insoluble in alcohol, chloroform or bromoform. The starch ether reacted violet red with iodine, contained 4.1% ash and 18.55% methoxyl. Calculated for $(C_6H_9O_5.CH_3)_x$, methoxyl is 17.60, or, without taking out for ash, 17.8%. Molecular weight determination in water gave 500, at another time 800, and in phenol, 1259. The high ash content was primarily due to silver compounds.

1. P. Karrer and C. Nageli, Helv. Chim. Acta, 1921, **4**, 185; abst. C. A. 1921, **15**, 2629; J. S. C. I. 1921, **40**, 361-A; Chem. Zentr. 1921, I, 934.

2. Compt. rend. 1910, **150**, 710; abst. J. S. C. I. 1910, **29**, 506; J. C. S. 1910, **98**, i, 301; C. A. 1910, **4**, 1556; Chem. Zentr. 1910, I, 2074; Jahr. Chem. 1910, **63**, II, 408. Compt. rend. 1910, **151**, 817; abst. J. S. C. I. 1910, **29**, 1402; J. C. S. 1910, **98**, i, 817; C. A. 1911, **5**, 1345; Chem. Zentr. 1911, I, 17; Jahr. Chem. 1910, **63**, II, 407; Wag. Jahr. 1910, **56**, II, 257. See also G. Malfitano, Compt. rend. 1904, **139**, 1221; 1906, **143**, 400; Rev. gén. sci. 1908, **19**, 614; J. C. S. 1906, **90**, i, 804; Chem. Zentr. 1906, II, 1312; Jahr. Chem. 1905-1908, II, 939.

In the methylation of potato starch with methyl sulfate and baryta water, the latter produces a colloidal, aqueous starch solution, which precipitates a starch-barium compound[1], the starch, however, being methylable in this form, the compound with barium dissolving in the reaction mass as etherification proceeds. For the methylation of 10 gms. starch there was used 1320 gms. crystalline barium hydroxide and 504 gms. methyl sulfate. Notwithstanding the large excess of etherifiant, not more than two methoxyl groups could be introduced into the C_6 complex. Even with 2604 barium hydroxide and 1000 methyl sulfate per 10 of starch, the methylation remained stationary at this point. After completion of methylation, the product is evaporated to dryness and the methyl starch extracted with chloroform.

From starch 10, crystalline $Ba(OH)_2$ 1320, methyl sulfate 500, starch ether was obtained readily soluble in water, hot alcohol, chloroform, bromoform, acetone, phenol and methyl iodide; insoluble in ether. Ash 0.4%, methoxyl 32.6%, mol. wt. in water 990, and not reducing Fehling's solution. The molecular weight of methyl starch cannot be well determined in chloroform ebullioscopically, on account of the fact that during solution in the solvent minute bubbles are released in the heating, whereby a considerable lowering of the thermometer takes place. Solutions of methyl starch in water or in chloroform show the Tyndall phenomena and colloidal particles in the ultramicroscope, but such solutions may be ultra-filtered and are then non-reactive in the ultramicroscope, and give no Tyndall effects in a cone of light, indicating that colloidal particles have been replaced by genuine crystals. Methyl starch is unaffected by such enzymes as diastase or ptyalin. *Bacillus macerans* which decomposes ordinary starch into crystalline dextrin, does not grow in a methyl starch solution, and causes no depolymerization. By repeated methylation of

1. C. Lintner, Zts. ang. Chem. 1888, **1**, 232; abst. Ber. 1888, **21**, 454; J. C. S. 1889, **56**, 316.

potato starch, a maximum of 35.5% methoxyl was obtained, equivalent to about 2.2-methyl starch (2.2 methyl groups).

In the methylation of starch with methyl sulfate and NaOH solution, a colloidal solution of starch was methylated at 50-100° through alternate additions of NaOH and methyl sulfate, using starch 1, NaOH 9, methyl sulfate 12.6. Toward the close of the etherification the methyl starch is precipitated (salted out) by salt enrichment occurring in the reaction vessel. The methyl starch so produced dissolves to clear solutions in cold water, but becomes turbid when the aqueous solution is heated, methylated starch precipitating. Upon cooling the starch ether passes into solution, this phenomenon being utilizable for its purification. Readily soluble in chloroform or bromoform. Ash 0.34%, methoxyl 35.38-35.5%, mol. wt. in water 1830. Preparations of methyl starch are colloid-chemically heterogeneous, the larger portion being ultrafilterable, a small portion colloidal and incapable of dialysis. If the optically blank filtered solution is frozen or heated, there appears a turbidity, eventually a precipitate of methyl starch. This re-formation of colloidal particles takes place especially readily in chloroform and bromoform solutions. The disappearance of the typical iodine reaction with increasing methylation of starch is indicative that a dispersion of the colloidal particles continues, in addition to the bearing which follows substitution of hydroxyl groups by alkyl. From the fact that two of the three hydroxyls in starch may be methylated more readily than the third, it is indicative to P. Karrer that all three hydroxyls are not the same.

The details of the three processes of Karrer for introducing the methyl group into starch are as follows:

I. *Methylation with Methyl Iodide and Silver Oxide.* 10 gms. purified starch dissolved in 300 gms. water in an autoclave at 130°, and the clear, filtered solution treated with 64 gms. powdered silver oxide and 28 gms. methyl iodide, and heated with stirring at 43-45°. When the major portion of methyl iodide has gone into combination, the

temperature is slowly raised to 65° during 15 min., the mass cooled to 40° and 28 gms. additional methyl iodide added, the process repeated, and 28 gms. added a third time. The reaction mass is then held at 65° with vigorous stirring for 2 hrs., suction filtered and the AgI precipitate boiled with water, clarified, decolorized, the whole methylation process repeated, finally evaporated to dryness, powdered, washed with alcohol and ether and vacuum dried at 100°. Yield 5 gms. The product was readily soluble in water, insoluble in alcohol or chloroform, the aqueous solution being un-ultrafilterable. Methoxyl 17.8%.

II. *Methylation with Methyl Sulfate and Baryta Water.* 10 potato starch, dissolved to a granule-free paste by shaking with water 800, treated with 330 of crystalline barium hydroxide in 800 of hot water with stirring. 126 methyl sulfate was dropped in while the mass was heated to boiling under constant stirring. After the vigorous reaction has subsided, it is boiled 1 hr., and the same amounts of $Ba(OH)_2$ and methyl sulfate added. It is now cooked 24 hrs. to convert as much as possible of barium into the sulfate, which is then filtered off, rubbed with water 800, and the mash exactly neutralized while stirring in order to remove excess adhering $Ba(OH)_2$, and to bring some of the precipitated starch again into solution. The filtrates are then combined and the above methylation process repeated. Finally the solution is cooked until the major portion of the barium methylsulfate has been decomposed (requiring 2-3 days), and the liquid exactly neutralized with sulfuric acid, evaporated to dryness at 30-40°, and the methyl starch obtained by extraction with chloroform. Yield, 4.5. The methyl ether obtained was colorless, readily soluble in water, hot alcohol, chloroform, acetone, bromoform and methyl iodide, the aqueous solution becoming turbid upon heating. Ash 0.4%, methoxyl 32.6%.

III. *Methylation with Methyl Sulfate and Sodium Hydroxide Solution.* Starch 10 dissolved in 250 of water at 130°, to which was added 45 NaOH in 50 of water and 63

of methyl sulfate, drop-by-drop. After 30 min. the same amounts of NaOH and methyl sulfate were again added, and the mass heated under stirring. The salted out methyl starch was collected, dissolved in hot chloroform, and the latter solution evaporated to dryness. The product is readily soluble in cold water, partly precipitates therefrom on heating and redissolves on cooling. Readily soluble in chloroform.

J. Irvine and J. MacDonald[1] find that methyl groups are fairly readily introduced into starch by means of methyl sulfate and alkali, but the methoxyl content quickly reaches a limit of 36-37%, this value indicating that "only seven hydroxyl groups out of nine have undergone alkylation." Methylated starch of this composition appears to be a definite compound possessing a characteristic optical activity, and readily acetylated. Another distinguishing property displayed by starch during methylation is that the reaction is definitely arrested at the dimethyl stage when conducted by means of silver oxide and methyi iodide, as when these reagents are applied to a methylated starch containing less than 2 OH groups per C_6 molecule, the methoxyl content rises to 32-33% but no further. Similarly, the same reagents exert but a limited effect in raising the methoxyl content when applied to methylated starch alkylated by methyl sulfate beyond the dimethyl stage.

As methylation of starch proceeds, the color reaction with iodine progressively vanishes, the rotation increases in a dextro-sense, the protein and inorganic constituents are eliminated, particularly when the silver oxide reaction is employed, for they are then precipitated in the form of insoluble double compounds with silver oxide. It is important to observe that these precipitates contain combined carbohydrate indicative that N and P form a portion of the polymerized aggregate.

1. J. C. S. 1926, **129**, 1502; abst. C. A. 1926, **20**, 2830; Chem. Zentr. 1926, II, 1265.

Using a purified rice starch, 4 etherifications with methyl sulfate and NaOH formed a methyl starch of 37% methoxyl, and 24 treatments raised the methoxyl content to 43.7% which closely agrees with that required for a trimethyl ether (C_6 cellulose). There appear to be three distinct stages observable in the methylation of starch, the products in each case displaying a constancy of composition and properties warranting the assumption that they are three consecutive compounds. They obtained dimethyl starch, 32.7% methoxyl, hexamethyl starch on a 9 OH-starch molecule; methylated starch, 36.3% methoxyl, heptamethyl starch; and trimethyl starch, 43.7% methoxyl, nonamethyl starch. The specific rotation increases regularly (from + 135.7-216.5° in chloroform) with rise in methoxyl content. In the hydrolysis of the above three products with HCl in methyl alcohol, dimethyl starch gave essentially a dimethyl methylglucoside, methylated starch a mixture from which 2.3.6-trimethyl methylglucoside (1 mol.) and dimethyl methylglucoside (2 mols.) were isolated, and trimethyl starch yielded 2.3.6-trimethyl methylglucoside, m. pt. 57.5°, in excellent yield, the ratio of these two glucosides being 1.85 : 1.

In the starch methylation researches of W. Haworth, E. Hirst and J. Webb[1], starch was first acetylated and then methylated. They stirred 20 gms. starch into 600 cc. water, and after 30 min. heating, the starch was precipitated by the addition of ethyl alcohol to the warm paste, the precipitate ground with warm ethyl alcohol, washed with ether and dried. This powdered starch was treated with 6 times its weight of glacial acetic acid through which chlorine had been bubbled for a few seconds, and the mixture stirred 30 min. at 20°. 20 parts acetic anhydride containing an amount of SO_2 equivalent to the Cl in the acetic acid was then added, and the mixture stirred 1 hr. at room tempera-

1. J. C. S. 1928, **131**, 2681; abst. C. A. 1929, **23**, 818; Chem. Zentr. 1929, I, 992.

ture, then 4 hrs. at 55°. Yield, 96.5 % starch triacetate, identical with that obtained by M. Bergmann and E. Knehe[1].

Whereas Irvine and MacDonald obtained but a 25% yield from 24 methylations of starch, Haworth *et al* obtained after 6 methylations, 89% of the theoretical yield of trimethyl starch, by taking advantage of the solubility of starch triacetate in acetone. The addition of methyl sulfate and dilute alkali to such a solution introduced in one operation 36% methoxyl, and a progressive increase in methoxyl content was obtained on each subsequent methylation. Hydrolysis of this trimethyl starch with methyl alcohol-HCl (2%) gave 80% pure trimethyl methylglucoside and 8% of a mixture of the latter with dimethyl methylglucoside, leaving a 6% unhydrolyzed residue.

By dispensing with the use of acetone as solvent for starch triacetate during methylation, dimethyl starch results in 80% yield, methoxyl 31.8%, and giving on hydrolysis a mixture of trimethyl-, dimethyl- and monomethyl-glucose, the former being present to the extent of about 20%, and indicating that all of the OH groups are exposed to simultaneous methylation,—a well marked difference between cellulose and starch in this respect.

Their work is epitomized under the following six headings:

I. *Methylation of Potato Starch.* When a method of simultaneous deacetylation and methylation is applied to starch, etherification is both rapid and substantially complete, and renders the methylated starch so produced the most suitable intermediate for the preparation of 2.3.6-trimethylglucose.

II. *Methylation in Presence of Water Only.* 20 gms. powdered starch triacetate were treated with 224 cc. 30% NaOH solution and 80 cc. methyl sulfate, the latter added gradually and with stirring. Temperature, 50° for 75 min., thereafter at 70° for 75 min. longer, care being taken to avoid acidity at any stage. After nearly neutralizing with

1. Ann. 1927, **452**, 151; abst. C. A. 1927, **21**, 1448.

sulfuric acid, it is filtered and the residue extracted with boiling chloroform. The aqueous portion is treated with excess of CO_2, evaporated to dryness in presence of barium carbonate and the residue extracted with chloroform. The united chloroformic extracts gave a white, flaky solid, slightly soluble in water or chloroform. Methoxyl 31.8%. Dimethyl starch requires 32.7% methoxyl.

III. *Hydrolysis of Dimethyl Starch.* The starch ether was boiled 24 hrs. in 2% HCl, the acid neutralized by lead carbonate, 4.55 gms. viscous syrup being obtained from which dimethyl methylglucoside (41.9% methoxyl) and trimethyl methylglucoside (52.5%) were obtained. Further methylations gave a progressive increase in methoxyl content, the simultaneous deacetylation and methylation by heating dimethyl starch with acetic anhydride and fused sodium acetate at 100° for 1.5 hrs.

IV. *Methylation with Acetone as Solvent.* The following method gives in one operation, a methylated starch of 36% methoxyl, and facilitates the formation of trimethyl starch in almost quantitative yield, and comprises the simultaneous deacetylation and methylation of starch triacetate dissolved in acetone, with efficient stirring and provided with a reflux condenser. The methoxyl content may be varied by employing a smaller quantity of acetone, methylated starches of 28-36% methoxyl having thus been obtained.

V. *Preparation of Methylated Starch (Methoxyl 36%).* 25 gms. powdered starch triacetate are dissolved in 250 cc. acetone and treated with 280 cc. 30% NaOH solution and 100 cc. methyl sulfate. The latter was added in 10 equal portions at 10 min. intervals, the temperature being maintained at 56°. After heating 30 min. at 100°, during which time acetone was allowed to evaporate, the mixture was nearly neutralized by sulfuric acid, CO_2 added, and filtered, then extracted with chloroform, and the chloroform evaporated off. White, impalpable powder. Ash 1.6%,

methoxyl 36.0%. Two additional methylations raised the methoxyl 4%. Three additional methylations gave 44.0% methoxyl, ash 0.04%, final yield 92% of theory, or 89.4% yield on the original starch. No advantage was apparent by acetylating after the first methylation, solubility in acetone of methylated starch being the decisive factor in etherification. The maximum of methylation gave a product of 45% methoxyl.

VI. *Trimethyl Starch and its Hydrolysis.* The maximum methylated starch is a white powder, m. pt. 145° with previous softening. When boiled 24 hrs. with methyl alcohol containing 2% HCl there was obtained both trimethyl methylglucoside and dimethyl methylglucoside. Hydrolysis with 5% HCl gave 2.3.6-trimethylglucose, tetramethylglucose being absent.

J. Irvine[1] has demonstrated that in the etherification of starch, the methylation may be arrested at two definite intermediate stages before substitution is maximum, which appears at variance with the methylation of cellulose in which the introduction of three methyl groups per C_6 molecule proceeds regularly. Maximum methylation is possible with potato, rice and maize starch to the limiting methoxyl value, 45.5%. When the methoxyl content has been raised to 35-36%, the product may be subjected to the action of thionyl chloride followed by sodium methoxide, and the methylation completed by the action of methyl iodide and

1. See "A Comprehensive Survey of Starch Chemistry" Walton, 1928, **1**, 16. He found (Rev. trav. chim. 1929, **48**, 813; abst. C. A. 1929, **23**, 5345) that three distinct compounds are recognizable as the essential products of the methylation of starch, *viz.* dimethylstarch giving 2.3-dimethylglucose on hydrolysis; methylated starch with 37% methoxyl, giving a mixture of 2.3-dimethyl- and 2.3.6-trimethylglucose on hydrolysis; and trimethylstarch giving only 2.3.6-trimethylglucose on hydrolysis. In this respect starch shows an exact parallelism with glycogen and also certain similarities with inulin, but differs markedly from cellulose where methylation proceeds regularly until the formation of trimethylcellulose, which, on hydrolysis, gives 2.3.6-trimethylglucose. This sugar, however, possesses the tendency to exist in two interconvertible forms, a butylene-oxidic and an amylene-oxidic one, a fact which renders it an uncertain reference compound in structural studies.

silver oxide. Although this method gives a completely methylated product, it is accompanied by extensive depolymerization.

After 27 methylations of potato starch with diazomethane in the hands of L. Schmidt and M. Zentner[1], a methylated starch results containing 21.5% methoxyl, unchanged by further methylation. Upon hydrolysis with 1% HCl in methyl alcohol and the product extracted with acetone, three fractions are obtained of methoxyl 35.3%, 25.23% and 20.01% respectively. Further hydrolysis of the first fraction yielded a dimethylglucose. Oxidation with nitric acid gives an acid, the methyl ester of which contains but three methoxyl groups, from which the inference is drawn that one of the methylated hydroxy groups in the dimethylglucose is in position 6. Their work is summarized under three headings as follows:

I. *Methylation of Starch.* 3.5 gms. potato starch previously vacuum dried at 100°, with 50 cc. ether, were methylated by distilling in diazomethane. In order to hinder as far as possible self-decomposition of diazomethane to polymethylene, this was so prepared that after the nitrosomethylurethane was decomposed by methyl alcoholic KOH solution, the diazomethane was distilled into absolute ether, cooled with ice, in a stream of N. For one methylation, 4 cc. nitrosomethylurethane were used, corresponding to 0.7 gm. diazomethane. The diazomethane was added 10 times to the starch, after which but a weak reaction was observable, but diazomethane was added once more. The viscid methylation mass was washed with ether, then alcohol, then digested with absolute alcohol, obtaining an alcohol-soluble portion (23.41% methoxyl), and an alcohol-insoluble (22.71% methoxyl).

When starch is treated as above 27 times with diazomethane the methoxyl content is not appreciably altered,

1. Monatsh. 1928, **49**, 111; abst. C. A. 1928, **22**, 3395; J. S. C. I. 1928, **47**, 742-A.

21.3-21.5% methoxyl being found, against 17.62 for monomethyl starch.

II. *Hydrolysis of Methylated Starch.* An 8% solution of 4 gms. methyl starch (21.5% methoxyl) heated 46 hrs. with 1% HCl in methyl alcohol at 100°, and 12 hrs. more at 130°, then neutralized with silver carbonate, the AgCl filtered off, animal charcoal added to remove colloidal silver, filtered, and vacuum evaporated to dryness. Upon extraction with acetone and evaporating, the product gave 35.3% methoxyl.

III. *Hydrolysis to Sugar.* 2.5 gms. of the glucoside above, was treated with 50 cc. 5% HCl (sp. gr. 1.024) for 4 hrs. at 80°, and then 30 min. at 80-90°. The product obtained gave equivalent to 29-29.7% methoxyl.

For data on starch glycollic ethers and benzyl starch, consult the respective topics.

Starch Ethers Manufacture. The commercial production of the starch ethers—primarily methyl and ethyl starch—is based upon the disclosures of (1) Lilienfeld, (2) I. G. Farbenindustrie chemists, and (3) Miscellaneous Processes, as outlined below:

(1) *L. Lilienfeld Processes.* Pages 10-22 herein attempted to present a substantially complete outline of the Lilienfeld patent of 1912, which, however, is primarily concerned with the use of cellulose in some form as the initial carbohydrate material for ether formation, as in the patent issued in 1917[1]. In 1920 appeared a process for alkylstarch manufacture[2], as indicated in the following three illustrative examples:

1. U. S. P. 1217028; abst. J. S. C. I. 1917, **36**, 383; Mon. Sci. 1918, **85**, 4.

2. U. S. P. 1350820; abst. C. A. 1920, **14**, 3251; J. S. C. I. 1920, **39**, 654-A; Paper, 1921, **17**, No. 20, 19. E. P. 3370, 1914, abst. J. S. C. I. 1916, **35**, 534; Kunst. 1918, **8**, 42; J. Soc. Dyers, 1916, **32**, 181. F. P. 468162; 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; abst. C. A. 1923, **17**, 1803; Chem. Ztg. 1920, **44**, 877; Chem. Zentr. 1921, IV, 41; J. C. S. 1921, **119**, 650. Ital. P. 140506; abst. Chem. Ztg. 1914, **38**, 1027. D. R. P. 360415; abst. Chem. Tech. Rep.

(a) 100 parts starch are dissolved in either 400 parts 10% NaOH solution or 900 parts 10% NaOH, to which is afterwards added 100-200 parts 30% NaOH solution, gently heated on the water bath, and 100-200 parts ethyl sulfate gradually added. The mixture is then heated 0.5-2 hrs. on the water bath, and the reaction mixture then incorporated with 300-600 parts powdered NaOH. After again heating, 300-1200 parts ethyl sulfate are gradually added, whereupon the ethyl starch separates with a rise in temperature and frothing of the mass. The reaction mixture is then acidulated with dilute HCl or sulfuric acid, the precipitate washed to neutrality and dried. The starch is insoluble in water, and may be purified by solution in alcohol, filtration, and re-precipitation with water. It is a white powder, also insoluble in hot water, but readily soluble in methyl or ethyl alcohols, formic acid, glacial acetic acid, aniline, pyridine, quinoline, picoline, di- or epi-chlorhydrin, methyl acetate; ethyl acetate, phthalate, sebacate, citrate, succinate, tartrate, benzoate, levulinate; butyl or amyl acetates, acetone, tetra- or penta-chlorethane, trichlorethylene, acetylene dichloride, carbon tetrachloride, chloroform, benzene, toluene, xylene, nitrophenols, *o*-cresol, naphthalene, toluidine, formanilid, acetanilid, turpentine oil, camphor, castor oil, linseed oil, Chinese wood oil, olive oil, vaseline, paraffin oil, stearin, beeswax, Japan wax, lanolin, nitromethane, phenyl ether, triphenyl phosphate, tricresyl phosphate. There is no cellulose ester either with inorganic (nitrocellulose) or organic (cellulose acetate) radical attached, that has this variety of solubility in low boiling, high boiling, plastifying and softening liquids and solids.

(b) 100 parts starch are dissolved either in 400 parts 10% NaOH, or 900 parts 10% NaOH, to which is then added 520-800 parts 30% NaOH solution and 1000 parts

1922, **46**, 366; Chem. Zentr. 1923, II, 264. Aust. P. Appl. 2182, 1920; abst. Chem. Ztg. 1922, **46**, 687. Nor. P. 27507; abst. C. A. 1917, **11**, 1748. Can. P. 248226; abst. C. A. 1925, **19**, 3491. E. P. 149319. F. P. Addn. 16144 to F. P. 417392. D. R. P. 246443. Aust. P. 54710.

ethyl iodide, and the mixture heated in a digester at 100° for a considerable period, and the product purified as outlined in (a). It is obtained as a white powder soluble in alcohol, methyl alcohol, dichlorhydrin, glacial acetic acid, tetrachlorethane. It is obvious that any alkylating agent involving employment of iodine is too expensive for commercial exploitation.

(c) 100 parts starch are dissolved in 900 parts 10% NaOH, the solution gently heated with 200-400 parts 30% NaOH, and then 200-500 parts ethyl sulfate added gradually. The precipitated diethyl starch may be immediately collected on a hot water filter, washed with hot water, neutralized, washed to neutrality and dried. A white substance is obtained soluble in cold water, but substantially insoluble in hot water.

In 1924 appeared an amplification of this process[1], in which it is advised to heat the starch with at least 15 times its weight of 30-50% solution of alkali, the ethers produced being insoluble in water.

(2) *I. G. Farbenindustrie Methods* are indicated in the following processes.

It is claimed to be more advantageous in that more complete and uniform penetration of starch by etherifying agent is possile, if the alkylating ester is in the vapor phase, an example being[2] to knead starch 10 gms. with 30 gms. 30% NaOH solution at 20° until a loose powder of alkali-starch has formed. This product is then placed in a tumbling autoclave and methylated with methyl chloride for 6 hrs. at 40°, under 5 atms. pressure. After the mass has been purified by dialysis, a methyl starch is obtained which constitutes an excellent adhesive for paper and cardboard.

1. U. S. P. 1488355; abst. C. A. 1924, **18**, 1750; J. S. C. I. 1924, **43**, 374-B; Chem. Zentr. 1924, II, 1645. E. P. 163017; abst. C. A. 1921, **15**, 3207; J. S. C. I. 1922, **41**, 10-A; Chem. Zentr. 1921, IV, 586. F. P. 534778; abst. Caout. et Gutta. 1922, **19**, 11425; Chem. Zentr. 1922, IV, 248. D. R. P. 488030; abst. C. A. 1930, **24**, 2291. Aust. P. 93928 Addn. to 78217. See U. S. P. 1505043.

2. E. P. 302191; abst. J. S. C. I. 1929, **48**, 167-B. F. P. 640174; abst. C. A. 1929, **23**, 846; Chem. Zentr. 1928, II, 1616. Can. P. 283917.

Where the carbohydrate is simultaneously subjected to a desiccating and etherifying treatment at reaction temperature[1], the etherification may be conducted simply, in a one-stage process and with improved results, by employing an autoclave as shown in Fig. 8, provided with a stirring device *2*. In the upper part of the autoclave there is suspended a perforated receptacle, as a basket *3*, enclosing the stirrer *2*, provided with a perforated bottom *4*, in which is placed the starch or cellulose to be etherified. The lower portion of the autoclave is filled with desiccating material *5*, as fused calcium chloride; *6* represents means for the ingress and egress of etherifying fluid. The receptacle *3* is

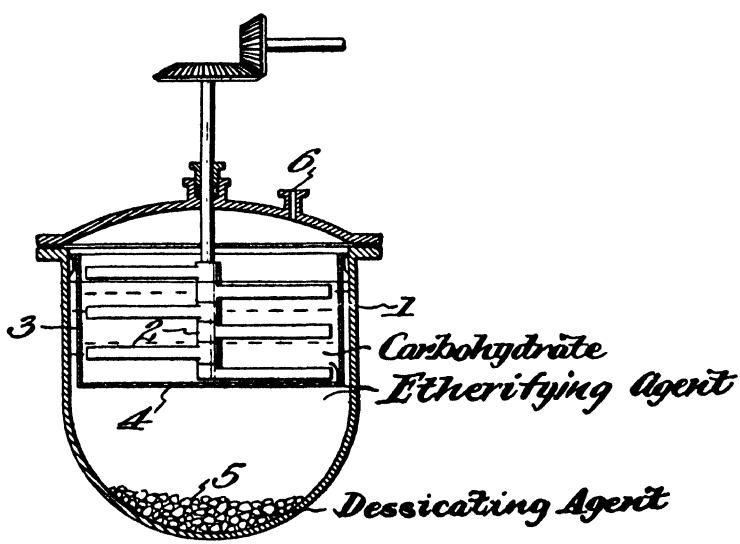


Fig. 8. Leuchs' Process for Carbohydrate Etherification.

charged with carbohydrate, the desired amount of etherifiant introduced, preferably with agitation of the carbohydrate, simultaneous etherification and desiccation taking place, and being continued, heat being applied as desired.

1. F. P. 676344; abst. C. A. 1930, **24**, 2914. O. Leuchs and I. G. Farbenindustrie A. G., U. S. P. 1746663; abst. C. A. 1930, **24**, 1759; J. S. C. I. 1930, **49**, 1127-B; Plastics, 1930, **6**, #9, 519. D. R. P. 492319; abst. C. A. 1930, **24**, 2756. Cf. E. P. 302191.

The calcium chloride absorbs water from the starting materials and from the reaction products concurrently with ether formation.

Or[1], into a mixing and kneading apparatus is introduced 160 gms. starch and 320 gms. 50% NaOH solution, which are intimately mixed. The resulting alkali-starch preparation which contains about 30% starch, 30% NaOH and 40% water (the moisture content of the starch), is mixed with 100-600 gms. sodium sulfate and warmed in a closed pressure vessel under stirring, with 240 gms. ethyl chloride for 4 hrs. at 120-130°. After washing out the reactants, there is left ethyl starch as a white powder.

Where the alkylating agent is caused to act on the semi-moist carbohydrate or starch, and the mass subjected to continuous agitation during the etherification step, water-resistant methyl and ethyl starches are formed of great stability and uniformity of composition.

(3) *Other Starch Etherification Processes.* G. Young[2] prepares methyl, ethyl and benzyl starches by soaking cellulose 30 min. in 40% NaOH solution, gently pressing, the amount of the water being not more than half the NaOH by weight. The alkyl chloride is then added in the proportion of 20 mol. to 1 mol. carbohydrate, and the mass is heated at 100-130° for 6-8 hrs. The ethers formed are characterized by being insoluble in methyl or ethyl alcohol or in benzine.

In the process of D. Smith[3], 100 gms. corn starch are dissolved in 900 cc. 10% NaOH solution, 200 cc. 30% NaOH added, the solution warmed to 40-60° and 200 cc. ethyl sulfate slowly added. The mixture is heated to induce pre-

1. G. Balle, D. R. P. 494917; abst. C. A. 1930, **24**, 6040. See F. P. 687119; abst. C. A. 1931, **25**, 833. E. P. 326865; abst. C. A. 1930, **24**, 4931.

2. U. S. P. 1504178; abst. C. A. 1924, **18**, 3272; J. S. C. I. 1924, **43**, 743-B; Chem. Zentr. 1925, I, 2050. E. P. 184825; abst. C. A. 1923, **17**, 878; J. S. C. I. 1922, **41**, 854-A; Chem. Zentr. 1923, II, 591; Kunst. 1923, **13**, 56; Chim. et Ind. 1923, **10**, 542. F. P. 555279; abst. Chem. Zentr. 1923, IV, 681.

3. **E. P. 244543; abst. Pulp & Paper Mag. 1927, 25, 1197.** See E. P. 216648.

liminary reaction, then 500-600 gms. solid NaOH and 600 cc. ethyl sulfate added by stirring into the mass, which is then heated to 85-95° for 1-2 hrs., or until the reaction which sets in, has subsided. The starch ether separates out, is removed, washed with water, then with dilute acid, then with water and dried.

A. Davis[1] dissolves 100 gms. high grade commercial cornstarch in 10% NaOH solution, then adds 200 cc. 30% NaOH, the mass being warmed on the water bath to 40-60°, when there are added 200 cc. diethyl sulfate. The mass is now heated 0.5-2 hrs. on the water bath to bring about a preliminary reaction, during which the mass becomes more fluid. Agitation is constant. There is then added 500-600 gms. pulverized NaOH followed by 600 cc. ethyl sulfate with constant stirring, and the temperature raised to 85-90° for 1-2 hrs., or until reaction sets in which is shown by foaming up sharply and the temperature spontaneously rises to 120°. During this reaction the starch is converted into the ethyl ether, and since it is insoluble in the supernatant ether, separates as a gelatinous mass which quickly hardens. It is then removed and purified as above described.

According to J. Irvine[2], three distinct compounds are recognizable as the essential products of the methylation of starch, viz: dimethylstarch, giving 2.3-dimethylglucose on hydrolysis; methylated starch with 37% methoxyl, giving a mixture of 2.3-dimethyl- and 2.3.6-trimethyl- glucose on hydrolysis; and trimethylstarch, giving only 2.3.6-trimethylglucose on hydrolysis. In this respect starch shows an exact parellelism with glycogen and also certain similarities with inulin, but differs markedly from cellulose, where methylation proceeds comparatively regularly with the formation of trimethylglucose, which, on hydrolysis, gives 2.3.6-trimethylglucose.

1. U. S. P. 1594769; abst. Chem. Zentr. 1926, II, 1707.
2. Rec. trav. chim. 1929, **48**, 813; abst. C. A. 1929, **23**, 5345.

Applications of the Starch Ethers. On account of the water-solubility of the lower etherified derivatives, especially of the alkyl starches, which in presence of hot or cold water give very viscous solutions, the starch ethers as methyl and ethyl starch have been recommended as adhesives and pastes and protective colloids[1]. Due to their unusual inertness and chemical and physical resistance, antiseptic and bactericidal ingredients may be incorporated, and after evaporation of the volatile portion, pliant elastic skins result, excellent for coapting the edges of a wound, or protecting an abraded surface. Likewise, for subcutaneous, intramuscular and intravenous injections of medicaments, these highly viscous but innocuous starch ethers should find a distinct field of usefulness. Combined with coumarone resins[2], for the manufacture of artificial leather and plastic bodies in conjunction with high boiling solvents, due to the fact that the starch ethers are miscible with drying and non-drying oils and petroleum products, a field of usefulness is indicated of growing importance[3].

In the preparation of stencil sheets for mimeograph and duplicator work, D. Smith[4] ethylates corn starch, and combines with a tempering agent as castor oil and a chlorinated naphthalene, Japan wax and benzyl alcohol, impregnating Japanese or Yoshino paper with this composition. A. Davis[5] prepares a 12.5% starch ether solution in ethyl

1. L. Lilienfeld, U. S. P. 1444257; abst. C. A. 1923, **17**, 1310; J. S. C. I. 1923, **42**, 292-A; Chem. Zentr. 1923, IV, 436. Aust. P. 89859; abst. Chem. Zentr. 1924, I, 2450. Aust. P. 92914 Addn. to 89859; abst. Chem. Zentr. 1924, I, 2450.

2. *Ibid.* U. S. P. 1625415; abst. C. A. 1927, **21**, 2054; J. S. C. I. 1927, **46**, 518-B; Chem. Zentr. 1927, II, 362. E. P. 163271; abst. C. A. 1922, **16**, 141; J. S. C. I. 1922, **41**, 50-A; Chem. Zentr. 1922, II, 543.

3. *Ibid.* U. S. P. 1625416; abst. C. A. 1927, **21**, 2054; J. S. C. I. 1927, **46**, 519-B; Plastics, 1927, **3**, 608. E. P. 171661; abst. C. A. 1922, **16**, 1301; J. S. C. I. 1922, **41**, 53-A; Chem. Zentr. 1922, II, 544; Kunst. 1923, **13**, 9. F. P. 535132; abst. Caout. et Gutta. 1922, **19**, 11495; Chem. Zentr. 1922, IV, 274. D. R. P. 504226; abst. C. A. 1930, **24**, 5444. Can. P. 249773; abst. Chem. Zentr. 1926, I, 2757. Dan. P. 29621. Aust. P. 91680.

4. E. P. 244543; abst. Pulp & Paper Mag. 1927, **25**, 1197. E. P. 216648.

5. U. S. P. 1594769; abst. Chem. Zentr. 1926, II, 1707.

acetate, into which is poured a mass consisting of 15 gms. chlorinated naphthalene, 12 gms. japan wax, and 8 cc. benzyl alcohol. Sheets of Yoshino paper are then drawn through this composition for the preparation of stencil sheets.

Starch Ether Esters. *Esterified Starch Ethers. Etherified Starch Esters.* The abietate, benzoate, laurate, linoleate, oleate, palmitate, phenylacetate, salicylate, stearate and undecylenate of ethyl starch have been described, as yet, of no particular technical significance[1]. Methyl starch glycollate[2] has been disclosed by J. Chowdhury, and a starch methylphenylethylene oxide compound by Farbenfabriken vorm. F. Bayer & Co.[3].

Butylstarch linoleate may be made by gradually introducing 10 parts butylstarch (45% butoxyl) into 50 parts linoleic acid, and the mixture heating with stirring to 110-150°, until a test portion withdrawn from the reaction mass appears homogeneous. The reaction product is then dissolved in a little benzene, and the butylstarch linoleate precipitated by means of alcohol. It is a highly viscous mass, dissolving in any proportion in aromatic hydrocarbons, yielding lacquer coatings which absorb oxygen from the air and thereby being converted into solid, elastic films. These films are no longer soluble in the solvent after drying. Addition of driers materially assists the film forming process[4].

The alkyl starches, especially methyl starch and ethyl starch, when etherified only partially, are either soluble in or swollen by cold or hot water. In general, it has been found that the esterification to a relatively slight degree

1. I. G. Farbenindustrie, E. P. 334897; abst. Br. Plastics, 1931, **2**, 317; J. S. C. I. 1930, **49**, 1146-B. F. P. 695323; abst. C. A. 1931, **25**, 2866.
2. J. Chowdhury, Biochem. Zts. 1924, **148**, 76; abst. C. A. 1925, **19**, 640; J. C. S. 1924, **126**, i, 1029; Chem. Zentr. 1924, II, 622. See D. R. P. 332203; abst. Chem. Zentr. 1921, II, 672.
3. D. R. P. 368413; abst. J. S. C. I. 1923, **42**, 620-A; Chem. Zentr. 1923, II, 755; Chem. Tech. Uebers. 1923, **47**, 77.
4. I. G. Farbenindustrie, E. P. 334897.

(usually less than 5% on the weight of the original starch) of these partially or incompletely etherified starches, especially where acids of relatively high molecular weight are introduced, materially lowers the sensitivity of the starch ether towards water.

Starch Esters of the organic acids, in contradistinction to the nitrated starches, have been known for the past fifty years, and have established themselves in various fields of technical usefulness, especially as thickening agents, adhesives and in the application to textiles. The formate and especially acetate, are best known and most important. Their close relationship to the starch ether-esters and the starch ethers, merits brief consideration herein.

Starch Formate. Made by simple immersion of anhydrous starch in absolute formic acid. Has been investigated by A. Kldiaschwili[1] and J. Traquair[2], and methods for manufacture have been patented[3]. It is a white powder, soluble in hot water.

Starch Acetate[4]. First prepared in 1870[5], and subse-

1. J. Russ. Phys. Chem. Soc. 1904, **36**, 905; abst. J. C. S. 1904, **86**, i, 798; Bull. Soc. Chim. 1905, (3), **34**, 1173; Chem. Zentr. 1904, II, 1029.

2. J. S. C. I. 1909, **28**, 288; abst. Zts. ang. Chem. 1909, **22**, 2346; Bull. Soc. Chim. 1909, (4), **6**, 1152.

3. C. Cross and J. Traquair (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, I, 1295; Chem. Ztg. Rep. 1907, **31**, 177; Jahr. Chem. 1905-8, II, 3724; Mon. Sci. 1909, **71**, 77. Belg. P. 171743, 1903. C. Cross, E. Bevan and J. Traquair, Chem. Ztg. 1905, **29**, 527. J. Traquair, J. S. C. I. 1909, **28**, 288; abst. Zts. ang. Chem. 1909, **22**, 2346; Bull. Soc. Chim. 1909, (4), **6**, 1053; C. A. 1909, **3**, 2070. J. S. C. I. 1910, **29**, 323; abst. Bull. Soc. Chim. 1910, (4), **8**, 1150.

4. See E. Worden, Kunst. 1913, **3**, 61; abst. C. A. 1913, **7**, 1633; Zts. ang. Chem. 1913, **26**, II, 320. He made an unsuccessful effort (J. S. C. I. 1912, **31**, 1064; abst. C. A. 1913, **7**, 888, 2304) to partially hydrate cellulose formate.

5. Ann. Chim. Phys. 1870, (4), **21**, 235; abst. Chem. Centr. 1871, **42**, 568. Reproduced Ann. 1871, **160**, 74; abst. Chem. Centr. 1871, **42**, 740; J. C. S. 1872, **25**, 66.

quently investigated by L. Schulze[1], A. Michael[2], Z. Skraup and H. Hamburger[3], D. Law[4], F. Pregl[5], K. Zuhlkowsky[6], J. Traquair[7], C. Cross and E. Bevan[8], A. Kldiaschwili[9], and W. de Conick and A. Raynaud[10]. Z. Skraup in 1899

1. J. prakt. chem. 1883, **136**, 324; abst. Chem. Centr. 1884, **55**, 217; Jahr. Chem. 1883, **36**, 1366; J. C. S. 1884, **46**, 284; Bull. Soc. Chim. 1884, **42**, II, 292; Jahr. Chem. 1883, **36**, 1366.

2. Amer. Chem. J. 1883-1884, **5**, 359; abst. J. C. S. 1884, **46**, 420; Bull. Soc. Chim. 1884, **42**, II, 354; Jahr. Chem. 1883, **36**, 1366.

3. Ber. 1899, **32**, 2413; abst. J. S. C. I. 1899, **18**, 941; Chem. Zentr. 1899, II, 752; Jahr. Chem. 1899, **51**, 1288; J. C. S. 1908, **94**, 321.

4. Chem. Ztg. 1908, **32**, 365; abst. J. C. S. 1908, **94**, 321; Bull. Soc. Chim. 1909, (4), **6**, 157; Zts. ang. Chem. 1908, **21**, 1377; Chem. Zentr. 1908, I, 183; Jahr. Chem. 1905-1908, II, 55.

5. Wien. Akad. Ber. 1901, **110**, II-b, 881; Monatsh. Chem. 1901, **22**, 1049; J. C. S. 1902, **82**, 135; J. S. C. I. 1902, **21**, 129; Bull. Soc. Chim. 1902, (3), **28**, 929; Chem. Zentr. 1902, I, 182; Jahr. Chem. 1901, **54**, 880.

6. Wien. Akad. Ber. 1880, **72**, II, 384; Ber. 1880, **13**, 1395; 1890, **23**, 3295; Chem. Zentr. 1880, **51**, 613; Jahr. Chem. 1880, **33**, 1005. Monatsh. Chem. 1905, **26**, 1420. J. C. S. 1891, **60**, 165; Chem. Zentr. 1888, **59**, 1060; J. C. S. 1889, **56**, 116. K. Zuhlkowsky and B. Franz, Ber. oesterr. Ges. zur Foerderung d. chem. Ind. 1894, **16**, 120.

7. J. S. C. I. 1909, **28**, 288; abst. Zts. ang. Chem. 1909, **22**, 2346; Bull. Soc. Chim. 1909, (4), **6**, 1152; Chem. Zentr. 1909, I, 1989; Jahr. Chem. 1909, **62**, 378. For reactions of starch with acetic anhydride, see P. Schützenberger, Ann. Chim. Phys. 1870, (4), **21**, 235; abst. Chem. Zentr. 1871, **42**, 568; Ann. 1871, **160**, 74; J. C. S. 1872, **25**, 366; abst. Chem. Zentr. 1871, **42**, 740.

8. C. Cross, E. Bevan and J. Briggs, Jour. Soc. Dyers Col. 1907, **23**, 250. C. Cross, E. Bevan and J. Traquair, Chem. Ztg. 1905, **29**, 527; Wag. Jahr. 1905, **51**, II, 197; Chem. Zentr. 1905, II, 36.

9. J. Russ. Phys. Chem. Soc. 1905, **37**, 421; abst. Brewers Jour. 1905, **41**, 688; J. S. C. I. 1905, **24**, 1246; Jahr. Chem. 1905-1908, II, 954; Chem. Zentr. 1905, II, 1029; J. C. S. 1904, **86**, i, 798. Compare also Z. Skraup, E. Geinsperger, E. v. Knaffl-Lenz, F. Menter and H. Sirk, Monatsh. 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. Zentr. 1906, II, 655; Jahr. Chem. 1905-1908, II, 929. J. Boeseken, J. van den Berg and A. Kerstjens (Rec. trav. chim. Pays-Bas, 1916, **35**, 320; abst. J. C. S. 1916, **109**, i, 308; C. A. 1917, **11**, 39) have found that the velocity of acetylation of starch is less than that of cellulose, hydriodic acid being the best catalyst. In the case of sulfuric acid, an increase in the amount of acid used produces an acceleration in esterification, but not to an extent proportional to the amount of catalyst employed.

10. Bull. Acad. Roy. Belg. 1911, 213, 335; abst. J. C. S. 1911, **100**, 423; Chem. Zentr. 1911, II, 855; C. A. 1911, **5**, 2443. For the hydrolyzing action of formic acid on starch, see W. Oechsner de Conick, Bull. Acad. Roy. Belg. 1910, 515, 586; abst. C. A. 1911, **5**, 394; J. C. S. 1910, **98**, 654; Chem. Zentr. 1910, II, 1459. See also L. Schulze, J. prakt. Chem. 1883, **136**, 324; I. Frankhausen, Dingl. Poly. 1887, **266**, 303. For the preparation of soluble starch by heat-

studied the action of sulfuric acid as an aid in starch acetylation[1], and in 1922 H. Pringsheim and M. Lassmann[2] published physical constants of starch acetate and inulin triacetate. Y. Tsuzuki[3] described a method of starch acetylation using zinc chloride as catalyst, and determined the molecular weight cryoscopically and by means of the ebullioscope. E. Peiser[4], K. Hess, H. Friese and F. Smith[5], and P. Brigl and R. Schinle[6] published refinements in manufacture. P. Karrer and E. v. Krauss[7] studied the action of hot glycerol on acetated starch, and H. Clarke and H. Gillespie[8] investigated the esterification of potato starch by boiling acetic acid. In one process of manufacture air is removed from the starch in order to insure maximum, uniform acetylation[9], in another, dry alkali-starch is treated

ing with dilute acetic acid, see E. Blumer, D. R. P. 137330, 1901; abst. Chem. Zentr. 1903, I, 306; Jahr. Chem. 1903, **56**, 1005; Zts. ang. Chem. 1903, **16**, 90. F. P. 322206, 1902; abst. J. S. C. I. 1903, **22**, 310. E. P. 10872, 1902. Aust. P. 14886, 1904. Farbenfabriken vorm. F. Bayer & Co., D. R. P. 200145; abst. Jahr. Chem. 1905-1908, II, 941.

1. 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; 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. Zentr. 1901, 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.

2. Ber. 1922, **55B**, 1409; abst. C. A. 1922, **16**, 3878. See also H. Pringsheim and A. Aronowsky, Ber. 1922, **55B**, 1414.

3. Bull. Chem. Soc. Japan, 1928, **3**, 276; 1929, **4**, 153; abst. C. A. 1929, **23**, 1393; 1930, **24**, 260.

4. Zts. physiol. Chem. 1927, **167**, 88; abst. C. A. 1927, **21**, 2881.

5. Ber. 1928, **61B**, 1975; abst. C. A. 1929, **23**, 302.

6. Ber. 1929, **62B**, 99; abst. C. A. 1929, **23**, 2426. See P. Brigl and H. Keppler, Zts. physiol. Chem. 1929, **180**, 38.

7. Helv. Chim. Acta, 1930, **13**, 1071; abst. J. S. C. I. 1930, **49**, 1415-A.

8. J. A. C. S. 1932, **54**, 2083; abst. C. A. 1932, **26**, 3235.

9. I. G. Farbenindustrie, E. P. 293757; abst. C. A. 1929, **23**, 1750.

with a slight excess of acetyl chloride[1], while J. Randall[2] esterifies alkali-cellulose with calcium acetate.

The starch acetates have been patented for use as a component in bronzing liquid[3], for attaching rubber to paper[4], as a finish and paint remover[5], as binding agent, in match manufacture[6], and in the production of plastic masses[7]. The methods of stencil preparation for mimeograph work of S. Horii[8] and D. Gestetner[9] utilize acetated starch.

Treatment of acetylstarch suspended in toluene with phosphorous pentachloride at 105° gives a product which contains 1 Cl to every 8 groupings, an aldehyde group being liberated in the chlorination[10]. Starch acetate (44.7% acetyl) when heated in glycerol at 200-220° is deacetylated to a product containing 7-10% acetyl[11]. H. Pringsheim and P. Meyersohn[12] have cryoscopically determined the molecular weights of diamylose acetate and hexa-amylose acetate.

Starch Benzoate has been investigated by C. Cross and

1. E. Stern, D. R. P. 411156; abst. J. S. C. I. 1925, **34**, 563-B; Ann. Rep. S. C. I. 1925, **10**, 476.
2. U. S. P. 1338040; abst. C. A. 1920, **14**, 1835.
3. W. Doerflinger, U. S. P. 884475.
4. R. Rose and H. Cude, U. S. P. 1773201; abst. C. A. 1930, **24**, 5159.
5. C. Ellis, U. S. P. 1169783.
6. W. Dixon, E. P. 27491, 1911; abst. J. S. C. I. 1913, **32**, 214.
7. W. Mooser-Schiess, U. S. P. 1317721.
8. U. S. P. 1587954, Re-17267; 1594525, 1645141, 1664777, 1753204, 1753205, 1790987, 1792095, 1799793. E. P. 250798, 261203, 275747, 289511, 310181. Jap. P. 44216. See also R. Escales and H. Levy, Kunst. 1923, **13**, 25. S. Halen, Kunst. 1921, **11**, 121; 1922, **12**, 73; abst. C. A. 1922, **16**, 657, 2600; Chim. et Ind. 1922, **7**, 548.
9. D. Gestetner, U. S. P. 1371157.
10. E. Peiser, Zts. physiol. Chem. 1927, **167**, 88; abst. C. A. 1927, **21**, 668, 2881.
11. P. Karrer and E. v. Krauss, Helv. Chim. Acta, 1930, **13**, 1071; abst. C. A. 1931, **25**, 1224.
12. Ber. 1927, **60B**, 1709; abst. C. A. 1927, **21**, 3602.

E. Bevan[1], E. Baumann[2], O. Hauser and H. Muschner[3], and H. Ost and F. Klein[4]. The process of A. Wohl[5] comprises heating starch with benzoyl chloride in the presence of pyridine to 110-130° with nitrobenzene as solvent for the ester formed. The starch and cellulose benzoates possess very desirable technical properties, but the present cost of production makes it non-competitive with the corresponding acetic esters.

Starch Glycollate. The process of J. Chowdhury is detailed on pp. 56-57.

Starch Lactate. Starch Phthalate. When starch is condensed with formaldehyde in the presence of concentrated lactic or phthalic acids[6], these two esters result, which, on account of their plasticity and softening power, appear to have desirable technical applications.

Starch Higher Fatty Acid Esters. A dilaurate, dipalmitate and distearate of starch have been described[7], and methods for the preparation of starch linoleate, linolenate and oleate[8], starch palmitate[9], stearate[10], and hexapalmi-

1. J. C. S. 1893, **26**, 837; Chem. News, 1890, **61**, 87. C. Cross, E. Bevan and R. Jenks, Ber. 1901, **34**, 2496. C. Cross and E. Bevan, Ber. 1901, **34**, 1514; J. C. S. 1901, **80**, i, 452; Chem. Zentr. 1901, II, 94; Jahr. Chem. 1901, **54**, 891.

2. Ber. 1886, **19**, 3218; abst. J. C. S. 1887, **52**, 228; Jahr. Chem. 1886, **39**, 1426.

3. Zts. ang. Chem. 1913, **26**, 137; J. S. C. I. 1913, **32**, 357; Chem. Zentr. 1913, I, 1412; J. Dyers and Col. 1913, **29**, 194; Kunst. 1913, **3**, 330; C. A. 1913, **7**, 2854; J. C. S. 1913, **104**, i, 363.

4. Zts. ang. Chem. 1913, **26**, 437; J. S. C. I. 1913, **32**, 823; Kunst. 1913, **3**, 331; C. A. 1913, **7**, 3661; J. C. S. 1913, **104**, i, 1043; Chem. Zentr. 1913, II, 1293.

5. D. R. P. 139669; abst. Zts. ang. Chem. 1903, **16**, 285.

6. Herold, A. G., D. R. P. 507997; abst. C. A. 1931, **25**, 784.

7. H. Hele-Shaw and J. Pickard, Can. P. 281702. H. Gault, Compt. rend. 1923, **177**, 592; abst. C. A. 1924, **18**, 80; J. C. S. 1923, **124**, i, 1064. I. G. Farbenind. A. G., D. R. P. 539470; abst. C. A. 1932, **26**, 1783. F. P. 699217; abst. C. A. 1931, **25**, 3482.

8. Farbenfabriken, vorm. F. Bayer & Co., E. P. 239726; abst. C. A. 1926, **20**, 2167. D. R. P. 411990. Cites E. P. 208685.

9. Soc. de Stearinerie et Savonnerie de Lyon and P. Berthon, 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. In U. S. P. 1651366, P. Berthon describes starch esters of the higher fatty acids which are soluble in benzene, toluene, chloroform and carbon tetrachloride, and may be prepared by reacting upon starch

tate[1] have been detailed. They constitute a new class of compounds, having many desirable properties, and are discussed under "Cellulose Higher Fatty Acid Esters."

Starch Phenolsulfonate. When alkali-starch is esterified with phenolsulfonic acid[2], starch phenolsulfonates result, soluble in a wide variety of solvents, and upon evaporation of solutions lustrous films result. Dextrin phenolsulfonate is known.

Alkylated Glycogen. On account of its physiological importance, glycogen has been the subject of repeated investigation. P. Karrer[3] has pointed out that the action of methyl sulfate and barium or sodium hydroxide converts glycogen into a methyloglycogen, the properties of which are in singular agreement with the corresponding methylated starch, from which Karrer deduced that starch and glycogen are fundamentally identical, a view not held by H. Pringsheim and M. Lassmann[4]. A. Macbeth and J. Mackay[5] methylated glycogen, after several operations obtaining a product with 37% methoxyl (dimethylglycogen requires 32% methoxyl). The glycogen ether was very resistant to further alkylation. By repeated methylation, a product was eventually obtained containing 40% methoxyl.

J. Irvine and J. MacDonald[6] first succeeded in obtaining a trimethylstarch, the complete methylation of glycogen

directly by the acid chloride in the presence of pyridine, quinoline or zinc chloride. For instance, if 100 gms. dry starch are moistened with a mixture of 400 gms. benzene and 600 gms. palmityl chloride and 400 gms. added in portions, after heating on the water bath at 60° for 0.5 hr. with continual stirring, the ester may be precipitated out by the addition of alcohol. From a benzene solution, starch palmitate gives a colorless, translucent, uninflammable film.

10. I. G. Farbenindustrie, D. R. P. 484242; abst. C. A. 1930, **24**, 962.

1. P. Karrer and Z. Zega, Helv. Chim. Acta, 1923, **6**, 822; abst. C. A. 1924, **18**, 80.

2. I. Fukushima and Y. Takamatsu, J. S. C. I. Japan, 1929, **32**, 130; Suppl. Binding, **32**, 42-B; abst. C. A. 1929, **23**, 5058.

3. Helv. Chim. Acta, 1921, **4**, 994; abst. C. A. 1922, **16**, 1216.

4. Ber. 1922, **55**-B, 1409; abst. C. A. 1922, **16**, 3878.

5. J. C. S. 1924, **125**, 1513.

6. J. C. S. 1926, **129**, 1502; abst. C. A. 1926, **20**, 2830.

having been accomplished in 1929 by W. Haworth, E. Hirst and J. Webb[1] in 1929. The glycogen was purified by precipitation of its aqueous solutions by alcohol, and further purified by electro-dialysis, and was methylated from glycogen triacetate, by treating an acetone solution of the triacetate at 50° during 90 min. with 30% NaOH solution and methyl sulfate with vigorous stirring. After being heated 30 min. at 100°, the solution was cooled with ice, sulfuric acid added until the solution was faintly alkaline, neutralization of the NaOH being completed by CO_2. Yield 97-98% of theory. The trimethylglycogen melted at 147° as against 145° for trimethylstarch. Did not reduce Fehling's solution. Soluble in chloroform or acetone, becoming gelatinous without dissolving, in alcohol or water, insoluble in ether or petroleum ether. Upon boiling with 2 % methyl alcohol-HCl the glycogen ether hydrolyzes to crystalline 2.3.6-trimethylglucose in 76% yield.

This work was repeated and extended by G. Hughes, A. Macbeth and F. Winzor[2] on the methylation of glycogen by the action of NaOH and methyl sulfate upon an acetone solution of glycogen triacetate, and also by the methylation of glycogen direct in the absence of acetone. In the first instance, they obtained nearly the theoretical of 45.6% methoxyl for trimethylglycogen; in the second instance, the maximum methylation of glycogen was 36% after six methylations.

No technical application of the methylated glycogens has as yet been evolved, insofar as aware.

Alkyl Saccharides and Polyatomic Alcohols[3]. While at the present time these bodies have little or no technical value, yet for completeness of presentation, a short statement of the more important of these alkylated derivatives has been included, with references to the original sources

1. J. C. S. 1929, **132**, 2479; abst. C. A. 1930, **24**, 1353.
2. J. C. S. 1932, **135**, 2026.
3. Much information in this topic has been obtained from H. Coles, Iowa State Coll. Jour. Sci. 1931, **5**, 61-83, 243-250, all references having been checked against the originals.

of information for more detailed data. With the meticulous search now going on in the entire field of organic chemistry for suitable plasticizing, flexilizing, softening and auxiliary solvent bodies both liquid and solid some of these alkylated compounds may be found applicable in obtaining special properties to cellulose ether compositions, and in this possibility lies the value of their enumeration.

1. *Trioses. Glycerose.* Glycerol has been methylated to mono-[1], di-[2], and tri-methyl glycerol. Various glyceryl ethers having been described by A. Fairbourne[3]. Benzylidene- and ethylidene-methylglycerol have been prepared[4], as well as hexamethylglycerol glucoside. M. Ulmann and K. Hess[5] have described endecamethyltriose (obtained by acetolysis of cellulose), indicating that the compound is octa-methylcellobiose.

2. *Erythrose.* The oxidation of monomethyl-*a*-fructose yields monomethyl-*d*-erythronic acid (dihydroxymethoxybutyric acid)[6], while 2.4-dimethyl-*d*-erythronic acid (hydroxydimethoxybutyric acid)[7] is obtained from the lactol acid of tetramethylfructose, methylating to methyl 2.3.4-trimethoxy-*d*-erythronate (methyl trimethoxybutyrate)[8]. 2.3-Dimethyl-*d*-erythronolactone is claimed to result upon acting upon tetramethylfructose with potassium permanganate.

3. *Threose.* It is claimed dimethoxy-*d*-succinic acid may be prepared from 1-methyl-arabonolactone[9], from tetramethylgluconolactone and nitric acid[10], and from 2.3.5-trimethylxylonolactone[11]. Dimethoxy-*l*-succinic acid is ob-

1. J. Irvine, J. MacDonald and C. Soutar, J. C. S. 1915, **107**, 337.
2. H. Gilchrist and C. Purves, J. C. S. 1925, **127**, 2735.
3. A. Fairbourne, J. C. S. 1929, **132**, 1151.
4. H. Hill, A. Hill and H. Hibbert, J. A. C. S. 1928, **50**, 2242.
5. Naturwiss. 1932, **20**, 316; abst. J. S. C. I. 1932, **51**, 725-A.
6. J. Irvine and A. Hynd, J. C. S. 1909, **95**, 1220.
7. J. Avery, W. Haworth and E. Hirst, J. C. S. 1927, **130**, 2308.
8. J. Irvine and J. Patterson, J. C. S. 1922, **121**, 2696.
9. W. Haworth, E. Hirst and A. Learner, J. C. S. 1927, **130**, 2432.
10. W. Haworth, E. Hirst and E. Miller, J. C. S. 1927, **130**, 2436.
11. W. Haworth and C. Porter, J. C. S. 1928, **131**, 611.

tained from *d*-2.3.5-trimethylarabonolactone, or from the breaking down of the lactol acid of 1.3.4.5-tetramethylfructose[1].

4. *Erythrulose.* Tetramethylfructose when oxidized with nitric acid[2] gives an indefinitely characterized ester, methyl dimethylerythrulonic acid.

5. *Rhamnose.* The cautious methylation of acetonerhamnose yields dimethylacetonerhamnose[3], which hydrolyzes to dimethylrhamnose[4], and forms a methylrhamnoside[5]. When methylated, acetonemethylrhamnoside gives trimethyl-*a*-methyl-*l*-rhamnoside[6], oxidizing to *l*-arabotrimethylglutaric acid[7]; and this on hydrolysis forms trimethyl-*l*-rhamnose[8], the latter giving trimethylrhamnonic acid on oxidation[9]. Triacetyl-, monoacetyldimethyl-, and monoacetyl-methylrhamnoside[10] have been prepared. *iso*-Rhamnose forms[11] *b*-tetra-acetyl*iso*rhamnose, m. pt. 147°. Methylation of *l*-fucose produces *a*- and *b*-*l*-methylfucoside (methylhodeose)[12], first obtained by E. Votocek and F. Valentin[13], and which probably contains some *b*-*d*-methylfucoside.

6. *Ribose.* An alkyl compound of *d*-ribose has been isolated from animal tissues[14]. P. Levene and R. Tipson[15] have prepared the isomeric triacetyl-1-methyl-*d*-ribosides,

1. T. Purdie and R. Rose, J. C. S. 1906, **89**, 1204.
2. W. Haworth, Ann. Reports Prog. Chem. 1926, **23**, 74.
3. O. Svanberg, Ber. 1924, **56B**, 2195.
4. J. Irvine and J. Patterson, J. C. S. 1922, **121**, 2146.
5. T. Purdie and C. Young, J. C. S. 1906, **89**, 1194.
6. C. Hudson, J. A. C. S. 1926, **48**, 1424.
7. E. Hirst and G. Robertson, J. C. S. 1925, **127**, 358.
8. H. Fenton, Ann. Reports Prog. Chem. 1906, **3**, 89.
9. E. Hirst, J. C. S. 1926, **129**, 350.
10. W. Haworth, E. Hirst and H. Samuels, J. C. S. 1931, **134**, 2861.
11. B. Helferich and N. Bigelow, Z. Physiol. Chem. 1931, **200**, 263; abst. J. S. C. I. 1931, **50**, 1275-A. Cf. J. S. C. I. 1929, **48**, 1280-A.
12. J. Minsaas, Rec. trav. chim. 1932, **51**, 475; abst. J. S. C. I. 1932, **51**, 723-A.
13. Coll. Czech. Chim. Comm. 1930, **2**, 36; abst. J. S. C. I. 1930, **49**, 326-A.
14. L. Winter, Biochem. Jour. 1927, **21**, 467.
15. J. Biol. Chem. 1931, **92**, 109; abst. C. A. 1931, **25**, 4229; cf. C. A. 1931, **25**, 1805.

including methylated *l*-bromtriacetyl-*d*-ribose, and triacetylmethyl-*d*-riboside.

7. *Lyxose.* Trimethylmethyl-lyxoside results from the methylation of *a*-methyl-lyxoside[1], a colorless oil, giving *d*-trimethoxyglutaric acid with nitric acid which consists of *a*-isomerides, on removing the glycoside group therefrom, 2.3.4-trimethyl-lyxose is obtained[2] as needles, m. pt. 79°, and forming trimethyl-lyxonolactone on oxidation[3]. H. Bott, E. Hirst and J. Smith[4] have described the methylation of methyl-lyxofuranoside to trimethyl methyl-lyxofuranoside and methyl-lyxopyranoside to the tri-methyl derivative. Upon slow distillation, 2.3.4-trimethyl-lyxofuranose forms hexamethyldipentose, needles, m. pt. 77°.

8. *Arabinose.* 2.4-Dimethylarabinose has been reported upon by G. Zemplen and G. Braun[5], 2.5-dimethyl-*d*-arabonolactone being obtained by treating 2.3.5.6-tetramethylglucose with hydrogen dioxide[6]. 2.3.4.6-Tetramethylglucose upon oxidation yields dimethyl-*d*-arabonolactone[7]. Dimethylarabinose results by hydrolyzing hexamethylmethylmaltoside[8], forming a methylarabinoside which may be methylated to trimethylmethylarabinoside. 2.3.4-Trimethyl-*l*-arabinose (1.5) oxidizes to 2.3.4-trimethylarabonolactone[9], oxidizable with nitric acid to *l*-arabotrimethoxyglutaric acid[10], the latter being directly obtainable from trimethyl-*l*-arabinose[11]. It forms a methyl amide, a diamide, a methyl ester[12], and a dimethyl ester[13].

1. W. Haworth and E. Hirst, Ann. Report Progress Chem. 1928, **25**, 97.
2. J. Ambler, J. Chem. Education, 1930, **7**, 1599.
3. W. Haworth and C. Long, J. C. S. 1929, **132**, 345.
4. J. C. S. 1930, **133**, 658.
5. Ber. 1926, **59**, 2230.
6. W. Lewis and E. Gustus; abst. from Org. Div., A. C. S. Baltimore, April, 1925.
7. *Ibid.* J. A. C. S. 1927, **49**, 1512.
8. J. Irvine and J. Dick, J. C. S. 1919, **115**, 593.
9. W. Haworth, Ann. Reports Prog. Chem. 1926, **23**, 74.
10. W. Haworth, E. Hirst and D. Jones, J. C. S. 1927, **130**, 2428.
11. G. McOwan, J. C. S. 1926, **129**, 1737.
12. E. Hirst and G. Robertson, J. C. S. 1925, **127**, 358.
13. G. McOwan, J. C. S. 1926, **129**, 1747.

2.3.4-Trimethylarabinose (1.5) has been condensed with methyl chlorformate and potassium cyanide to trimethylarabomethoxymannonitrile and gluconitrile[1]. *l*-1.2.-3.4-Trimethyl-*b*-methylarabinoside has been prepared[2]. 2.3.4-*d*-Trimethyl-*b*-methylarabinoside has been prepared. 2.3.4.*d*-Trimethyl-*a*-methylarabinoside forms a 2.3.4-trimethyl-*d*-methyl-*d*-arabinose[3]. H. Neher and W. Lewis[4] have prepared crystalline trimethyl-*l*-arabinose. When 2.4.6-trimethyl-[5] and 1.3.4.6-tetramethyl-fructose are degraded, *d*-2.3.5-trimethylarabonolactone results. Methylarabinoside methylates to a mixture of *a*- and *b*-trimethylmethylarabinosides, yielding on hydrolysis *l*-2.3.5-trimethylarabinose[6] forming a lactone of trimethoxyhydroxyvaleric acid, which in turn yields dimethyltrimethoxyglutarate. *l*-2.3.5-Trimethylarabinose also forms on milder oxidation[7], *l*-2.3.5-trimethoxyarabonolactone, colorless needles. *d*-Arabotrimethoxyglutaric acid[8] may be prepared from 1.3.4.5-tetramethylfructose[9], trimethyl-lyxonolactone[10], trimethyl-*d*-arabinose or tetramethylmannonolactone[11]. *d*-2.3.-4-Trimethylarabonolactone[12] has been described as being obtained from 1.3.4.5-tetramethylfructose. Acetoiodomaltose[13] may be methylated to hexamethylmethylglucoarabinoside.

9. *Alkylxyloses.* Mono- and di-methylacetonexyloses result from refluxing monoacetonexylose with methyl iodide and silver oxide, the latter sugar upon hydrolysis forming

1. W. Haworth and S. Peat, J. C. S. 1929, **132**, 350.
2. J. Pryde and R. Humphreys, J. C. S. 1927, **130**, 559.
3. J. Ambler, J. Chem. Education, 1930, **7**, 1599.
4. J. A. C. S. 1931, **53**, 4411.
5. W. Haworth and A. Learner, J. C. S. 1928, **131**, 619.
6. S. Baker and W. Haworth, J. C. S. 1925, **127**, 365.
7. W. Haworth, E. Hirst and A. Learner, J. C. S. 1927, **130**, 2432.
8. K. Josephson, Svensk. Keb. Tids. 1929, **41**, 24.
9. W. Haworth, E. Hirst and A. Learner, J. C. S. 1927, **130**, 1040.
10. E. Hirst and J. Smith, J. C. S. 1928, **131**, 3147.
11. E. Goodyear and W. Haworth, J. C. S. 1927, **130**, 3136.
12. C. Anderson, W. Charlton, W. Haworth and V. Nicholson, J. C. S. 1929, **132**, 1337.
13. G. Zemplen, Ber. 1927, **60B**, 1555.

dimethylmethylxylose, oxidizing to 3.5-dimethylxylonolactone. W. Haworth and E. Percival[1] have isolated 2.3.4-trimethylxylose and 2.3.5-trimethyl-*v*-xylonolactone, while R. Hockett and C. Hudson[2] have described *b*-methyl-*d*-xyloside obtained by condensing *d*-xylose with methyl alcohol. Cold acetylation gives a mixture of *a*- and *b*-methylxyloside tetra-acetates. E. Heuser and W. Ruppel[3] have described dimethylxylan, yielding on hydrolysis 2.3-dimethylmethylxyloside[4]. When *b*-xylochloralose is methylated, dimethyl *b*-xylochloralose results, acetylating to a monoacetyldimethyl-*b*-xylochloralose[5]. Dilute alkali acting on trimethylxylose[6] gives trimethyl-lyxose. 2.3.4-Trimethylmethylxyloside prepared from *b*-methylxyloside[7] has m. pt. 46.8°[8] to 51°, *l*-2.3.4-trimethylxylose resulting when the glycosidic group is removed, and *l*-2.3.4-trimethylxylonolactone formed on oxidation. However, 2.3.4-trimethylxylose gives 2.3.4-trimethylxylonic acid on oxidation[9]. *a*-Methylxyloside may be methylated to 2.3.4-trimethyl-*a*-methylxyloside[10].

10. *Gentiobiose.* G. Zemplen and Z. Brucker[11] have described 2.3.4-triacetyl-1-*b*-methylglucose, 1-*b*-methylgentiobioside hepta-acetate, 1-*b*-methyl-6-*a*-glucosidoglucose heptabenzoate, heptamethyl-1-*b*-methyl-6-*a*-glucosidoglucose and 1-*b*-methylgentiobioside heptabenzoate.

11. *Monomethylgalactose.* K. Freudenberg and K. Smeykal[12] report diacetone-6-methylgalactose having b. pt.

1. J. C. S. 1931, **134**, 2850.
2. J. A. C. S. 1931, **53**, 4454; abst. C. A. 1932, **26**, 423.
3. Ber. 1922, **55B**, 2084; abst. C. A. 1923, **17**, 390; J. C. S. 1922, **122**, i, 810; Chem. Zentr. 1922, III, 667.
4. S. Komatsu, T. Inoue and R. Nakai, Mem. Coll. Sci. Kyoto Univ. 1923, **7**, 25; abst. C. A. 1924, **18**, 666.
5. L. Goodhue, A. White and R. Hixon, J. A. C. S. 1930, **52**, 3191.
6. C. Gross and W. Lewis, J. A. C. S. 1931, **53**, 2772; abst. C. A. 1931, **25**, 4230; J. S. C. I. 1931, **50**, 1037-A.
7. F. Phelps and C. Purves, J. A. C. S. 1929, **51**, 2443.
8. A. Carruthers and E. Hirst, J. C. S. 1922, **121**, 2299.
9. E. Hirst and C. Purves, J. C. S. 1923, **123**, 1352.
10. J. Avery and E. Hirst, J. Chem. Soc. 1929, **132**, 2466.
11. Ber. 1931, **64B**, 1852; abst. J. S. C. I. 1931, **50**, 1040-A.
12. Ber. 1926, **59B**, 100.

109-115° at 0.5 m., forming 6-methylgalactose on hydrolysis and producing a monomethylgalactonic acid. Dimethylgalactose is said to give a monomethylgalactosazone[1]. K. Freudenberg, W. Belz and C. Niemann[2] have described 6-methylgalactose. *b*-Galactose penta-acetate is convertible to *a*-acetobromgalactose[3], alkylating to acetomethylgalactose, which may be transformed into *b*-methylgalactoside-6-triphenylmethyl ether, m. pt. 167-169°.

12. *Dimethylgalactose.* According to J. Irvine and J. Oldham[4] dimethylgalactose forms a monomethylgalactosazone.

13. *Trimethylgalactose.* The methylation of *a*-methylgalactoside forms a trimethyl-*a*-methylgalactoside[5]; *d*-galactose upon methylation and oxidation giving 2.3.4-trimethoxy-*l*-glutaric acid.

14. *Tetramethylgalactose.* J. Irvine and A. Cameron[6] have described tetramethylgalactose and the isomeric tetramethyl-*a*-(and -*b*-)methylgalactoside. The statement appears[7] that methylated dihydrosphingosine (obtained from the partial cleavage of cerebrosides), forms tetramethylgalactose. 2.3.4.6-Tetramethylgalactose may be obtained from octamethyllactose[8], octamethylmelibiose[9], hendecamethylraffinose[10], methyloctamethyl-lactobionate[11] or tetramethylgalactoside[12], and forms a characteristic tetramethylgalactose anilid[13], m. pt. 192-193°[14]. It may be oxidized to

1. J. Irvine, J. C. S. 1922, **123**, 898.
2. Ber. 1929, **62**, 1554.
3. A. Müller, Ber. 1931, **64B**, 1820; abst. J. S. C. I. 1931, **50**, 1039-A.
4. J. C. S. 1925, **127**, 2903.
5. W. Haworth, J. C. S. 1915, **107**, 8-T.
6. J. C. S. 1904, **85**, 1071-T.
7. E. Klenk and R. Härle, Z. physiol. Chem. 1928, **178**, 221.
8. W. Haworth and G. Leitch, J. C. S. 1918, **113**, 188.
9. W. Haworth, J. Loach and C. Long, J. C. S. 1927, **130**, 3146.
10. W. Haworth, E. Hirst and D. Ruell, J. C. S. 1923, **123**, 3125.
11. W. Haworth and C. Long, J. C. S. 1927, **130**, 544.
12. J. Pryde and R. Humphreys, Biochem. J. 1926, **20**, 825.
13. W. Haworth, E. Hirst and D. Ruell, J. C. S. 1923, **123**, 3125.
14. W. Charlton, W. Haworth and W. Hickinbottom, J. C. S. 1927, **130**, 1527.

tetramethylgalactonic acid[1] and 2.3.4.6-tetramethylgalactonolactone[2]. 2.3.5.6-Tetramethylgalactose upon oxidation forms 2.3.5.6-tetramethylgalactonolactone[3], also obtainable by methylating galactonolactone[4]. *a*-Methylgalactoside when methylated, forms tetramethyl-*a*-methylgalactoside[5], readily soluble in organic solvents.

15. *Pentamethylgalactose.* P. Levene and G. Meyer[6] have described a pentamethyldiethylmercaptogalactose, b. pt. 155-160°, and M. Wolfrom[7] a liquid aldehydo pentamethylgalactose.

16. *Monomethylmannose.* Diacetonemannose may be methylated to diacetonemethylmannose[8], m. pt. 111-115°[9]. An isomer, methyldiacetonemannose[10] has been reported. Details have also been published for the preparation[11] of 4-*b*-glucoside-*a*-methylmannoside and its hydrolysis to heptamethyl-4-*b*-glucosido-*a*-methylmannoside, and the methylation of 4-*b*-glucosidomannoic acid and its hydrolysis to methyloctamethyl 4-*b*-glucosidomannonate. Mannitan dioleate dehydrates to *iso*mannide dioleate, which methylates to monomethyl*iso*mannide[12]. *a*-Methylmannoside reacts with triphenylmethyl chloride[13]. Methylation of mannosediacetone[14] gives γ-methylmannoside.

1. P. Levene and H. Simms, J. Biol. Chem. 1925, **65**, 31.
2. W. Haworth, D. Ruell and G. Westgarth, J. C. S. 1924, **125**, 2468.
3. J. Irvine and R. Gilmour, J. C. S. 1908, **93**, 1429.
4. J. Irvine and A. Moodie, J. C. S. 1905, **87**, 1462.
5. H. Schlubach and H. Firgau, Ber. 1926, **59**, 2100.
6. P. Levene and G. Meyer, J. Biol. Chem. 1927, **74**, 695.
7. J. A. C. S. 1930, **52**, 2464.
8. H. Ohle, Ber. 1924, **57**, 403.
9. K. Freudenberg, W. Durr and H. v. Hochstetter, Ber. 1928, **61B**, 1735.
10. P. Levene and G. Meyer, J. Biol. Chem. 1924, **59**, 145.
11. W. Haworth, E. Hirst and H. Streight, J. C. S. 1931, **134**, 1349.
12. J. Irvine and H. Gilchrist, J. C. S. 1924, **125**, 10; abst. C. A. 1924, **18**, 973.
13. R. Hockett and C. Hudson, J. A. C. S. 1931, **53**, 4456; abst. C. A. 1932, **26**, 425.
14. J. Irvine and A. Skinner, J. C. S. 1926, **129**, 1089; abst. C. A. 1926, **20**, 2663.

17. *Dimethylmannose.* Vegetable ivory has been claimed as a source of dimethylmannose[1]. On methylation of diacetone mannitol[2], 5.6-dimethylmannitoldiacetone results, which, upon removal of the acetone residue, leaves 5.6-dimethylmannitol[3], and this oxidizes to 5-6-dimethylmannonolactone. Methylation of dimethylmannitol[4] gave chiefly pentamethylmannitol, and a little hexamethylmannitol, yielding on oxidation pentamethylmannonic acid.

18. *Trimethylmannose.* When *a*-methylmannoside is methylated, trimethylmethylmannoside[5] is obtained.

19. *Tetramethylmannose* has been obtained by J. Irvine, A. Fyfe and T. Hogg[6], E. Hirst and G. Robertson[7], and P. Shaffer and T. Friedemann[8]. 2.3.4.6-Tetramethyl-*a*-methylmannoside[9] and the *b*-isomeride[10] hydrolyze to tetramethylmannose and oxidize to 2.3.4.6-tetramethylmannonic acid[11] and *d*-2.3.4.6-tetramethylmannonolactone[12].

When mannitolmonoacetone is methylated[13], 3.4.5.6-tetramethylmannitolmonoacetone is formed, 3.4.5.6-tetramethylmannitol remaining when the acetone residue is removed, and which oxidizes to 3.4.5.6-tetramethylmannoic acid. 1.2.3.4-Tetramethyl-5-ethylmannitol has been described.

20. *Pentamethylmannose.* 2.3.4.5.6-Pentamethylmannitol has been prepared. When diethylmercaptomannose is methylated[14], pentamethyldiethylmercaptomannose results, and upon removal of the diethylmercapto group, penta-

1. J. Patterson, J. C. S. 1923, **123**, 1139.
2. J. Irvine and B. Paterson, Chem. News, 1912, **106**, 167.
3. *Ibid.* J. C. S. 1914, **105**, 898.
4. *Ibid.* J. C. S. 1914, **105**, 915; abst. C. A. 1914, **8**, 2342.
5. P. Levene and G. Meyer, J. Biol. Chem. 1928, **76**, 809.
6. J. C. S. 1915, **107**, 524.
7. J. C. S. 1925, **127**, 358.
8. J. Biol. Chem. 1930, **86**, 345.
9. W. Haworth, J. C. S. 1915, **107**, 8-T.
10. H. Bott, W. Haworth and E. Hirst, J. C. S. 1930, **133**, 1395.
11. P. Levene and H. Simms, J. Biol. Chem. 1925, **65**, 31.
12. S. Carter, W. Haworth and R. Robinson, J. C. S. 1930, **133**, 2125.
13. M. Bridel, Bull. Soc. Chim. 1923, **33**, 1005.
14. P. Levene and G. Meyer, J. Biol. Chem. 1927, **74**, 695.

methylmannose is formed. It readily condenses with alcohol to form pentamethylmannosedimethylacetal. J. Irvine and B. Paterson have methylated dimethylmannitol to penta- and hexa-methylmannitol, yielding pentamethylmannonic acid on oxidation.

21. *Monomethylfructose.* Triacetylfructose upon methylation[1] forms monomethyltriacetylfructose. *a*-Diacetonefructose methylates to 3-monomethylfructose[2]. 3-Methyl-*a*-diacetone fructose[3] appears to be non-fermentable. A 6-methyl-*a*-(or -*b*-)fructose has been described[4]. E. Hersant and W. Linnell[5] have formed *dl*-5-methoxyfructose, yellow crystals, m. pt. 80-85°; T. Purdie and D. Paul[6] the alkylation of *d*-fructose, and W. Haworth, E. Hirst and M. Plant[7], the methylation of 4-*b*-galactosido-*a*-methylmannoside.

22. *Dimethylfructose.* *l*-Dimethylinulin is said to form a dimethylfructose[8], on further methylation forming a dextro-rotatory tetramethylmethylfructoside.

23. *Trimethylfructose.* Upon hydrolysis of trimethyllevan[9], or octamethylturanose[10], it is claimed 1.3.4-trimethylfructose results, oxidizable to dimethoxyhydroxyglutaric acid. Hydrolysis of the acetyl groups in triacetyl anhydro-fructose leaves trimethyl-anhydro-fructose[11]. Distillation induces molecular association to di-(trimethylanhydrofructose)[12]. Acetone may be removed from 3.4.5-trimethylfructosemonoacetone, leaving laevo 3.4.5-tri-

1. Reviewed by C. Desch and A. Lapworth, Ann. Reports Prog. Chem. 1909, **6**, 80.
2. J. Irvine and A. Hynd, J. C. S. 1909, **95**, 1220.
3. A. Kendall and C. Gross, J. Infect. Dis. 1930, **47**, 249.
4. J. Irvine, Proc. Chem. Soc. 1913, **29**, 69.
5. Quart. J. Pharm. Pharmacol. 1931, **4**, 52; abst. C. A. 1931, **25**, 5402.
6. J. Chem. Soc. 1907, **91**, 289; abst. C. A. 1907, **1**, 1696.
7. J. C. S. 1931, **134**, 1354.
8. J. Irvine, Reports Brit. Ass'n Adv. Sci. 1922, 33; cf. J. Irvine, E. Steele and M. Shannon, J. C. S. 1922, **121**, 1060.
9. H. Hibbert and R. Tipson, J. A. C. S. 1930, **52**, 2582.
10. G. Zemplen and G. Braun, Ber. 1926, **59**, 2230.
11. H. Schlubach and W. Flörsheim, Ber. 1929, **62**, 1491.
12. J. Irvine and J. Stevenson, J. A. C. S. 1929, **51**, 2197.

methylfructose. 3.4.6-Trimethyl-*d*-fructose[1] may be obtained from hendecamethyl-melezitose[2], methylated sinistrin, or from trimethylinulin[3]. It forms 3.4.6-trimethylmethylfructoside which produces a trimethylfructose monoacetone[4]. A 1-methyl-2-fluorotriacetyl- and 2-fluoro-3-methyltriacetyl- fructose have been described[5], as well as 1.3.4-trimethylmethylfructoside[6].

24. *Tetramethylfructose.* 1.3.4.6-*d*-Fructose results from methylation of trimethyl-*d*-fructose[7], from the sucrose residue of methylraffinose[8], and from the mixture of methylated fructosides from fructose. On oxidation with nitric acid, 3.4.6-trimethylfructuronic acid is first formed[9], which forms an ethyl tetramethylfructuronate, stable towards alkalis. *b*-Methylhexoside on methylation, forms tetramethyl-*b*-methylhexoside, and upon removal of the glycoside group, *ab*-tetramethylhexose remains[10]. A dextro tetramethylmethylfructoside is obtainable from dimethyl-*d*-fructose[11].

1.3.4.5-Tetramethylfructose is obtained by the hydrolysis of tetramethyl-*b*-methylfructoside obtained by methylation of normal *b*-methylfructoside, or from the corresponding methylated *a*-methylfructoside[12], or tetramethylfructose[13]. 1.3.4.5-Tetramethyl-*b*-methylfructoside may be

1. J. Irvine and J. Patterson, J. C. S. 1922, **121**, 2696.
2. G. Leitch, J. C. S. 1927, **130**, 588.
3. J. Irvine, J. C. S. 1923, **123**, 898.
4. J. Irvine, W. Denham and E. Hirst, Reports Brit. Ass'n. Adv. Sci. 1922, 33; abst. J. S. C. I. 1922, **41**, 362-R.
5. D. Brauns and H. Frush, Bur. Standards J. Research, 1931, **6**, 449; abst. C. A. 1931, **25**, 4231.
6. H. Hibbert, R. Tipson and F. Brauns, Can. J. Res. 1931, **4**, 221; abst. J. S. C. I. 1931, **50**, 827-A.
7. W. Haworth, E. Hirst and A. Learner, J. C. S. 1927, **130**, 1040.
8. W. Haworth, E. Hirst and D. Ruell, J. C. S. 1923, **123**, 3125; abst. J. S. C. I. 1924, **43**, 190-B.
9. J. Avery, W. Haworth and E. Hirst, J. C. S. 1927, **130**, 2308.
10. W. Morgan and R. Robison, Biochem. J. 1928, **22**, 1270; abst. J. S. C. I. 1928, **47**, 1214-A.
11. R. Menzies, J. C. S. 1922, **121**, 2238.
12. H. Schlubach and G. Schröter, Ber. 1928, **61**, 1216.
13. E. Hirst and G. Robertson, J. C. S. 1925, **127**, 358.

obtained from *b*-methylfructoside[1], or from trimethylfructose[2]. The corresponding 1.3.4.5-tetramethyl-*a*-methylfructoside may be obtained by methylating *a*-methylfructoside[3]. When 1.3.4.5-tetramethylfructose is reduced with sodium amalgam[4], tetramethylhexitol results. J. Irvine and G. Robertson[5] have described a reactive form of methylfructoside.

25. *Alkylated Glucoses.* W. Haworth[6] has methylated sucrose to heptamethylsucrose, *a*-methylglucoside to tetramethyl-*a*-methylglucoside, *a*-methylmannoside to the tri- and tetra-methylmannoside, methylgalactoside to the tri- and tetra-derivative, and salicin to dimethylsalicin. L. Maquenne has described the preparation of *b*-methylglucoside[7], and J. Irvine and H. Gilchrist[8] monomethylmethylglucoside. The alkylation and rotatory power of partially methylated glucoses[9] have been detailed, including the preparation of monomethyl-levulose and its derivatives[10]. The methylation of *b*-methyl-*a*-glucoheptoside[11] and the preparation of penta-acetyl-*a*-(and -*b*-)methyl-*a*-glucoheptoside were reported upon in 1931. Trideca-acetyl-1-*b*-methyl-6′-*b*-cellobiosidogentiobiose has been prepared[12].

26. *Glucose.* D. Loder and W. Lewis[13] have converted 3-methylglucose into 3-methylfructose, and B. Helferich and

1. W. Haworth, The Constitution of Sugars. London: Edward Arnold & Co., 1929.
2. J. Irvine and J. Patterson, J. C. S. 1922, **121**, 2146.
3. H. Schlubach and G. Schröter, Ber. 1930, **63**, 364.
4. W. Haworth and J. Mitchell, J. C. S. 1923, **123**, 301.
5. J. C. S. 1916, **109**, 1305; abst. C. A. 1917, **11**, 575.
6. J. C. S. 1915, **107**, 8; abst. C. A. 1915, **9**, 1034.
7. Leon Maquenne, Bull. Soc. chim. 1905, (3), **33**, 469; abst. J. C. S. 1905, **88**, 415.
8. J. C. S. 1924, **125**, 1; abst. C. A. 1924, **18**, 973.
9. J. Irvine and J. Scott, Chem. News, 1912, **106**, 151; abst. C. A. 1913, **7**, 1167.
10. J. Irvine and A. Hynd, J. C. S. 1909, **95**, 1220; abst. C. A. 1909, **3**, 2933.
11. W. Haworth, E. Hirst and M. Stacey, J. C. S. 1931, **134**, 2864.
12. G. Zemplen and A. Gerecs, Ber. 1931, **64B**, 2458; abst. C. A. 1932, **26**, 98.
13. J. A. C. S. 1932, **54**, 1040; abst. C. A. 1932, **26**, 2433.

E. Guenther[1] described derivatives of 6-methyl-*d*-glucose. E. Pacsu[2] has prepared a 4-methylglucose, said by R. Schinle[3] to be 2-methylglucose. Methylglucoside, ethylarabinoside, ethylrhamnoside, ethylglucoside and benzylglucoside have been made[4], and α-monomethylglucose isolated[5] 2.3.4-Triacetyl-β-methyl-*d*-glucosenide and its 6-methyl ether[6], and mono- and di-methylanhydromethylglucoside[7] have been synthesized.

B. Helferich and O. Lang[8] prepared 3-methyl-β-methyl-6-glucoside from β-tetraacetyl-3-methyl-*d*-glucose and described 2.4-diacetyl-3-methyl-6-triphenylmethyl-β-methyl-*d*-glucoside, m. pt. 144-145°. When 3.5.6-tribenzyl*iso*propylideneglucose[9] is hydrolyzed, and the resulting 3.5.6-tribenzoylglucose converted into its methylglucoside, methylation and debenzoylation give 2-methylmethylglucoside, hydrolyzable to 2-methylglucose.

Compounds of 2.3-dimethyl-β-methylglucoside have been reported upon by J. Oldham and J. Rutherford[10]; 2.3.6-trimethylglucose, trimethylmethylglucoside, heptamethylmethyl-cellobioside and -lactoside by J. Irvine and E. Hirst[11]; and trimethylglucose from cellulose by W. Denham and H. Woodhouse[12]. Methylation of 2.3.4-triacetyl-

1. Ber. 1931, **64B**, 1276; abst. C. A. 1931, **25**, 4230.
2. Ber. 1932, **65B**, 51; abst. J. S. C. I. 1932, **51**, 254-A; C. A. 1932, **26**, 2173.
3. Ber. 1931, **64B**, 2361; abst. C. A. 1932, **26**, 96; J. S. C. I. 1931, **50**, 1399-A.
4. Ber. 1893, **26**, 2410; abst. J. C. S. 1894, **66**, 3.
5. J. Irvine and T. Hogg, J. C. S. 1914, **105**, 1386; abst. C. A. 1914, **8**, 2682.
6. B. Helferich and E. Himmen, Ber. 1929, **62B**, 2136; abst. J. S. C. I. 1929, **48**, 1280-A.
7. J. Irvine and H. Gilchrist, J. C. S. 1924, **125**, 1; abst. C. A. 1924, **18**, 973; Chem. Zentr. 1924, I, 2102.
8. J. prakt. Chem. 1932, (ii), **132**, 321; abst. J. S. C. I. 1932, **51**, 255-A.
9. J. Oldham and J. Rutherford, J. A. C. S. 1932, **54**, 1086; abst. J. S. C. I. 1932, **51**, 500-A.
10. *Ibid.* J. A. C. S. 1932, **54**, 366; abst. J. S. C. I. 1932, **51**, 254-A.
11. J. C. S. 1922, **121**, 1213; abst. C. A. 1922, **16**, 3071; Chem. Zentr. 1922, III, 1331.
12. J. C. S. 1917, **111**, 244; abst. C. A. 1917, **11**, 1953; J. S. C. I. 1917, **36**, 607; Chem. Zentr. 1918, I, 80.

α-methylglucoside[1]; 2.3.4-trimethylglucose and oxidation to 2.3.4-trimethyl-β-methylglucoside[2]; and monomethylglucosediacetone[3] have been detailed. Triacetyldibromglucose[4], trimethyl-α-methylglucoside[5] and 2.3-dimethylmethyl glucoside and its 4:6-dinitrate[6] have also been made.

Tetramethylgluconic acid from α-methylglucoside, a pentamethylglucose isomeric with tetramethyl-α-methylglucoside, and tetramethylmethylfructoside are products described by T. Purdie and J. Irvine[7]. 2.3.6- (or 2.3.4-)trimethylglucose has been synthesized, and 3.5.6-trimethylmethylglucoside prepared from trimethylacetoneglucose[8]. Glucal can be methylated to trimethylglucal[9], oxidizable to a trimethylglucose, which can be further methylated to 2.3.4.6-tetramethylglucopyranose.

Tetramethyl-pentitol, -gluconolactone and -sorbitol have been described[10], and maltose transformed into methylmaltoside, methylheptamethylmaltoside, tetra- and tri-methylglucose[11]. J. Kerb[12] has patented the manufacture of tetraglucosan, and J. Irvine and A. Moodie[13] have

1. W. Haworth, E. Hirst and E. Teece, J. C. S. 1931, **134**, 2858.
2. W. Charlton, W. Haworth and R. Herbert, J. C. S. 1931, **134**, 2855.
3. J. Irvine and J. Scott, J. C. S. 1913, **103**, 564; abst. C. A. 1913, **7**, 2383.
4. J. Irvine and J. Oldham, J. C. S. 1925, **127**, 2729; abst. C. A. 1926, **20**, 376.
5. T. Purdie and R. Bridgett, J. C. S. 1903, **83**, 1037.
6. J. Irvine and J. Rutherford, J. A. C. S. 1932, **54**, 1491; abst. J. S. C. I. 1932, **51**, 603-A.
7. J. C. S. 1903, **83**, 1021; abst. J. S. C. I. 1903, **22**, 888.
8. P. Levene and G. Meyer, J. Biol. Chem. 1921, **48**, 233; abst. C. A. 1922, **16**, 60; Chem. Zentr. 1921, III, 1319. See also P. Levene and M. Yamagawa, J. Biol. Chem. 1920, **43**, 323; abst. C. A. 1920, **14**, 3645.
9. E. Hirst and C. Woolvin, J. C. S. 1931, **134**, 1131; abst. J. S. C. I. 1931, **50**, 1399-A.
10. J. Irvine, A. Fyfe and T. Hogg, J. C. S. 1915, **107**, 524; abst. C. A. 1915, **9**, 1907; J. S. C. I. 1915, **34**, 627; Chem. Zentr. 1915, II, 267; Meyer Jahr. Chem. 1915, **25**, 108.
11. J. Irvine and J. Dick, J. C. S. 1919, **115**, 593; abst. C. A. 1919, **13**, 3166.
12. Holl. P. 17538.
13. J. Irvine and A. Moodie, J. C. S. 1908, **93**, 95; abst. C. A. 1908, **2**, 1553.

described derivatives of tetramethylglucose. Pentamethylglucose has been prepared by E. Fischer[1].

Monomethyl-levulose, tetramethyldextrose, octamethylsucrose and tetramethyldextrose[2]; heptamethylmethylmaltoside[3]; heptamethylsucrose[4]; and neotrehalose[5] have been prepared. Compounds of 2.3.6-trimethylglucose[6] were described in 1932. P. Karrer and J. Peyer in the methylation of *d*-saccharic acid and mucic acid have formed dimethyltetramethyl-mucate and -*d*-saccharate and dimethyltrimethylmucate[7].

In the acetolysis of cellulose derivatives, octamethylcellobiose, hendecamethylcellotriose, and a methylated cellodextrin (cellotetrose?) have been isolated[8], and cellobiose (cellose) investigated[9]. The methylation of biosan to hexamethylbiosan[10] has been reported, K. Freudenberg[11] considering the former as a high-molecular chain of decomposition products of cellulose. From cellulose has been prepared a crystalline methylcellotriose[12], and heptamethyl-*b*-methylcellobioside, 2.3.6-trimethyl-*b*-methylglucoside, heptamethylcellobiose and decamethyl-*b*-cellotrioside synthesized.

1. Ber. 1914, **47**, 1980; abst. C. A. 1914, **8**, 3036.
2. T. Purdie and J. Irvine, J. C. S. 1905, **87**, 1022; abst. J. S. C. I. 1905, **24**, 906.
3. W. Haworth and G. Leitch, J. C. S. 1919, **115**, 809.
4. J. Irvine and E. Stiller, J. A. C. S. 1932, **54**, 1486; abst. J. S. C. I. 1932, **51**, 255-A.
5. W. Haworth and W. Hickinbottom, J. C. S. 1931, **134**, 2847; abst. C. A. 1932, **26**, 969.
6. J. Irvine and R. McGlynn, J. A. C. S. 1932, **54**, 356; abst. J. S. C. I. 1932, **51**, 255-A.
7. P. Karrer and J. Peyer, Helv. Chim. Acta, 1922, **5**, 577; abst. C. A. 1922, **16**, 3874.
8. W. Haworth, E. Hirst and H. Thomas, J. C. S. 1931, **134**, 825.
9. W. Haworth and E. Hirst, J. C. S. 1921, **119**, 193; abst. C. A. 1921, **15**, 1505.
10. K. Hess and H. Friese, Annalen, 1926, **450**, 40; abst. C. A. 1927, **21**, 174; J. S. C. I. 1927, **46**, 44-A; J. C. S. 1927, **132**, 44. See also K. Hess, W. Weltzien and R. Singer, Annalen, 1925, **443**, 71; abst. J. C. S. 1925, **128**, i, 641. J. Irvine and G. Robertson, J. C. S. 1926, **129**, 1488; abst. J. S. C. I. 1926, **45**, 823-A.
11. Naturwissenschaften, 1929, **17**, 959; abst. C. A. 1930, **24**, 1213; J. S. C. I. 1930, **49**, 198-A.
12. K. Freudenberg, C. Andersen, Y. Go, K. Friedrich and N. Richtmyer, Ber. 1930, **63B**, 1961; abst. C. A. 1931, **25**, 85; J. S. C. I. 1930, **49**, 1412-A.

CHAPTER IX

CARBOHYDRATE ARYL AND ARALKYL ETHERS. BENZYLCELLULOSE.

Most important of these bodies are the benzylated celluloses, usually prepared by the action of a benzyl halide upon cellulose which has previously been treated with alkali. On the assumption that cellulose is represented by the simple formula $C_6H_{10}O_5$, in which it is generally conceded there are a maximum of three replaceable hydroxyls, $C_6H_7O_2(OH)_3$, the action of benzyl alcohol upon cellulose comprises the replacement of one, two or three hydroxyl hydrogens by the benzyl group, as below indicated:

$$\begin{array}{rl} C_6H_5CH_2OH + & HO \\ & HO\text{-}C_6H_7O_2 = C_6H_5CH_2.O(OH)_2.C_6H_7O_2 \\ & HO \\ \text{Benzyl alcohol} + & \text{Cellulose} = \text{Monobenzylcellulose} \end{array}$$

$$\begin{array}{rl} C_6H_5CH_2OH & HO \\ + & HO\text{-}C_6H_7O_2 = (C_6H_5CH_2)_2O_2.OH.C_6H_7O_2 \\ C_6H_5CH_2OH & HO \\ \text{Benzyl alcohol} + & \text{Cellulose} = \text{Dibenzylcellulose} \end{array}$$

$$\begin{array}{rl} C_6H_5CH_2OH & HO \\ C_6H_5CH_2OH + & HO\text{-}C_6H_7O_2 = (C_6H_5CH_2)_3O_3.C_6H_7O_2 \\ C_6H_5CH_2OH & HO \\ \text{Benzyl alcohol} + & \text{Cellulose} = \text{Tribenzylcellulose} \end{array}$$

Assuming the atomic weight of C = 12.0; H 1.008 and O, 16.0, then cellulose has mol. wt. 162.08, C 44.42%, H 6.22%; monobenzylcellulose, mol. wt. 252.13, C 61.87%, H 6.39%; dibenzyl-, mol. wt. 342.18, C 70.12%, H 6.48%, and tribenzyl-, mol. wt. 432.22, C 74.96%, H 6.53%.

These benzyl derivatives have been imperfectly studied as yet, yet they offer most interesting commercial possi-

bilities, and are readily soluble in the commercial state in mixtures of acetone, alcohol and benzene, and in general, in the cheaper solvents. The main technical drawback at the moment to the extensive technical utilization of these cellulose benzyl ethers is the cost of the benzylating agent and the large amount required for maximum benzyl introduction into the cellulose aggregate.

Benzylcellulose.[1] Outside of the two alkylcelluloses methyl and ethyl, benzylcellulose is the best known representative of the etherified carbohydrates, its technical usefulness being based on its stability toward concentrated alkali solutions, its apparent ease of production, and to the commercial advantage of the preponderance in weight of the benzyl group ($C_6H_5CH_2$) over that of methyl or ethyl when in the etherified condition attached to cellulose. The cellulose ethers are all solids, and sold on a weight basis. On the assumption of a triether-derivative and based on a C_6 molecule for cellulose, a trimethyl derivative adds 45 by weight, a triethyl 87, but a tribenzylcellulose adds 273. The economic advantage of this is at once apparent, especially as benzyl chloride is readily obtainable at a not prohibitive price.

The physical constants and methods of preparation of the benzylcelluloses show a wide range of dissimilar results —more so than with the analogous methyl- and ethyl-cellulose, and this is explainable on the following classes of variants involved in their production:

1. Condition of the cellulose operated upon as to the composition, maturity and alkaline content of the alkali-cellulose prepared therefrom. Sufficient attention has as yet not been centered upon uniform methods of alkali-

1. For chronological development of benzylcellulose advancement, see this work, pages 4, 10, 39, 45, 46, 48, 49, 58, 60, 62, 64, 69, 86, 87, 91, 93, 96, 101, 102, 103, 104, 107, 109, 110, 113, 122, 123, 126, 136, 137, 140, 141, 143, 152, 158, 159, 162, 164, 169, 171, 173, 174, 175, 176, 177, 178, 183, 184, 188, 193, 202, 204, 206, 207, 212, 213, 214, 223, 224, 227, 232, 234, 235, 237, 240, 244, 245, 246, 247, 248, 249, 253, 256, 257, 259, 260, 266, 268, 269, 270, 272, 278, 282, 285, 290, 292, 293, 294, 295, 297, 302, 304, 305 and 306.

cellulose production for benzylating purposes, as exemplified, for instance, by the meticulous researches which have been made on the optimum alkalicellulose required for viscose rayon manufacture.

Conditions of etherification as to temperature, concentration, and details of the etherification step whether conducted as a unitary operation or by a plurality of treatments.

3. The composition and purity of the etherifying agent. Commercial benzyl chloride usually contains benzal chloride (benzylidene chloride) which exists in several isomeric forms, benzotrichloride which likewise has several isomerides, benzyl alcohol and sometimes unchanged toluene. This complexity of etherifier is not present in methyl or ethyl chlorides or sulfates. Too much emphasis can not be laid upon the importance of using benzyl chloride of maximum purity in all operations involving etherification of the carbohydrates.

4. The degree of substitution of benzyl for replaceable hydroxyl hydrogen in the cellulose aggregate, and the manipulation of the steps of etherification and subsequent purification so that the maximum of mono-, di- or tri-benzylcellulose results. The difficulty of removal of unused benzyl chloride and benzyl alcohol formed at the close of the etherifying process is a point of prime importance, because it is quite easy to modify the physical properties of the benzylcelluloses after formation, especially those desirable properties of water-insolubility, viscosity and solubility in relatively inexpensive solvents.

O. Leuchs in his patent application executed Jan. 26, 1917[1], has given the first workable process for benzylcellulose formation, his directions being to mix 40 gms. cellulose with 400 gms. NaOH 10%, then add 800 gms. NaOH, and heat the mixture with 500 gms. benzyl chloride for 50-70 hrs. at 100°. The mass obtained is washed with ether-alcohol, then with water, being a pure, white powder

1. U. S. Ser. No. 185198, filed Aug. 8, 1917.

when dried. The benzylcellulose dissolved in benzene, or mixture of benzene with alcohol and chloroform. Nothing is said as to the yield, but from the color and solubility, it is apparent that the ether was washed with ether-alcohol and water until only a cellulose of high benzylation was left. The temperature to which the etherification was carried on accounts in a measure for the lightness in color of the ether produced.

The first comprehensive academic investigation of the benzylated carbohydrates was made in 1921 by M. Gomberg and C. Buchler[1], who expanded upon their previous work on the manufacture of benzyl esters[2] by including the carbohydrates cellulose, starch, glucose, sucrose and dextrin, basing their method of procedure somewhat upon the earlier work on the alkylation of carbohydrates, as touched upon on page 2 of this work. No attempt was made to ascertain the optimum conditions for the most complete alkylation, but merely to establish the generalities of the reaction. The general method of procedure was to dissolve, or suspend, the individual carbohydrates in water which contained sufficient NaOH to keep the solution alkaline throughout the entire period of reaction, benzyl chloride being added in the proportion of slightly more than 1 mol. of the chloride for each hydroxyl group used in the carbohydrate, the mixture being well stirred. After the reaction was deemed to have been completed, excess of benzyl chloride was removed by steam distillation, and the subsequent treatment applied as described below for the individual carbohydrate. For analysis, the purified products were dried for 6-10 hrs. at 100°.

Benzylation of Cellulose. Unless previously subjected to a "hydration" treatment, normal or natural cellulose benzylated but slightly. It was found that benzylcellulose is

1. J. A. C. S. 1921, **43**, 1904; abst. C. A. 1922, **16**, 59; J. C. S. 1922, **122**, i, 112; J. S. C. I. 1922, **41**, 71-A; Chem. Zentr. 1927, I, 1396; Ann. Rep. S. C. I. 1922, **7**, 136; Bull. Soc. Chim. 1922, **32**, 454.
2. J. A. C. S. 1920, **42**, 2059; abst. C. A. 1921, **15**, 95.

insoluble in Schweitzer's reagent, which considerably facilitated the purification of the etherified products.

(a) Absorbent cotton, previously subjected to hydration by means of zinc chloride and HCl, washed free and dried, was benzylated as above indicated at 90-95°, the resulting product being partially soluble in cuprammonium solution, analysis indicating benzylation equivalent to less than a mono-ether.

(b) 5 gms. absorbent cotton were dissolved in Schweitzer's reagent, allowed to stand over night, then precipitated by alcohol and freed from copper. It was then digested 12 hrs. with 11 gms. NaOH in 73 cc. water, 22 gms. benzyl chloride then added, and the mixture heated for 7 hrs. at 90-95°. After steam distillation, the product was thoroughly washed with water, alcohol and ether. The gray powder was then insoluble in copperammonia solution, in chloroform, chlorhydrin, acetone, acetic acid, benzene and nitrobenzene. Analysis indicated half-monobenzylcellulose (C_6 molecule), *and yet was insoluble in water.*

(c) 5 gms. cellulose were converted into hydrocellulose by means of HCl, the neutral material then digested 3 hrs. with 50 cc. NaOH 15%, then 10 cc. water and 18 gms. benzyl chloride added, and the mixture heated 4 hrs. The benzylated product was then digested for several hours with cuprammonium solution, filtered, washed, then digested in several changes of dilute HCl, and washed with water, alcohol and ether. The benzylated product amounting to 4 gms. consisted of white, very short fibers, indicating but superficial or incomplete benzylation. Analysis indicated the introduction of a half benzyl group in a C_6 cellulose.

(d) 4 gms. filter paper soaked 12 hrs. in 30 cc. NaOH 20%, 45 cc. water added, and the mixture heated an hour at 90-95° with no apparent change. 17 gms. benzyl chloride then introduced and heating continued 5 hrs. Analysis indicated a half-monobenzylcellulose formed.

(e) 5 gms. filter paper were digested 2 days at room temperature with 10 gms. NaOH and 30 cc. water, 30 gms.

benzyl chloride then added and mixture heated 7 hrs. at 100°. After removal of unchanged benzyl chloride by steam distillation, washing, the material weighed 6 gms., analysis indicating a 1.5-benzylcellulose. The benzylation was repeated with but little increment in benzyl. The half-benzyl compound did not show signs of softening at 250°, the 1.5-benzylcellulose melting at 208-210°, while the product of the double benzylation under (e) softened at 165°, and melted at 175-177°. The 1.5-benzylcellulose appeared as fully insoluble in the various organic solvents as the ½-benzyl ether shown under (b), while the product of double benzylation was soluble in chlorhydrin, chloroform, nitrobenzene, ethyl acetate and gelatinized by acetone.

It is apparent that with the possible exception of the twice benzylated product, all the ethers produced were of too low degree of benzylation to be of industrial value.

Benzyldextrin. The dextrin used was from potato starch and completely soluble in water. One mol. dextrin, 3.5 mols. benzyl chloride and 4.5 mols. NaOH (9%) were heated at 80-85° for 4 hrs. Upon addition of ether to the concentrated chloroform solution of the reaction mixture, 16 gms. dextrin gave 18 gms. insoluble benzyl derivative, of analysis ½-benzyl dextrin, a white, amorphous, tasteless powder, m. pt. 208-210°, insoluble in water, acetone and ether; slightly soluble in benzene and nitrobenzene. Swelled in alcohol and in ethyl acetate, and with chloroform, chlorhydrin and acetic acid gave colloidal, transparent solutions, filterable with difficulty.

Benzylated Starch. A potato and a corn starch were used. In each case the reaction temperature was 85-90°, the relative proportion of reactants being the same as with dextrin. "Potato starch took up one benzyl group for each C_{12} molecule, while corn starch took up two." Monobenzyl starch (on a C_{12} basis) melted at 200-203°, the dibenzyl at 203-205°. Both were soluble in chloroform, benzene, nitrobenzene, ethyl acetate and benzyl benzoate.

Benzylated Sucrose. It was difficult to judge the progress of benzylation of sucrose, because the benzylated products dissolved in the excess of benzyl chloride. When 1 mol. sucrose, 8.8 mols. benzyl chloride and 12 mols. NaOH (10%) were heated for 4.5 hrs. at 85°, and after steam distillation the residual gum dissolved in chloroform-benzene, the solution dried and absolute ether added, analysis showed the mixture to be a monobenzyl derivative (C_{12} cellulose) with higher alkylated products. If heating is at 100° for 3 hrs., the product consists almost wholly of dibenzyl sucrose (C. 58.2, H 6.1). Twice benzylated at 100° for 4 hrs. gave a mixture of di- and penta-benzyl sucrose (C_{12}), possessing a most persistent bitter taste. The two compounds are insoluble in water, soluble in alcohol, acetic acid, chloroform, chlorhydrin, ethyl acetate, benzene and nitrobenzene. The pentabenzyl was soluble also in ether and in acetone, while the dibenzyl sucrose was only slightly soluble in acetone and not at all in ether. Both are insoluble in petroleum ether.

Benzylated Glucose. On account of unsatisfactory results in benzylation of glucose, *a*-methylglucoside of E. Fischer[1] was benzylated as above, benzylglucoside, dibenzylmethylglucoside and tetrabenzyl-benzylglucoside being formed. The dibenzylmethylglucoside is a semi-solid material, soluble in benzene and in chloroform, cloudy with acetone or ethyl acetate, slightly soluble in alcohol or acetic acid, insoluble in absolute ether or petroleum ether. Tetrabenzyl-benzylglucoside is an oil, soluble in a great variety of organic solvents, including ether and petroleum ether.

In 1928 appeared the general resume of the applications of benzylcellulose by L. Clement and C. Riviere[2] in which was described a method of producing this ether, giving a body soluble in acetone and in a mixture of alcohol and benzene or toluene, indicating the formation of a highly benzylated product, probably of unusually low viscosity.

1. Ber. 1895, **28**, 1145; abst. J. C. S. 1895, **68**, i, 437.
2. Chim. et Ind. 1928, **19**, 670; abst. Chem. Zentr. 1929, I, 955; Zts. ang. Chem. 1927, **40**, 1579.

They have detailed the uses of benzylcellulose for lacquers and varnishes, films, filaments and plastic masses.

T. Nakashima[1] carried further the benzylation researches of Gomberg and Buchler, and by heating at higher temperature and for longer periods obtained a more nearly complete benzylation, and hence more favorable solubilities from a commercial viewpoint. He etherified with benzyl chloride dissolved in benzene or toluene, and in a single treatment obtained a di-ether on a C_6 cellulose basis, the yield being practically quantitative. Ethers higher than dibenzyl were difficult to obtain.

The alkalicellulose prepared with 10-20% NaOH solution gave an ether of benzyl content less than ½ mol. per mol. C_6 cellulose, in conformity with the results obtained by Gomberg, but by shaking this ether with copperammonia solution to dissolve the unchanged cellulose a mono-ether remained, soluble in chloroform, benzene, carbon tetrachloride; insoluble in alcohol, ether and water. His method of procedure was to immerse cotton paper in 40-50% NaOH (by vol.) solution, which, after 24 hrs. was pressed to 3-4 times the original weight of the cellulose, and heated with benzyl chloride at 110° for 50-60 hrs. As the reaction progresses, two layers slowly separate out, the upper being a toluene or benzene solution containing benzylcellulose, benzyl chloride and benzyl alcohol, whereas the lower layer consists of alkali, sodium chloride and unacted-upon cellulose. The upper layer when treated with acetic acid, impurities removed by steam distillation, extracted with alcohol, dissolved in chloroform and precipitated by alcohol or ether, produces a white powder, corresponding to the di-ether. If 10-20% NaOH solution is used in excess, instead of the 40-50%, and the material etherified immediately at 100° with benzyl chloride, the cellulose swells

1. Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 261; Abstracts, 1929, **2**, 31; abst. C. A. 1929, **23**, 3572; J. S. C. I. 1929, **48**, 684-A. See Chem. Zentr. 1929, I, 1678, 1679. T. Nakashima, Sci. Papers Inst. Phys. Chem. Research, Tokyo, 1929, **12**, 121; abst. C. A. 1930, **24**, 721; J. S. C. I. 1930, **49**, 72-A.

but does not lose its original form, and may be purified by treating with boiling water, alcohol and ether.

When 50 gms. paper are immersed in 400 cc. 20% NaOH solution, and warmed with 150 gms. benzyl chloride on the water bath for 20 hrs., a product containing less than ½ mol. per C_6 cellulose is obtained. The monobenzylcellulose and still lower etherified products melt on heating at 220°. The di-ether becomes soft at 160° and melts at 175°, while tribenzylcellulose softens at 150° and melts at 160°.

He found that by treatment of cotton paper which has been steeped in 40-50% NaOH solution with sufficient benzyl chloride in benzene or toluene, dibenzylcellulose is obtained in quantitative yield in a single operation, but if 10-20% NaOH solution be employed, a mixture of monobenzylcellulose and unchanged cellulose results, from which the latter may be removed by treatment with ammoniacal copper oxide solution.

Dibenzylcellulose may be converted into the tribenzyl ether according to T. Nakashima and I. Sakurada[1] by heating 10 gms. with 50 gms. benzyl chloride at 100° for 6 hrs., and adding gradually 45 gms. silver oxide.

H. Okada[2] has submitted the benzylcelluloses to intensive study, and arrived at the following conclusions:

(a) Alkalicellulose reacts more uniformly with benzyl chloride than with ethyl sulfate.

(b) A product almost completely soluble in benzene can be obtained by one-stage benzylation, by immersion

1. Bull. Inst. Phys. Chem. Research, Tokyo, 1929, **8**, 272; Abstracts, 1929, **2**, 33; abst. C. A. 1929, **23**, 3572; J. S. C. I. 1929, **48**, 684-A.

2. Cellulosechemie, 1931, **12**, 11; abst. C. A. 1931, **25**, 5759; J. S. C. I. 1931, **50**, 203-A. This investigation is of special value as it indicates practical commercial methods of manufacture by at most a two-stage process. His results, accompanied by practical tests as to suitability, are well worth reproducing in condensed form. He established that, although depolymerization of the cellulose was profound, a direct connection exists between the alkali concentration and the viscosity. In film form, in comparison with nitrocellulose, benzylcellulose has a proportionately greater extensibility in contrast to its

of cellulose in 30-50% NaOH solution, pressing free from excess alkali and treatment with benzyl chloride at 100°. The soluble portion contains 70-71% C., has relative vis-

diminished tensile strength, more to be ascribed to the softening action of the linked benzyl groups concerned, than to residual and contaminating traces of benzyl alcohol.

The products soluble in benzene to transparent solutions always have a somewhat higher carbon content, than do those benzyl ethers but partly soluble or capable of swelling in benzene, but clearly soluble in benzene containing alcohol. Thus, there is a sharp line of demarcation in the carbon content between the solubility on one hand in pure benzene, and in benzene containing alcohol.

A purified cellulose was used as initial material of alphacellulose 96%, copper number 0.70, and relative viscosity in 1% solution of the normal nitrate in acetone, 2430. The general method was to heat alkalicellulose of various compositions with benzyl chloride in an apparatus with reflux, with or without the presence of a solvent, the reaction first causing a breaking up of the fibers, and then a gelatinization or emulsification of the reaction mass. With unfavorable compositions, the fiber structure does not disappear until after many hours heating, the reaction mass not being homogeneous. Under the microscope, recognizable characteristics of the reaction mass are observable, which serve as indicia of the progress and completeness of the reaction. In order to purify the reaction mass, it was rubbed up with excess of salt, then either completely extracted with alcohol and washed with hot water, or else first steam distilled for removal of benzyl alcohol and benzyl chloride, then exhausted with alcohol and hot water.

The composition of the benzylcellulose furnished by I. G. Farbenindustrie was C, 71.68%, relative viscosity at 20° against solvent 2.8 (concentration 1 gm. per 100 cc., solvent benzene-alcohol 5:1) soluble in benzene to a clear solution. Another sample gave C, 71.37%, relative viscosity at 18°, 3.0; clearly soluble in benzene, tensile strength of film 4.7 kgm./sq.mm., extensibility of film 22.0%, creasing number 5.

The results obtained are subdivided into Series I, one-stage benzylation, and (2) two-stage benzylation, and this again into variants in procedure, consecutively numbered 1-12 inclusive.

Series 1. *Single-stage Benzylation.* From each 5.5 gms. air-dry cellulose, various alkalicelluloses were prepared, separated into fibers, and heated with benzyl chloride at 80-100°. Change in appearance of reaction mixture was observed macroscopically and under the microscope, the period of heating after gelatinization, in each instance, being fairly long. From a benzene and benzene-alcohol mixture of the purified benzylcellulose, connection between composition of solvent and solubility power as shown by turbidity approach, was observed. The content of soluble portion of each sample was quantitatively determined in the solvent composition of highest dissolving power. Viscosity of each sample was determined in the previously extracted soluble portions, and the *relative* viscosity of a 1% solution measured against the solvent. Films were prepared from the soluble portion and tensile strength and extensibility (Schopper machine) and creasing number (with both hands) obtained. Results obtained are shown in Tables XIV and XV, on pages 1529 and 1530.

cosities of 2-4 (1% solution compared to solvent), and yields films with satisfactory properties.

(c) Alkalicellulose obtained by use of too great con-

Series II. *Two-stage Benzylation.* These researches were conducted in two different ways; in one, the intermediate products after the first stage of benzylation were isolated, in the other, they were not. The finished products in both processes were approximately identical.

1. Air-dry cellulose 5.5 gms. were soaked in 17.5% NaOH solution, pressed to 23 gms. (ratio 4.2:1 on the cellulose), heated with 75 gms. benzyl chloride, 7 hrs., at 100°. The fiber structure was retained. Then 16 gms. solid NaOH (90%) and 4 gms. water were added, the temperature rising considerably. Proportionate amounts, cellulose 1, NaOH 3.5, water 4.08. Reaction mass rapidly emulsifies and in 2.4 hrs. becomes homogeneous. No fibers distinguishable. Heating discontinued after 6 hrs. Yield 9.6 gms. Poorly soluble in benzene or benzene-alcohol 50:40. Relative viscosity 2.33 at 16°, concentration 1 gm/100 cc. Tensile strength of film, 4.3 kgm./sq. mm. Extensibility 17%. Creasing number 4. C 70.21%.

2. Cellulose 5.5 soaked in 17.5% NaOH, pressed to 14.7, and heated with 75 benzyl chloride, 5.5 hrs. at 100°. Then 18.2 solid NaOH added and kneaded. Proportionate amounts, cellulose 1, NaOH 3.70, water 1.88. Heating continued 9 hrs. The hard fiber lumps in the alkalicellulose remained intact. After removal of lumps from reaction mass by filtration, the product was extracted. Completely soluble in benzene or in benzene-alcohol 50:30. Alcohol greater than 30, poorly soluble. Relative viscosity 2.21 at 16°, concentration 1 gm/cc. Film, tensile strength 3:5 kgm/sq. mm. Extensibility 9%. Creasing number 1. C 72.13%.

3. Cellulose 5.5, 17.5 NaOH, pressed to 12.95, then heated with 75 benzyl chloride, 5.5 hrs. at 100°. Then 20 of 46.6% NaOH solution added at once. Proportionate amounts, cellulose 1, NaOH 2.24, water 3.40. Heating time 6 hrs. Many fiber particles remained behind. Relative viscosity of soluble portion, 2.9 at 16°, concentration 1 gm./100 cc., solvent used benzene-alcohol 50:20. Film from soluble portion, tensile strength 4.8 kgm./sq. mm. Extensibility 23%. Creasing number 4-5.

4. Cellulose 5.5 soaked in 17.5% NaOH, pressed to 22.1, heated with 30 benzyl chloride 3.5 hrs. at 100°. Then 19.5 solid NaOH, 3.5 water and 10 benzyl chloride added at once. Proportionate amounts, cellulose 1, NaOH 2.49, water 3.6. Heating stopped after 5 hrs. Yield 9.6. Partly soluble and capable of swelling in benzene; soluble in benzene-alcohol 15:40; poorly soluble in benzene-alcohol 50:40. Relative viscosity 4.0 at 17°, concentration 1 gm./100 cc., solvent used benzene-alcohol 50:20. Film, tensile strength 5.0 kgm./sq. mm. Creasing number 5. C 70.33%.

5. Cellulose 5.5 soaked in 25% NaOH, pressed to 25.1, and heated at 100° with 30 benzyl chloride 3 hrs. Then 8.6 solid NaOH, 2.8 water and 10 benzyl chloride added, and heated 5 hrs. longer. Proportionate amounts, cellulose 1, NaOH 2.55, water 3.74. Yield 9.9. Solubility, same as 4, but content of soluble portion in benzene-alcohol 77:23 was 98.5%. Viscosity of soluble portion, 3.06 at 18° and 3.30 at 14°, in benzene-alcohol 77:23. Film, 5.0 kgm./sq. mm. Creasing number 5. C 70.62%.

centration of NaOH was unsatisfactory, as reaction velocity and viscosity were too greatly reduced.

(d) By a two-stage benzylation, a product completely soluble in benzene is obtainable, 17.5% NaOH solution can

6. In the following runs the intermediate product was isolated and the C content immediately determined on the products obtained from the reaction mass. *First stage* . Cellulose 11 gms. were soaked 2 days in 17.5% NaOH, pressed to 34.7 gms. and heated with 16 gms. benzyl chloride 2.5 hrs. at 100°. Fiber structure retained. The residual NaOH required 20 cc. *N*/1 sulfuric acid. After removal of benzyl chloride and benzyl alcohol by steam distillation, the product was washed with hot water and pressed. *Second stage.* Calculated amount of NaOH and water previously mixed was added to the pressed and wet fibrous product, so that it was soaked in about 15 times its weight of 50% NaOH, allowed to stand 1 hr., pressed to 53.5 gms., heated 3.5 hrs., with 60 gms. benzyl chloride at 100°. Gelatinization ensued quickly (0.5 hr. from beginning of heating). 40 gms. toluene added after 1 hr. heating. Product treated with salt and alcohol as previously stated. Completely soluble in benzene and benzene-alcohol 50:40. Relative viscosity 2.01 at 20° in benzene-alcohol 50:10. C 72.78%. Ash 0.25%.

7. *Amount of benzyl chloride decreased.* Cellulose 11 soaked overnight in 17.5% NaOH, pressed to 30 and heated with 10 benzyl chloride and 20 toluene, 2 hrs. at 100°. *Second stage.* Product from first stage treated as in 6, pressed to 30, heated 15.5 hrs. with 30 benzyl chloride and 30 toluene at 100°. Compared with 6, reaction was very slow, probably on account of the harmful action of the toluene. First stage, C 44.0%, ash 0.2%, indicating little etherification. Finished product, C 67.85%, ash 0.25%. Solubility in benzene and benzene-alcohol unsatisfactory.

8. *Reaction course in absence of solvent. First stage.* Cellulose 7.5 stood overnight with 17.5% NaOH, pressed to 22, heated "fairly long" with 10 benzyl chloride at 100°. Residual NaOH solution titrated with *N*/1 acid, and benzyl chloride used calculated on assumption that the alkalicellulose at first contained 14.5% NaOH and about 0.38 NaOH was used up by the cellulose even in absence of benzyl chloride. "A", time of heating 2 hrs., benzyl chloride used 5.7 gms., carbon 56.26%. "B", 4 hrs., 7.9 gms., 59.2% C. "C", 6 hrs., 8.5 gms., 60.24% C. The portion of the wet product obtained after steam distillation, washing and pressing, corresponded to 5.6 gms. cellulose (non-etherified), and was subjected to the next operation. Residual portion was analyzed. *Second stage.* The wet product containing 5.6 gms. cellulose, treated as in 6, so that it was soaked in 50% NaOH, pressed to 23.7 gms. (A) , or 24.5 gms. (B) or 22.3 gms. (C), and heated 3.5 hrs. with 20 gms. benzyl chloride at 100°. Reaction course was as rapid as in 6, and approximately the same with A, B and C. Properties of finished product as follows: Completely soluble in benzene and in benzene-alcohol 50:35. Poorly soluble in benzene-alcohol 50:40. Relative viscosity, A. 2.16, B. 2.40, C. 2.00 (all) at 20°, solvent benzene-alcohol 50:10. Carbon, A, 72.10%, B, 71.74%, C, 71.83%, ash 0.15%.

9. *Benzyl chloride further decreased; influence NaOH concentration in second stage studied. First stage.* Cellulose 5.5 soaked in

be used, and a weight of benzyl chloride in excess of the weight of cellulose, followed by the second-stage immersion in 50% NaOH by weight, and 3-4 times the quantity of

17.5% NaOH 2 days, pressed to 15, and heated with 5 benzyl chloride 3 hrs. at 100°, and separated by steam distillation and washing. *Second stage.* "A" treated with 50% NaOH, pressed to 20, heated with 15 benzyl chloride, 4 hrs. at 100°. Benzyl chloride used, for A, 9.5 gms; for B, 5.2 gms. Properties; solubility, "A", completely in benzene and benzene-alcohol 50:35; viscosity, 2.24 at 20° in benzene-alcohol 50:10; C 71.61%. "B", swells only in benzene, partly soluble in benzene-alcohol 50:10; relative viscosity 2.30 at 20° in benzene-alcohol 50:10; C 68.5%.

10. *Influence of time of heating with 33% NaOH. First stage.* Cellulose 5.5 soaked in 17.5% NaOH, pressed to 15.5, heated with 5 benzyl chloride 3 hrs. at 100°. *Second stage.* The cellulose obtained as above and isolated wet was soaked in 33% NaOH, pressed to 18, heated to 100° with 15 benzyl chloride, the residual alkali titrated with normal acid and the benzyl chloride used calculated as above. "A", time of heating 3 hrs., benzyl chloride was 6.9 gms; "B", 6 hrs., 8.9 gms; "C", 9 hrs., 9.2 gms. Properties: Swells in benzene, partly soluble in benzene-alcohol 50; 15-45. Relative viscosity, 3.20 at 20°, concentration, "B", 0.939 gms./100 cc.; "C", 0.97 gms./100 cc.

11. *Confirming harmful influence added solvents. First stage.* Cellulose 5.5 soaked in 17.5% NaOH, pressed to 15.5, heated (A) with benzyl chloride, or (B) with 15 each benzyl chloride and toluene, 3 hrs. at 100°. Residual NaOH titrated, and benzyl chloride used was (A) 4.67 gms., (B) 0.98 gms. Therefore the harmful action of the solvent in the first stage can be seen. After steam distillation, in order to study the solvent effect in the second stage, "A" was soaked in 50% NaOH as above, pressed to 20.5, heated 3.5 hrs. at 100° with 20 each benzyl chloride and toluene. Benzyl chloride used, 10.3 gms. Partly soluble in benzene and in benzene-alcohol 50:10. Relative viscosity, 2.35 at 20°, 0.953 gms./100 cc. in benzene-alcohol 50:10. The benzyl chloride used in second stage is no different from that used in absence of toluene, but here, complete solubility in benzene was not obtained.

12. *Influence of decrease of temperature. First stage.* Cellulose 5.5 soaked in 17.5% NaOH, pressed to 17, heated at 80° with 5 benzyl chloride. For the three portions A, B and C, the time of heating, benzyl chloride gms. used, and C % was 3 hrs., 1.32 gms. —%; 6.75 hrs., 3.89 gms., 55.71% C.; 10 hrs., 4.32 gms., 56.41% C., showing the course of the reaction to be quite slow. *Second stage.* About 5/6th of B or C was soaked in 50% NaOH solution, pressed to either 17.8 gms. (B), or 18. gms. (C), and heated with 15 gms. benzyl chloride, 5.6 hrs. at 80°. Benzyl chloride used 7.18 gms. (B), or 7.38 gms. (C). Solubility (B) 67.6% soluble in benzene, 83.6% soluble benzene-alcohol 50:10. (C), 96.5% soluble in benzene, 96.5% in benzene-alcohol 50:10. Relative viscosity at 20°, (B), solvent, benzene, 676 gms./100 cc., 1.58; in benzene-alcohol, 50:10, 0.836 gms./100 cc., 1.58. (C), solvent benzene, 0.965 gms./100 cc., 2.30; benzene-alcohol, 50:10, 0.965 gms./100 cc., 1.76. Film, relatively brittle. Carbon, (B) 70.15%; (C) 70.77%. Thus in general, decrease of reaction temperature is harmful, or at least disadvantageous, especially shown in the viscosity of the product which does not increase.

benzyl chloride. In the two-stage process, the first stage reaction is completed in 2-3 hrs., and the second stage in 3-4 hrs.

(e) With 30% NaOH the product is not completely soluble in benzene, unless it contains a little ethyl alcohol. Use of benzene or toluene reduces reaction velocity, and temperatures under 100° induce depolymerization of cellulose rather than benzylation. In comparison with nitrocellulose film, a benzylcellulose film has a greater elasticity but lower tensile strength. A sharp division is noted in carbon percent in products completely soluble in pure benzene when compared with those soluble in benzene containing ethyl alcohol.

In 1929 appeared an exhaustive investigation of benzyl-, *p*-chlorbenzyl-, and 1.2.4-chlordinitrobenzyl-cellulose by H. Neithammer and W. Koenig[1] in order to study those cellulose ethers which are analytically demonstrable. They used a specially purified cellulose (*α*-cellulose 99.84%, ash 0.26%, copper number 0.17, cellulose number 0.28), and a standard cotton cellulose[2] (*α*-cellulose 99.62-99.83%, ash 0.07-0.16%, copper number 0.07-0.12, and cellulose number 0.19-0.29). Their work is divided into three sections, i.e., action on alkalicellulose of (a) benzyl chloride, (b) chlorbenzyl chloride, and (c) 1.2.4-chlordinitrobenzene.

(a) *Action of Benzyl Chloride on Alkalicellulose.* On the assumption of a C_{12} molecule for cellulose, monobenzylcellulose has the composition C 55.04%, H 6.33%; dibenzylcellulose, C 61.87%, H 6.39%; tribenzylcellulose C 66.63%, H 6.45%; tetrabenzylcellulose C 70.12%, H 6.48%. The results obtained in the benzylation of cellulose are indicated in the following table:

1. Cellulosechem. 1929, **10**, 201; abst. C. A. 1930, **24**, 3641; J. S. C. I. 1930, **49**, 72-A.

2. Report of The Committee of The Division of Cellulose Chemistry of The American Chemical Society, I. E. C. 1923, **15**, 748.

(b) *Action of Chlorbenzyl Chloride on Alkalicellulose.* The higher *p*-chlorbenzylcelluloses are more difficult of preparation than are the benzylcelluloses, explainable by the more difficult penetration of the larger chlorbenzyl chloride in the cellulose aggregate. It has been demonstrated that it is quite possible to produce higher ethers of cellulose with *p*-chlorbenzyl chloride, that they dissolve in definite solvents, and that the masses obtained are plastic. *o*-Chlorbenzyl chloride behaves entirely differently from the *p*-compound or benzyl chloride, and although the cellulose appeared attacked, the products obtained dissolve in Schweitzer's reagent and contain but a small amount of chlorine. Results obtained using the *p*-compound are shown in Table XII, remembering that, calculated on cellulose as C_{12}, the theoretical composition is, monochlorbenzylcellulose, Cl 7.90%; di-, 12.37%; tri-, 15.25%; tetra-, 17.25%; hexa-, 19.85%.

Table XI. Benzylation of Cellulose

Run #	Conc. of Alkali	Action of Alkali Soln.		Molar Ratio Cellulose $C_{12}(C_6)$: Bzd.	Dissolved in	Temp. in C°	Time in Hrs.	Purified with Schweitzer's Reagent	% C	% H
		Time in Hrs.	Temp. in °C							
1	20	72	18	1:17 (1:8.5)	Xylol	105	65	1 Mol	60.41	6.55
2	20	20	19	1:13.5 (1:6.75)	Xylol	105	120	1 Mol 43 hrs.	62.00	6.66
3	20	45	20	1:2 (1:1)	Xylol	105	100	1 Mol	52.74	6.25
					Xylol			again purified	54.32	6.41

The catalysts used in the course of the reaction showed no result in any case, attributed chiefly to the insolubility of the same in the solvents used for the compounds brought together in the reaction. Temperatures above 140° are harmful, and under 65° the velocity of reaction is very small.

Table XII. Chlorbenzylcellulose

Run #	Action of Caustic Alkali: Time in hours	Action of Caustic Alkali: Temp. in °C	Conc. of Alkali in %	Molar Ratio Cell. $C_{12}(C_6)$: p-Cl-Hyd	Dissolved in	Temp. in °C	Time in hours	Purified with Schweitzer's Reagent	% Cl	Remarks
1	21	0	34	1:5 (1:2.5)	Xylol	108	8½	1 time 48 hrs.	8.17	
2	20	18	20	1:15 (1:7.5)	Xylol	108	16	1 time 48 hrs.	3.26	not very pure
3	95	19	20	1:10 (1:5)	Amylalcohol	105	65		0.58	not purified
4	17	18	18	1:1 (1:0.5)	Xylol	105	60	1 time 67 hrs.	5.10	
5	48	18	19	1:2 (1:1)	Xylol	105	80	1 time 48 hrs.	6.55	
6	20	18	19	1:6 (1:3)	Ethylalcohol	65	110	.....	0.76	completely soluble in Schweitzer's Reagent
7	45	18	20	1:2 (1:1)	Xylol	105	60	3 times. Total 146 hrs.	7.32	$BaCl_2$ as catalyst
8	20	18	50	1:25 (1:12.5)	Amylalcohol	108	30	1 time 48 hrs.	10.91	
9	45	20	20	1:2 (1:1)	Xylol	105	100	3 times. Total 159 hrs.	9.12	
10a.	21	17	33	1:6 (1:3)	Xylol	10	76	1 time	16.25	$KHSO_4$ as catalyst
b.	18	17	17.5			105	60	1 time	17.36	

As an illustrative example of procedure, 10 gms. standard cellulose were treated at 20° for 45 hrs. with 80 cc. 20% NaOH solution, well pressed, treated with 10 gms. *p*-chlorbenzyl chloride dissolved in 75 cc. xylene. Then 0.5 gm. barium chloride was introduced and the whole heated 60 hrs. at 105°. The product was filtered, washed with alcohol, water and ether and dried. The yellowish fibers were then soaked in Schweitzer's reagent 147 hrs. in the cold, then for 17 hrs. with fresh reagent, washed and dried. Analysis gave 7.32% Cl.

(c) *Action of1.2.4-Chlordinitrobenzene on Alkalicellulose.* This compound, which reacts with alcohols and phenols with ether formation, readily reacts when brought in contact with alkalicellulose. The derivatives formed have the advantage of being readily analyzable by virtue of their nitrogen content, but also are particularly interesting through the possibility of reducing the nitro-group, diazotizing the resulting amino-group, and finally of diazo-coupling, a problem that was investigated for esters in 1913 by J. Briggs[1] and patented by F. Guenther[2] in 1926.

The results obtained are shown in Table XIII.

The ethers prepared are brownish in color, but may be obtained nearly white by the use of ethyl alcohol as chlordinitrobenzene solvent instead of amyl alcohol or xylene, and the reaction temperature correspondingly lowered. It was not possible to obtain a product rich in nitrogen. The dinitrophenylcellulose formed is accompanied by a breaking down of the cellulose, if the etherification is pushed beyond the stage of superficial attack on the cellulose fiber. The method may be carried out by allowing 3 gms. cellulose to stand 20 hrs. at 17° in 35 cc. 19% NaOH solution, pressing, and treating with 17 gms. chlordinitrobenzene dissolved in 50 cc. amyl alcohol and 30 cc. xylol. The whole is then heated 30 hrs. at 120°, filtered, washed several days with alcohol in a Soxhlet apparatus, then with water and drying.

1. Zts. ang. Chem. 1913, **26**, 255.
2. D. R. P. 433147.

Table XIII. Benzylation of Cellulose

Run #	Conc. of Alkali in %	Action of Alkali: Time in hours	Action of Alkali: Temp. in °C.	Molar Ratio Cellulose $C_{12}(C_6)$: Bzld. found	Dissolved in	Temp. in °C.	Time in hours	In Schweitzer's Reagent	% N	Remarks
1	15	17	18	1:6 (1:3)	Xylol	105	70	soluble	0.92	
2	19	20	17	1:10 (1:5)	Amyl alcohol	120	30	soluble	0.92	
2 b	....	....	....	.....	. ... ..	....	. .	soluble	0.94	Reduced with sulfur
2 B	....	....	....	.....	. .....	....	....	insoluble	7.14	Residue from H_2O filtration
3	20	50	17	1:6. 5 (1:3. 25)	Ethyl alcohol	70	130	soluble	0.74	
4	20	1.time 45 2.time 120	20	1:6 (1:3)	Xylol	105	1.time 22 2.time 60	insoluble	2.10	
4 a	....	....	....	.....	... ...	....	....	insoluble	6.91	Residue from H_2O filtration
5	30 (2.time 18)	1.time 45 2 time 120	20	1:6 (1:3)	Ethyl alcohol	70	1.time 23 2.time 60	soluble	0.74	
6	17.5	25	17	1:6 (1:3)	Xylol	105	175	soluble		In SO_4 as catalyst

Table XIV. Benzylation of Cellulose

Run #	Solubility in Variously Composed Solvents (expressed as cc. Alcohol added to 50 cc. Benzol. Thus "O" denotes pure Benzol).	% of Soluble Portion in Mixed Soln. of Composition Benzol: Alcohol in CC	Rel. viscosities of Soluble portion and Composition of Solvent Used. Benzol: Alcohol in CC.	Tensile Strength of Film in Kg/mm²	Extensibility of Film in %	Creasing No. of Film	Carbon Content of Soluble Portion in %
1	O: Capable of swelling, 5-20: most soluble, 0-5 and 20-40: fairly soluble, over 40: poorly soluble	97.2 (50:6.5)	3.23 (14°C) (50:20)	....	....	....	.....
2	O: Swellable, 4-10: most soluble, 10-50: fairly soluble, over 40: poorly soluble	97.6 (40:10)	2.77 (12°C) (40:10)	5.5	20	4-5	69.95
3	O: Swellable, 4-10: most soluble, 10-40: fairly soluble, 0-4 and over 40: poorly soluble	92.4 (40:10)	3 23 (14°C) (50:20)	5.0	23	4-5	.....
4	O: Swellable, 4-10: most soluble, 10-40: fairly soluble, 0-4 and over 40, poorly soluble	90.5 (40:10)	4 08 (14°C) (50:20)	5.5	27	7-8	70.31
5	3-5: most soluble, 5-10: fairly soluble, over 10: poorly soluble	96.1 (90:10)	1.48 (10°C) (90:10)	Too brittle Film could not be prepared			70.81
6	....	74.3 (90:10)	1.43 (12°C) (90:10)		"		71.14
7	O: Swellable, 3-6: most soluble, 6-20: fairly soluble, over 20: poorly soluble	99 0 (90:10)	1.48 (12°C) (90:10)		"		.....
8	O: swellable, 9-45: most soluble, 0-7 and over 45: poorly soluble	99.1 (50:20)	3.14 (13°C) (50:20)	5.2	22	5-6	70.60
9	O: Swellable, 9-45: most soluble, 0-7 and over 45: poorly soluble	99.1 (50:20)	3.28 (13°C) (50:20)	4.9	22	5-6	.....
10	O: Swellable, 9-45: most soluble, 0-7 and over 45: poorly soluble	92 5 (50:20)	3.24 (14°C) (50:20)	4.7	26	5-6	.....
11	O: Swellable, 9-45: most soluble, 0-7 and over 45: poorly soluble	82.3 (50:20)	2.79 (14°C) (50:20)	5.0	23	5-6	.....
12	O: Swellable, 8-35: most soluble, over 35: poorly soluble	83.3 (50:20)	1.77 (15°C) (50:20)	4.2	15	2	.....
13	O: Swellable, 8-35: most soluble, over 35: poorly soluble	99.4 (50:20)	1.84 (18°C) (50:20)	4.1	15	2-3	70.66
14	O: Swellable, 6-15: most soluble, 10-40: fairly soluble, 0-6 and over 40: poorly soluble	75.2 (50:20)	2.01 (13°C) (50:15)	4.5	17	4	70.33
15	Not analyzed, since it obviously gave a poor result.						
16	O: Soluble, 0-15: fairly soluble, over 20: poorly soluble	95.1 (50:0)	1.76 (15°C) (50:0)	Brittle Film cannot be prepared			72.80
17	O: Swellable, 3-10: most soluble, over 15: poorly soluble	82.0 (85:15)	1.80 (17°C) (80:20)	4.0	15	2	70.50
18	Not analyzed, since it obviously gave a poor result.						
19	O: Swellable, 3-10: most soluble, over 15: poorly soluble	81.8 (85:15)	1.66 (12°C) (85:15)	5.0	20	3	70.12

Table XV. Benzylation of Cellulose

Run #	Wt. of Cell. Used in Gms.	Conc. of Soaking Alkali in Wt. %	Amt. of Soaking Alkali in Gms.	Time of Soaking in Hours	Wt. of pressed Alkali Cell. in Gms.	Wt. of pressed Alkali Cell. in Gms. After Drying in H_2SO_4 Desiccator	Drying Time in Hours	Wt. of Benzyl Chloride used in Gms.	With or without Solvents	Reaction Temp. °C.	Appearance of Reaction Mass	Heating Time	Yield in grams
1	5.5	30	75	20	21.5	Without Drying	....	30	Without	100	Gelatinized after 7-8 hours	17.5	8.2
2	5.5	30	75	20	26.0	"	.. .	30	"	100	Gelatinized after 7-8 hours	24.5	8.8
3	5.5	30	75	20	33.0	"	....	30	"	100	Gelatinized after 7-8 hours	32.5	8.8
4	5.5	30	75	20	40.0	"	.. .	30	"	100	Gelatinized after 7-8 hours	40.5	8.8
5	5.5	68	75	1 with heating	22.0	"	...	30	"	100	Scarcely gelatinized after 25 hours	38.5	8.4
6	5.5	30	75	2	22.7	12.2	24	30	"	100	Gradually gelatinized after 23 hours	34.0	8.3
7	5.5	30	75	2	31.2	17.2	24	30	"	100	Gelatinized after 12 hours	22.5	10.0
8	5.5	30	75	48	26.5	Without Drying	.. .	75	"	100	Gelatinized after 3 hours. Emulsified after 7-8 hours.	14.0	9.22
9	5.5	30	75	48	29.75	"	....	75	"	100	Gelatinized after 3 hours. Emulsified after 7-8 hours.	14.0	9.03
10	5.5	30	75	48	41.0	"	....	75	"	100	Emulsified after 7-8 hours but not uniform.	15.0	9.37
11	5.5	30	75	48	50.5	"	....	75	"	100	Emulsified after 7-8 hours but not uniform.	14.5	8.90
12	5.5	46.6	75	24	19.5	"	.. .	75	"	100	Emulsified after 4 hours but fiber lumps remain to the end.	16.0	9.07
13	5.5	46.6	75	24	32.0	"	.. .	75	"	100	Emulsified after 4 hours and very uniform.	16.0	10.25
14	5.5	30	28.0	24	not pressed	"	....	75	"	70-80	Emulsified after 10 hours but fiber pieces remain.	29.5	7.4
15	5.5	46.6	32.0	24	"	"	....	75	"	70-80	Not emulsified until end, fiber structure retained.	29.5	.....
16	5.5	46.6	50.0	2	"	40	72	75	"	100	Gradually emulsified after 22 hours.	40.5	10.35
17	5.5	30	23	24	"	Without Drying	....	75	"	70-80	Emulsified after 20 hours.	32.5	7.0
18	5.5	30	23	24	"	"	....	25	Benzol 50	70-80	Insufficiently emulsified until the end.	62.0	.....
19	5.5	30	23	24	"	"	....	25	Toluol 50	100	Emulsified after 13-14 hours.	27.5	6.5

R. H. Ball and H. Hibbert[1] have developed a direct method for determination of the degree of benzylation of carbohydrates, and investigated the ethers formed from the reaction between cellulose, NaOH and benzyl chloride, resulting in the identification of monobenzylcellulose.

The method of oxybenzyl analysis involved decomposing benzylcellulose with hydriodic acid (sp. gr. 1.7) for 3 hrs. at 25°, and carefully neutralizing excess HI first with NaOH solution, and finally with disodium phosphate. The benzyl iodide thus liberated was ether-extracted, freed from iodine by shaking with sodium thiosulfate, and determined as silver iodide by precipitation with alcoholic silver nitrate solution.

Benzylation of cellulose was carried out according to the method of M. Gomberg and C. Buchler (see p. 1514), 5 gms. high *a*-cellulose wood pulp being steeped 12 hrs. in 30 cc. 20% NaOH solution, 45 cc. water then being added and the mixture heated 1 hr. at 95°, after which 17 gms. benzyl chloride were added and the mixture heated 5 hrs. longer at 95°. Excess benzyl chloride was removed by steam distillation, and the ether purified by washing with water, alcohol and ether. Soluble benzylcelluloses were then removed by ethyl acetate extraction, a small yield of these higher ethers being obtained. The unchanged cellulose was then removed by shaking 5 hrs. with a concentrated cuprammonium hydroxide solution made according to the method of R. Joyner[2]. The residue from this treatment had an oxybenzyl value of 90% of that calculated for monobenzylcellulose, cellulose being C_6. After three additional extractions with cuprammonium, the oxybenzyl value rose to 97.5% of theory, the product containing C 61.73, H 6.54 as against C 61.85, H 6.39 calculated for monobenzylcellulose. Thus from the reaction, three products were obtained: a cuprammonium hydroxide-soluble portion, a monobenzyl-

1. Can. J. Research, 1932.
2. J. C. S. 1922, **121**, 1511; abst. C. A. 1922, **16**, 3543; J. S. C. I. 1922, **41**, 276-R, 806-A.

cellulose, and a higher benzylcellulose soluble in ethyl acetate.

o-Chlorbenzylcellulose. An intensive study has been made on the effect of reaction time and temperature, alkali concentration, and ageing of alkalicellulose, on the nature and yield of the ethers formed from the reaction cellulose-NaOH-*o*-chlorbenzyl chloride, the products of reaction being separated into two fractions depending upon their solubility in chloroform, into *soluble* ethers having more than 1 OH group in cellulose replaced by *o*-chlorbenzyl, and *insoluble* ethers, comprising mono-*o*-chlorbenzylcellulose, together with any lower ethers and unchanged cellulose. The extent of benzylation was determined by chlorine analysis.

It was found that the cellulose ethers formed much more rapidly and in higher yield when excess of alkali solution was removed from the alkalicellulose before reaction, the presence of inert solvents also inhibiting the reaction. The typical procedure used was to steep 1 gm. wood pulp in 10 cc. NaOH solution of known concentration for 2 hrs., excess alkali solution being removed by suction and pressure, the sodacellulose thus prepared being heated with 16 gms. *o*-chlorbenzyl chloride for 10 hrs. at a predetermined temperature. The *o*-chlorbenzylcelluloses were recovered, separated into two fractions by chloroform extraction, purified and analyzed for chlorine.

The *o*-chlorbenzylcelluloses are sharply characterized by their dissolvability in chloroform, when not more than 1 OH of C_6 cellulose is substituted, the ethers are chloroform-insoluble, whereas cellulose ethers of a higher degree of benzylation are chloroform-soluble. There was, moreover, a peculiar break between the chlorine values of the insoluble and soluble ethers. The most highly substituted insoluble ether prepared contained 12.37% Cl, equivalent to mono-*o*-chlorbenzylcellulose. The *soluble* ether of lowest substitution contained 15.25% Cl, or the percentage calculated for sesqui-*o*-chlorbenzylcellulose, i.e., having 3 OH groups replaced in 2 glucose residues. This sesqui-ether was formed

in both the temperature and alkali concentration series, under the minimum conditions permitting formation of a chloroform-soluble ether. It appears sesqui-*o*-chlorbenzylcellulose, in the author's opinion, is a definite product in the reaction between alkalicellulose and *o*-chlorbenzyl chloride.

With NaOH concentration of 20 gms. per 100 cc. of solution, the degree of substitution at 90° was found to increase as a linear function of the time up to 9 hrs., with the rate of increase slowing up beyond this point. Under these conditions, the product contained only 12.5% Cl after 24 hrs. reaction. With a reaction time of 10 hrs., it was found the formation of chloroform-soluble ethers commenced at 89°, and rapidly increased both in yield and in degree of substitution above 110°. Under the above conditions, above 135° the soluble product contained 16.4% Cl. Both the yield and percentage of chlorine of the insoluble ethers increased to a maximum at 115-120°, decreasing thereafter. At this maximum point of benzylation, analysis showed the product to be mono-*o*-chlorbenzylcellulose.

With a temperature of 95° and a 10 hr. reaction period, the formation of chloroform-soluble benzylcellulose commenced at 13 gm. NaOH concentration per 100 cc. solution. Both yield and degree of substitution of the soluble ethers increased steadily as the concentration was raised above this point, until a di-*o*-chlorbenzylcellulose was obtained using an alkaline solution containing 50 gms. NaOH per 100 cc., while both the yield and chlorine percentage of the insoluble ethers passed through a maximum at 20-25 gms. NaOH per 100 cc.

A steeping period of a few minutes was found to be as satisfactory as several hours, increasing the mercerization period beyond 2 hrs. being detrimental both to the degree of benzylation and to the yield. With a mercerizing period of 12 hrs. or over, there were indications of an increase in the solubility of the insoluble fraction.

Table XVI. Experimental Results on *o*-Chlorbenzylcellulose

Steeping time, hrs.	Reaction time, hrs.	Alkali NaOH/100cc	Reaction temp. °C.	Insoluble Ethers		Soluble Ethers	
				Yield	% Cl	Yield	% Cl
2	2	20 gms.	90		1.25	not separated	
2	5	20	90		4.40	"	"
2	7.5	20	90		6.94	"	"
2	10	20	90		8.73	"	"
2	24	20	90		12.57	"	"
2	10	19.9	20	.86 g.	0	0	
2	10	19.9	60.5	.84	0.4	0	
2	10	19.9	75.5	.80	2.41	0	
2	10	19.9	82.5	.88	5.60	0	
2	10	19.9	89	.99	9.19	30 mg.	15.27
2	10	19.9	92	1.07	10.47	45 "	15.41
2	10	19.9	95	1.12	11.18	65	15.52
2	10	19.9	105	1.21	11.67	50	15.41
2	10	19.9	112	1.30	12.00	60	15.55
2	10	19.9	120	1.10	12.35	161	15.82
2	10	19.9	135	1.03	11.27	260	16.42
2	10	8.6	95	.98	4.62	0	
2	10	13.6	95	1.12	9.31	13 mg.	15.27
2	10	15.6	95	1.14	10.05	32 "	15.38
2	10	20.6	95	1.09	11.09	60	15.55
2	10	23.9	95	1.12	11.38	72	15.66
2	10	25.2	95	1.09	11.30	78	16.12
2	10	29.0	95	1.01	10.89	145	16.14
2	10	36.9	95	.84	8.71	170	16.72
2	10	43.1	95	.72	6.07	190	15.26
2	10	50.8	95	.66	3.87	150	17.26
5 min.	10	18.9	95	1.15	11.24	60	15.70
30 "	10	18.9	95	1.14	11.01	60	15.73
2 hrs.	10	18.9	95	1.12	11.18	65	15.52
12 "	10	18.9	95	1.14	11.09	55	14.14
48 "	10	18.9	95	1.12	10.83	50	14.14
2 "	10	50	120	.26	4.53	1.02 g.	16.85

Raising both the reaction temperature and NaOH concentration used for alkalicellulose formation increases both the yield and degree of etherification of the soluble fraction and reduces the chloroform-insoluble portion, this being confirmed by a reaction run at 120° using 50 gms. NaOH per 100 cc. in the steeping solution, a product being obtained comprising almost entirely the soluble *o*-chlorbenzylcellulose of chlorine content closely approaching that of the di-ether, and di-*o*-chlorbenzylcellulose representing the maximum degree of substitution producible.

A synopsis of the results obtained are shown in Table XVI, the theoretical interpretation being based on the equilibrium in the reaction between NaOH and cellulose, assuming a shift from the mono-sodium cellulosate to the sesqui- and di-sodium cellulosates as the temperature and alkali concentration are raised.

Manufacture of Benzylcellulose. The commercial production of the benzyl ethers of the carbohydrates in general, and those of cellulose in particular, is exemplified in detail in the patented processes divided into the following five classifications (1) H. Dreyfus, (2) Lilienfeld, (3) investigators of the I. G. Farbenindustrie, (4) chemists of the Imperial Chemical Industries, and (5) special and miscellaneous processes.

(1) *Dreyfus Processes.* The two Dreyfus processes[1] are addressed to the manufacture of benzylcellulose[2], and

1. H. Dreyfus, E. P. 164375; abst. C. A. 1922, **16**, 495; J. S. C. I. 1921, **40**, 540-A; Ann. Rep. S. C. I. 1921, **6**, 138; Chim. et Ind. 1922, **8**, 654; Chem. Tech. Uebers. 1921, **45**, 327. U. S. P. 1451330; abst. C. A. 1923, **17**, 2505; J. S. C. I. 1923, **42**, 447-A; Chem. Zentr. 1924, I, 2759. F. P. 530891; abst. Chem. Zentr. 1922, II, 899-R. F. P. Addn. 24082 to F. P. 530891. Australian P. 2543, 1921.

2. U. S. P. 1451331; abst. C. A. 1923, **17**, 2505; J. S. C. I. 1927, **46**, 447-A; E. P. 164377; abst. C. A. 1922, **16**, 494; Chem. Met. Eng. 1921, **25**, 714; J. S. C. I. 1921, **40**, 540-A; Chem. Tech. Uebers. 1921, **45**, 327. Belg. P. 290448. The British Celanese process for benzylated cellulose production (E. P. 315278; abst. C. A. 1930, **24**, 1740; J. S. C. I. 1930, **49**, 1022-B; Silk J. 1929, **6**, #66, 68; Brit. Plastics, 1930, **2**, 322) by treating cellulose with an etherifying agent in the presence of alkali for several hours at 45°, then with NaOH in solid form, the temperature being maintained at 30-60° until ether formation is complete.

to the production of mixed benzyl ethers as methylbenzylcellulose and ethylbenzylcellulose. The former process is detailed by the following two examples:

I. A conversion product insoluble in alkali as alkalicellulose is used, or cellulose is impregnated with 50% NaOH solution so that about 4 mol. equivalents of NaOH are contained in it relative to 1 mol. equiv. of cellulose C_6. The mass is then kneaded with 2-3 mol. equiv. of benzyl chloride. The reaction proceeds quickly if heated between 50-150°, preferably 50-100°. After 2 hrs. heating and mixing, 6 mol. equiv. additional of NaOH are added in powder form, and the mass kneaded with a further 3-5 mol. equiv. of benzyl chloride at a similar temperature. The benzylcellulose obtained is soluble in chloroform and in benzene, and gives excellent films. If a lower temperature of benzylation is used, the reaction requires a correspondingly longer period.

II. Or, the cellulose may be impregnated with 0.5-1.5 of water relative to the weight of the former and the alkali added in powdered form, carrying out the steps otherwise as above outlined. Benzyl bromide may replace the chloride, and the reaction may be carried out in the presence of a non-etherifying diluent as benzene. The reaction is facilitated in presence of traces of copper powder or copper salts or other suitable contact substance facilitating the exchange of halogen.

In the production of mixed benzylcelluloses, cellulose or its conversion product insoluble in alkalis is impregnated with NaOH solution as above, the mass being kneaded with 2 mols. benzyl chloride, and afterwards with 1 mol. ethyl sulfate. The reaction with benzyl chloride is carried out at 50-100°, and with ethyl sulfate at 50° or down to room temperature. After 2-4 hrs. 6 mols. NaOH are added in powder form, and the mass kneaded with a further 3 mols. benzyl chloride at 50-150°, and afterwards with 2 mols. ethyl sulfate at 50° or lower. After this addition, another 6 mols. NaOH powder are kneaded in and then another 3

mols. ethyl sulfate. Methyl sulfate may replace the corresponding ethyl ester. No solubilities or other physical constants of the mixed cellulose ethers are given.

(2) *Lilienfeld Procedure.* The essence of the two Lilienfeld processes for benzylcellulose formation is an attempt to reduce the amount of alkali required in order to obtain an ether of the desired solubility and other physical characteristics, by conducting the operation in two steps or stages, as shown in the following example, in which a lower degree of benzylation of cellulose is produced in the first operation, the ether produced being water-insoluble, which is solubilized into a benzyl ether by the second stage of operation, which is then also dissolvable in a wide range of organic solvents.

2400 parts of an aqueous solution of an alkali-soluble cellulose derivative (containing 200 each cellulose and NaOH)[1] are gradually mixed with 360-720 parts benzyl chloride during 1-2 hrs., the mass being meanwhile heated on the water bath[2]. Heating is continued up to 4 hrs., and until the mass has the consistency of a salve-like paste or viscous solution, and which contains in addition to the lower benzylcellulose insoluble in water or in glacial acetic acid, benzyl alcohol, benzyl ether, benzaldehyde, etc. These impurities may be removed at the close of the first step in benzylation as by steam distillation, or they may be allowed to remain in the reaction mass until the close of the second

1. L. Lilienfeld, U. S. P. 1483738; abst. C. A. 1924, **18**, 1198; J. S. C. I. 1924, **43**, 291-B. E. P. 149320; abst. C. A. 1921, **15**, 436; Chem. Met. Eng. 1920, **23**, 1269; Paper, 1921, **28**, 33; J. S. C. I. 1922, **41**, 53-A; Ann. Rep. S. C. I. 1921, **6**, 133, 138. F. P. 523931; abst. Chem. Zentr. 1921, IV, 1140. D. R. P. 475214; abst. C. A. 1929, **23**, 3232; Chem. Zentr. 1929, II, 237.

2. U. S. P. 1379351; abst. C. A. 1921, **15**, 339; J. S. C. I. 1921, **40**, 541-A; Mon. Sci. 1922, (5), **12**, 5. E. P. 14339, 1914; abst. J. S. C. I. 1915, **34**, 830; C. A. 1915, **9**, 3359. D. R. P. 155745; abst. Chem. Zentr. 1904, II, 1678; Jahr. Chem. 1904, 1163; Wag. Jahr. 1904, II, 389. Aust. P. 20407. In the preparation of cellulose for benzylation by the F. Klein process (E. P. 313538; abst. C. A. 1930, **24**, 1216), the moisture in the cellulose is nearly all replaced by glycerol or glycol, the reaction following, of course, being carried out in an alkaline medium.

step. The mass is then heated either in an open vessel or under vacuum for the removal of water, heating being continued until a granular mass results, and the mixture weighs 500-1400 parts, depending upon the amount of water to be removed and the initial amount of benzylating agent used. This mass is then powdered in any convenient manner, and after cooling, 70-150 parts of powdered NaOH are incorporated, and 300-800 parts benzyl chloride added, after which heat is applied, preferably with stirring, the range being 50-100° for 1-3 hrs., and until a test sample withdrawn shows the solubility and other constants desired. The mass is then admixed with water, neutralized, washed with hot and with cold water, and dried at a low temperature. The benzylcellulose may also be recovered by treatment with alcohol in which the benzylcellulose is insoluble, but in which the reaction products are soluble.

In a patent issued in 1932, Lilienfeld proceeds as follows[1]:

10 kilos cellulose are impregnated with 50-100 k. 18% NaOH solution and allowed to stand 1-3 days at room temperature, the mass freed from excess solution by pressure until the residue has a weight of 18-20 k.[2], the residue

1. U. S. P. 1858019. He also prepares benzylcellulose (E. P. 318088. Cf. E. P. 269531. Aust. P. 112620, 112623. Ital. P. 194918, 199196. Swiss P. 97634. F. P. 523931) by employing a cellulose which has been subjected to a preliminary treatment with NaOH and carbon bisulfide under such conditions that at least a substantial part of the product is soluble in water, whereby ease of etherification is greatly improved and the benzylcellulose ether has a relatively low viscosity in the dissolved condition. The method of G. Okada (Jap. P. 93058; abst. C. A. 1932, **26**, 4470) of isolating benzylcellulose from the reaction products of benzylation, the mixture of benzyl chloride, benzyl alcohol, sodium chloride, sodium hydroxide and water with formed benzylcellulose, is thoroughly mixed with NaCl or similar water-soluble salts, steam is passed through the mixture, and benzyl chloride and benzyl alcohol distilled off. From the residue benzylcellulose is easily isolated by washing with cold or hot water.

2. It is exceedingly difficult, if not impossible, to reduce an alkalicellulose which has been soaked in caustic soda solution of the strength given and for the time stated to a ratio of 1.8-2 on the original cellulose used, ratios being by weight. Our experience is that much better and more uniform results are to be obtained by soaking the cellulose in 18% NaOH solution as stated, at 18.5° for but 1.8-2.2 hrs., with constant circulation of alkali solution, then immediately

finely comminuted and 20-30 k. powdered NaOH incorporated, keeping the temperature down during addition of alkali by cooling. The final product is a white, fibrous mass, microscopically structureless. This mass is then treated with benzyl chloride in the ratio of 80-126 to 40 of NaOH, the benzyl chloride being added in a thin stream to the mass with constant stirring. At the close of the addition of benzylating agent, the autoclave is closed and heating applied for 2-12 hrs. at 60-130°. The lower the temperature, the longer the heating period and conversely. The benzylcellulose may be isolated in one of the two following ways:

(a) The reaction mixture is washed with water to remove sodium chloride and other water-soluble components, dried, dissolved in benzene, and this solution containing benzyl ether, benzyl alcohol, dibenzyl and unchanged benzyl chloride is treated with alcohol, whereby the benzylcellulose is precipitated from the above. The latter is then washed with water and dried.

(b) The reaction mixture is freed from volatile organic by-products by steam distillation, preferably under reduced pressure, the mass then washed with water, then alcohol and dried.

In another modification of this process, the initial cellulosic material may be prepared in one of the three ways:

(a) 375 parts by weight of a raw viscose containing 50 of cellulose and 13-20 of NaOH are diluted with 375 of water and heated with stirring on the water bath until complete coagulation ensues. The coagulated mass is washed, crushed, pressed to 500 parts, then dissolved in 100 of 50% NaOH and filtered from undissolved particles.

•(b) Cellulose is heated with 30-50% NaOH solution, the liquid poured off, and the resulting cellulose hydrate dissolved by the addition of water. The solution is then

press the product to a weight of 2.9-3.1, and disintegrate to a fine condition as with a Pfleidering machine, after which the "crumbs" of alkalicellulose are stored in a temperature regulated room in substantially airtight containers for 48-55 hrs. at 19-19.5°, when the additional NaOH may be added as disclosed in the patent, and the benzylating process initiated.

precipitated by dilute sulfuric acid or acetic acid, washed, and the precipitated cellulose hydrate dissolved in NaOH solution so that 12 parts of solutions contain 1 part each of cellulose hydrate and NaOH.

(c) Cellulose hydrate is precipitated by dilute sulfuric acid from a solution of cellulose in Schweitzer's reagent and dissolved in NaOH solution so that 12 parts of solution contain 1 part each cellulose hydrate and NaOH.

120 parts of solution resulting from the treatment under (a), (b) or (c), containing about 10 parts cellulose employed as a starting material and 10 of NaOH are gently heated, and 30 parts benzyl chloride gradually added, the addition requiring 0.5-2 hrs. During this addition, the temperature of the reaction mass slowly rises to 35-40°. After addition of benzyl chloride heating is continued until the temperature rises to 52-60°, this requiring an additional 1-2 hrs.

At this stage the reaction mixture is a whitish mass containing lower benzylcelluloses insoluble in water and organic solvents. The mass is now rubbed up with 30 parts powdered NaOH, gently heated, 36 parts benzyl chloride gradually added, and heating continued until 80-95° is reached, and kept at this temperature 0.5-2 hrs. Afterwards the reaction mass is again treated with 30 parts NaOH and 36 parts benzyl chloride. The reaction mass now containing the final product is diluted with water and agitated with benzene. The benzene-layer containing the benzylcellulose is separated from the aqueous portion, alcohol added thereto which precipitates benzylcellulose from the benzene solution. The precipitate is washed with water, then with alcohol and dried at a low temperature. The ether is soluble in benzene, toluene, xylene, chloroform and tetrachlorethane, insoluble in water or alcohol.

(3) *I. G. Farbenindustrie Benzylcellulose Manufacture.* According to one process[1], the direct conversion of

1. E. P. 343147; abst. C. A. 1931, **25**, 5557; J. S. C. I. 1931, **50**, 582-B.

straw, seaweed, esparto grass and similar materials which are encrusted but not turned into wood, may be benzylated into soluble, technically useful products, distinguished by their solubility in chloroform, benzene, toluene, benzyl alcohol, pyridine and trichlorethylene, from which useful films result from evaporation of the solution. The benzyl ethers are normally yellowed colored masses which may be readily bleached by treatment with sulfur dioxide, hydrogen dioxide or other similar treatment (see Topic "Bleaching").

The operation of the process is apparent from the following example:

100 parts wheat-, rye- or barley-straw are caused to swell somewhat with 200 parts 50-60% NaOH solution, 350 parts benzyl chloride then added, and heated for 6 hrs. at 100°, when the mass will have assumed a light yellow color. The reaction mass is washed with much water, finally with cold alcohol and dried[1]. E. Doerr has evolved a method for the isolation of benzylcellulose from the crude reaction mass containing in addition, benzyl alcohol and benzyl ether, which is claimed to be superior to extraction with alcohol in that the separation is much more perfect and the cost of purification correspondingly lowered. The method comprises mixing the crude reaction product with a water-soluble salt and extracting the resulting mixture with alcohol[2], or mixing with sodium chloride and extract-

1. See E. P. 12854, 1912; 6035, 1913.

2. U. S. P. 1771529; abst. C. A. 1930, **24**, 4631; J. S. C. I. 1930, **49**, 901-B; Plastics, 1930, **6**, #10, 608. E. P. 265491; abst. J. S. C. I. 1927, **46**, 296-B; C. A. 1928, **22**, 317; Chem. Zentr. 1927, I, 3162. D. R. P. 522170; abst. C. A. 1931, **25**, 3167. Details of the process are contained in the two following examples: 1 kilo crude benzylcellulose is well mixed with 1-2 kilos NaCl and then treated with benzine in an extraction apparatus until the outflowing extraction liquid no longer contains benzyl alcohol or benzyl ether. The salt content of the mass is then removed by washing with water. Or, when the benzylcellulose-salt mass is mixed to uniform consistency, 1 liter alcohol is added and the kneading continued for 0.5 hr., when the liquid is run off. If necessary, the mass may be thus treated a second time with an equal amount of alcohol, after which the salt is washed out with water and the final residues of benzyl alcohol and benzyl ether removed from the flocculent product with alcohol. Compare U. S. P. 1751685; abst. C. A. 1930, **24**, 2599.

ing with benzine[1], as indicated in the following two examples:

I. 1 kilo crude benzylcellulose (tough, gum-like mass) is well mixed with common salt 1-2 k., then extracted with benzene in an extraction apparatus until the outflowing extraction liquid no longer contains benzyl alcohol or benzyl ether. The salt content is then removed by washing with water and the benzyl cellulose dried.

II. 1 k. crude benzylcellulose is malaxated with 1-2 k. common salt, and when the mass has assumed a uniform consistency, 1 liter alcohol is added, and the mass kneaded 15-30 min., when the liquid is run off. Extraction is repeated until the final residue of benzyl alcohol and benzyl ether is removed, when the salt is washed out by water from the benzylcellulose, and the latter dried.

(4) *Imperial Chemical Industries Processes.* Apparently from practical experience in the viscose rayon industry, D. Traill[2] has described a highly intelligent pro-

1. U. S. P. 1751685; abst. C. A. 1930, **24**, 2599; Cellulose, 1930, **1**, 150.

2. E. P. 327714; abst. C. A. 1930, **24**, 5157; J. S. C. I. 1930, **49**, 610-B; Cellulose, 1930, **1**, 270. F. P. 682332; abst. C. A. 1930, **24**, 4390. Australian P. 23156. N. Bennett, H. Dodd, W. Sprent, F. Holt and Imperial Chemical Industries, Ltd., (U. S. P. 1872227) have described a method of benzyl chloride manufacture from treatment of the crude benzylcellulose reaction mass with an anhydrous alkaline material as sodium carbonate, then with an acid, followed by distillation, details being shown in the following examples:

a. The crude benzyl liquors containing benzyl alcohol are treated by mixing with 10% by weight of calcined sodium carbonate and filtered. 200 parts of the treated benzylcellulose liquor are mixed with 300 parts HCl, sp. gr. 1.14, and heated to 80-90° with constant agitation for 6 hrs. The aqueous portion is then separated from the crude benzyl chloride layer, the latter being filtered through soda ash and distilled. 120 parts benzyl chloride are recovered of 1.11 sp. gr. and containing 90% pure benzyl chloride.

b. 250 parts benzylcellulose liquor (after treatment with soda ash) are passed slowly down an externally heated, packed, silica tower, with counter-current of HCl gas led in at the bottom of the tower. The crude benzyl chloride is then treated as in Ex. 1, giving 128 parts benzyl chloride, 1.11 sp. gr., of 90% purity.

The benzylcellulose liquor referred to in the above examples is obtainable when alkalicellulose is treated in the presence of water with benzyl chloride. Some of the latter reacts to form benzylcellulose, some is hydrolyzed to form benzyl alcohol, and some reacts with this latter to form benzyl ether. The mixture is then a combination

cess for benzylcellulose production that is susceptible of producing a benzylated ether of uniform composition and excellent solubility and filament and film forming properties. A sample forwarded the author by this firm[1] was a greyish powder with yellowish cast interspersed with corneous lumps, of excellent solubility in a large number of organic solvents and producing films of high strength and tenuity.

The following two examples exemplify the salient points in this process:

I. Cellulose 100, mercerized 1 hr. in 15-50% NaOH solution, pressed to 200-400 parts and finely shredded in a Werner-Pfleiderer machine, is matured for 2 days between room temperature and 35°. Then 50-100 powdered NaOH is added and *intimately* mixed[2]. The mixture is then heated in a reaction vessel provided with reflux condenser and stirrer, the temperature of heating being about 100°, and for 8-10 hrs., 150-300 parts benzyl chloride having been previously added. A similar amount of benzyl chloride is then added, and the mixture heated for another 8-10 hrs., after which 100-200 parts more benzyl chloride are run in, and the final heating continued for 10-20 hrs. The gummy reaction mass is malaxated with alcohol and, after thorough mixing for 10-30 min., filtered. After several such alcohol treatments, the product becomes less gummy, and is ultimately obtained in granular form which is next treated with ether and filtered, being finally washed with water until free from NaCl. After final washing with alcohol it is

of benzyl alcohol, benzyl chloride, benzyl ether, benzylcellulose, sodium chloride, sodium hydroxide and water. This is extracted with a solvent which is a non-solvent for benzylcellulose and the sodium salts, *i. e.*, ethyl alcohol, the benzyl compounds being thus removed. The alcohol is distilled off, and the crude benzylation mixture results. It contains about 10-30% benzyl ether, 20-80% benzyl alcohol, 5-10% benzyl chloride, less than 5% condensation product, less than 5% water, and traces of iron.

1. Their Batch 16-N; letter, Apr. 14, 1932, H. S. M.

2. Observe that this is the opposite of the L. Lilienfeld process (U. S. P. 1858019) who ages from 1-3 days the alkalicellulose *while still submerged in NaOH solution,* which, in our judgment, is not the preferable method of procedure.

dried. The viscosity of a 10% solution of benzylcellulose produced in accordance with the above, when dissolved in benzene-alcohol (9:1 by volume), varies between 1 and 10 c.g.s. units, according to the concentration of caustic soda, time and temperature of maturing of the alkalicellulose, and conditions of time and temperature of benzylation.

II. 100 parts cellulose mercerized as in the preceding example is matured at 20-30° for 6 days[1], then benzylated and the benzyl ether treated as in the foregoing directions. Viscosity of 10% solutions in benzene-alcohol (9:1) is generally within the limits 0.02-1 c.g.s., this diminution of viscosity being also accompanied by a decrease in tensile strength, in our opinion, due to the fact that the alkalicellulose was over-matured.

As the water-soluble and alkali-soluble benzylcelluloses are admittedly of a relatively low degree of benzylation, it is essential that substantially, the maximum of benzyl groups should be introduced in the cellulosic aggregate. A typical analysis of benzyl-cellulose produced under this process is given as C 69.8%, H 6.40%, a dibenzylcellulose on a C_6 cellulose requiring C 70.17%, H 6.58%. This method of manufacture is said to be especially suitable when manipulating wood pulp as the source of cellulose, but in the ageing of alkalicellulose from wood pulp which seldom exceeds 89% alphacellulose on a bone-dry basis, the period

1. In our judgment, an entirely too long a period, even at the minimum temperature of 20° stated, and assuming that the minimum caustic concentration of 15% NaOH stated, has been used. Any increase in NaOH content, or elevation of temperature above 20°, would increase the deterioration of alkalicellulose, as evidenced, for instance in dry and wet strength and elongation in filament form, and clarity, tensile strength and elasticity when the benzylcellulose has been dissolved and cast in film form. When alkalicellulose reaches its optimum maturing period (which may be expressed as not to exceed 50 hrs. at the minimum temperature of 20° as stated by the patentee) it rapidly "rots," i. e. diminishes in tensile strength of methyl, ethyl or benzyl ether produced therefrom, and no manipulation of the etherification process can counterbalance this diminution in strength of the finished product, once the alkalicellulose has been allowed to mature beyond its period of optimum. For this reason primarily, Example I is considered a much preferable method of procedure than that laid down in Example II.

of ageing or maturing must be diminished by 10-20% in comparison to alkalicellulose made from cotton cellulose normally carrying 98-99% alphacellulose in its purified condition, and also due to the well known fact that cotton cellulose is more resistant to alkali than is wood cellulose, other factors being equal.

The benzyl ester produced by either Ex. I or II above is soluble in benzene-alcohol, toluene-alcohol, acetone-benzene, chlorethanes and ethylene-alcohol mixtures, cyclohexanol, furfural, and various plasticizers as triphenyl phosphate, tricresyl phosphate, dibutyl phthalate or camphor.

It is a fact that some benzylcelluloses give hazy or opalescent solutions difficult to clarify, and such solutions when evaporated to dryness deposit films of a more or less milky or mat appearance, which is not due to moisture absorption during the evaporative process. To overcome this technical defect, D. Traill[1] has proposed to combine an additional benzylation to partially etherified benzylcelluloses, in conjunction with a simultaneous treatment with steam, whereby the viscosity characteristics are lowered. The procedure is indicated by the following suggested method of treatment:

A benzylcellulose reaction mass containing about 20% benzyl chloride is treated in an autoclave with steam, at 50 lb. per sq. inch for 1 hr. The product is a creamy, spongy mass, which is in the form of a soft paste, due to the thermoplasticity of the benzylcellulose. The mass is allowed to harden by cooling, then ground to fine powder, when it will be found to dissolve in mixtures of benzene-alcohol and toluene-alcohol to a solution of high clarity and increased tenuity.

In the working up of the crude liquors in benzylcellulose manufacture[2], benzyl chloride is obtained by treating the crude mixture containing but little water, with an

1. E. P. 333902; abst. C. A. 1931, **25**, 812. F. P. 690216; abst. C. A. 1931, **25**, 1081.
2. Imperial Chemical Industries, Ltd., Can. P. 306349.

anhydrous alkali followed by treatment with chlorine and/or hydrochloric acid, the amount of chlorine being limited to avoid production of benzoyl chloride ($C_6H_5.CO.Cl$).

Benzylcellulose may also be separated by the use of up to 10% of a water-soluble wetting agent as a sulfonated oil or an alkylated naphthalenesulfonic acid[1], which is thoroughly incorporated with the reaction product, and this mixture then agitated for several hours with 4-20 times its weight of water. The resulting liquid containing most of the impurities in true or colloidal solution is then drawn off and the benzylcellulose then washed with water. The benzylcellulose may be further purified by washing it with organic solvents which have no coagulating action on the product, and only a very slight swelling action, e.g., a mixture of aliphatic and aromatic hydrocarbons, containing 20-80 wt./% of aromatic hydrocarbons, a 1:1 mixture being generally suitable.

It has been proposed to facilitate the purification of benzylcellulose by incorporating into the reaction mass a quantity of oil as castor oil, which is miscible with benzyl alcohol, then washing with methyl alcohol. Although the castor oil facilitates penetration of the reaction mass by alcohol, the residual castor oil, by virtue of its non-miscibility with water, is removable only with difficulty. This disadvantage may be removed by substituting a water-soluble fatty body as Turkey red oil[2] or other sulfonated oil, in about 10% of the weight of reaction mass to be treated. It is incorporated in a Werner-Pfleiderer mixer, and is usually complete in 15-30 min., after which it is transferred to a rapid mixer with 4-20 times its weight of water, and after thorough mixing for some hours the aqueous layer or emulsion is run off, and the residue washed with water to remove the sulfonated oil. Best results are said to be obtained in the rapid mixing operation, where the mixture

1. Imperial Chemical Industries, Ltd., A. Levesley and F. Randall, E. P. 364142; abst. J. S. C. I. 1932, **51**, 256-B. F. P. 723017.
2. Pathe Cinema, F. P. 615349; abst. J. S. C. I. 1927, **46**, 649-B; Chem. Zentr. 1927, I, 1392.

of solid and wash liquor is given a turbulent, circulatory motion by means of a vaned disc rotating at the base of a cone shaped shroud provided with a central opening through which the solid and wash liquors are admitted, these being impelled outwards through a series of holes round the bottom of the shroud by means of the rotating disc.

The following example illustrates the method: 100 parts benzylcellulose reaction mass, containing 45-75% benzylcellulose, are incorporated in a mixer up to 2 hrs. with 3-5 parts Turkey red oil. The reaction mass breaks up into small lumps, and is transferred to a rapid mixer, containing 800 parts water, where it is washed for 2-3 hrs., after which the white, aqueous layer, containing an appreciable amount of impurities—partly in solution and partly in the form of an aqueous emulsion—is run off, and the product again washed in the mixer with a further 800 parts water for 0.5-1 hr. The liquid is again run off and the benzylcellulose given two further washes of 0.5-1 hr. duration, first with 800 parts water containing 1% Turkey red oil, and then with water alone. The product is now thoroughly washed with water in the rapid mixer until all sulfonated oil has been removed. It is now in the form of fine granules, and when dry contains less than 0.1% benzyl chloride.

The benzylcellulose may be used in this condition, or may be further purified by treatment in a rapid mixer with 300-500 parts of toluene-alcohol 50:50. It is then centrifuged and dried, when it is obtained in the form of a white or whitish, fine granular powder.

In the working up of filter waste in connection with the use of benzylcellulose solutions in the arts[1], such as film cuttings, filter cloth residues and lacquer deposits, a pressure extractor is charged with a corresponding amount of the material, and this is extracted with liquid sulfur dioxide. After completion of the extraction, and if necessary after subsequent filtration, the major portion of the sulfur dioxide is distilled off under pressure, hot water

1. Aceta, G. m. b. H., D. R. P. 536890.

being then allowed to flow in to precipitate the cellulose derivative with violent agitation. The balance of SO_2 present is recovered by condensation, and any solvent present in the aqueous portion is recoverable by fractional distillation. Recovery of ethylbenzylcellulose is similarly made.

(5) *Miscellaneous Benzylcellulose Manufacturing Processes.* These are three in number, as follows:

(a). *Chatillon Process*[1]. Alkalicellulose is treated with benzyl chloride in the presence of benzene or other inert water-insoluble diluent forming an azeotropic mixture with water. The azeotropic mixture is distilled off during the reaction so that the concentration of alkali in the reaction mixture may be maintained. The operation of the process is indicated in Fig. 9, in which the vessel *A* is charged with the alkalicellulose, alkali and benzyl chloride, and then brought to the desired temperature by means of steam in the jacketed bottom *B*, then a small amount of hydrocarbon as benzene or benzine is added. At a definite temperature a mixture of hydrocarbon and steam begins to distill through the tube *C*, condenses in coil *D*, and collects in receiver, where it separates into the two layers *S* and *S'*, the upper being hydrocarbon which flows back to the reaction vessel through *R*, while the lower layer consists of water and is removed through the siphon *R'*.

By this arrangement the water removal is automatic and uniform, and the desired concentration of NaOH maintained in the reaction vessel. Example: The vessel is charged with 100 kgm. defibered alkalicellulose consisting of cellulose 30%, NaOH 15%, water 55%. To this is added 33 kgm. NaOH in powdered form and 120 kgm. benzyl chloride. The mixture is then heated to 95° and 20 kgm. benzene added. After 30 min. a stream of benzene vapor containing 6% water vapor begins to come off. If now the evaporated benzene is at once led back, and the total amount of water recovered measured, then after 4 hrs., 20 liters

1. A. Lautenberg and Chatillon (Societa Anon. Italiana per la Seta Artificiale), D. R. P. 542158; abst. C. A. 1932, **26**, 2317. F. P. 708181.

water has been recovered, after 8 hrs., 35 liters and after 12 hrs., 45 liters. When this point has been reached, the benzylcellulose formed will show the desired solubility. The

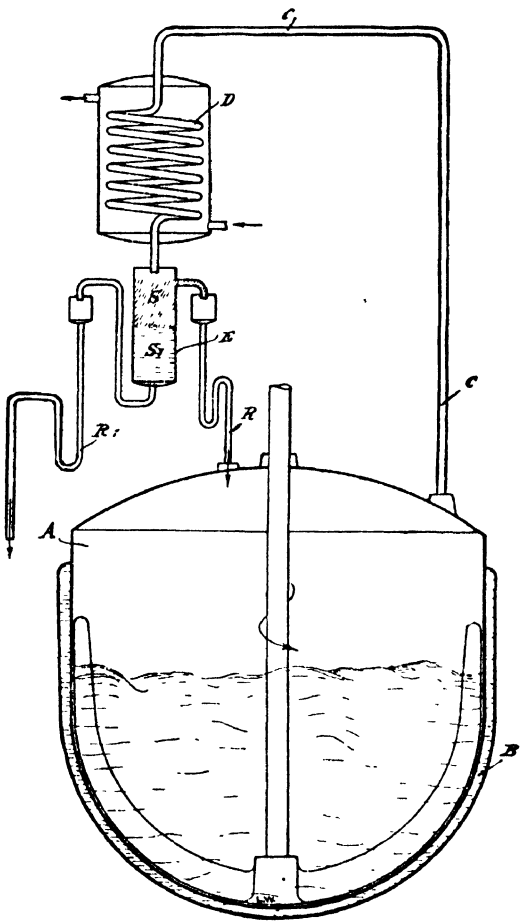


Fig. 9. Chatillon Process for Benzylcellulose Manufacture.

alkali and NaCl are washed out with water, the water distilled off, and the benzylcellulose separated.

It has been demonstrated in benzylcellulose manufacture, the reaction mass may be purified in a two-step process, the

first phase removing benzyl alcohol and benzyl chloride by extraction with methyl or ethyl alcohols, or denatured ethyl alcohol in which the denaturant is a relatively small proportion of acetone or benzine. The benzylcellulose containing water-soluble impurities as sodium chloride, is left behind. The second step involves removal of these impurities. The crude mass of benzylcellulose, benzyl alcohol, unaltered benzyl chloride, sodium chloride and water, is thoroughly mixed with castor oil in the proportion of approximately 2.5 liters to 500 gms. original cellulose, and sufficient methyl or ethyl alcohol, or ethyl alcohol denatured with acetone or benzine, added to dissolve out the castor oil, benzyl alcohol and benzyl chloride. The second step comprises treating with water to dissolve the sodium chloride, leaving the purified benzylcellulose as an impalpable powder. Any oil which is not a solvent of benzylcellulose but miscible with benzyl alcohol and the wash alcohol, may replace the castor oil.

(b) *J. Bouchet Process*[1]. Involves the treatment of 500 gms. cellulose which are impregnated with excess of 45% NaOH solution, the excess being removed by pressure until a mass results at least triple that of the original cellulose. This mass is then intimately incorporated with 850 gms. benzyl chloride which causes the temperature to rise to 70°, artificial heat then being applied up to 95-100°. This temperature is maintained until a test portion removed shows a complete solubility in benzene, which means a heating period of 8-10 hrs. As soon as the reaction has terminated, the temperature of the autoclave is lowered to 60° and 4 liters low boiling hydrocarbon liquid introduced which precipitates the benzylcellulose in a granular pulverulent mass. The benzyl alcohol, benzyl ether and unchanged benzyl chloride is then extracted in a Soxhlet apparatus, and the sodium chloride and sodium hydroxide eliminated by washing with water, leaving the benzylcellulose in a purified condition.

1. F. P. 693318; abst. C. A. 1931, **25**, 1671. See A. Lautenberg, Belg. P. 375513; Ital. P. Dec. 21, 1929.

Properties of Benzylcellulose. This ether comes into the market as a white, or yellowish grey powder interspersed with corneous lumps, the color depending upon the amount of bleaching treatment to which the ether has been subjected incident to manufacture. It is inodorous and tasteless, and of high stability in all ranges of normal conditions as to temperature and humidity. The commercial benzyl ether contains from 4-6% of moisture when vacuum dried over phosphorous pentoxide.

I. *Solubility in and Resistance to Water.* None of the benzylcelluloses, even those of benzylation lower than a monobenzyl-compound based on a C_6 cellulose are soluble in hot or cold water. The literature contains statements at variance with this[1], but close inspection of such results will show that the products were not pure benzylcelluloses and indefinitely characterized chemically, in some instances apparently being mixtures of benzylated cellulose and non-benzylated cellulose or hydrated cellulose. It is a generalization holding true for all classes of etherified carbohydrates, that with increasing increment of substituent radicals in the same group, the solubility in water or swelling by water diminishes with increase in molecular weight of the entering group, whether it be alkyl, aryl or aralkyl. That is, a mono-propylcellulose is less sensitive to cold or hot water than a mono-ethyl ether, and this in turn, less sensitive than a monomethylcellulose. In water sensitivity, a dimethylcellulose, of about the same molecular weight as a monoethylcellulose, is more resistant to water than is the latter. Diminishing the viscosity of a formed cellulose ether by intentional treatment, while increasing the range of

1. Anon. Chem. Age (London), 1932, **26**, 156; abst. J. Chem. Ed. 1932, **9**, 1128; Chemicals, 1932, **37**, 10; Chem. Markets, 1932, **30**, 243; Can. Chem. & Met. 1932, **16**, 77; Plastics, 1932, **8**, 163. Nitrocellulose, 1931, **2**, 58. "Ind. degli. ol. min. e dei grassi" VII, No. 8; Chem. Umschau, 1928, **35**, 295; abst. Farbe und Lack, 1929, No. 11, 134. Silk J. and Rayon World, 1932, **8**, 39. Plastics, 1932, **8**, 163. Industrial Chemist, Feb. 1932; abst. British Plastics, 1932, **3**, 386. P. Anief, Peintures, pigments, vernis, 1927, **4**, 376; abst. C. A. 1927, **21**, 3742. C. Mullin and H. Hunter, Chemical Markets, 1932, **30**, 244.

liquids which will dissolve the same, and increase the percentage solubility in a single solvent, affects but little, if at all, the action of hot or cold water on the viscosity-reduced cellulose ether over the same compound whose viscosity has not been intentionally diminished. In some arts the solubility or swelling in water of the partially etherified alkylcellulose has been a sought-for desideratum, whereas in other applications, as near as possible to absolute resistance to water is desired. M. Hagedorn and P. Moeller[1] have demonstrated as a generality, that with the cellulose ethers, water resistance increases in direct ratio with carbon content. We have been unable to prove as yet to our satisfaction that this increase in water resistivity has any *definite ratio* to the carbon content, while there is direct evidence to the contrary. For instance, it is well known that methylcellulose of the alkylation magnitude of one methyl group per C_6 cellulose molecule, is substantially entirely soluble in water. Let this methylcellulose be etherified by the introduction of but 1% of benzylcellulose or ethylbenzylcellulose—negligible as to increment of carbon content—and the methylcellulose becomes less soluble in water than if another methyl group had been introduced, i.e., if a dimethylcellulose had been produced, a fact well known to workers in this field.

The hygroscopicity of benzylcellulose ranges between 0.5% and 1%, being less as the degree of benzylation increases. However, the moisture regain in a bone dry benzylcellulose depends in a large measure upon the fineness of subdivision and porosity of the ether. Hard particles of the benzylated ether when subdivided to a known size, do not regain moisture from the bone-dry state as do the softer, non-corneous particles. The hygroscopicity of cellulose acetate of acetone solubility is 6-7%. It is obvious, therefore, that films and articles of benzylcellulose are practically impermeable to water, differing markedly in this

1. Cellulosechem. 1931, **12**, 29; abst. J. S. C. I. 1931, **50**, 436-B; Brit. Plastics, 1931, **3**, 180; Nitrocellulose, 1931, **2**, 39; C. A. 1931, **25**, 5982.

respect from the alkylcelluloses. This property is especially valuable in photographic film production, especially films intended for high magnification as in the moving picture industry, where a slight distortion is magnified on the screen.

II. *Solubility.* The range of solvents in which the benzylcelluloses are dissolvable is greatly in excess of that for the cellulose esters, either the inorganic (nitrocellulose) or organic (acetylcellulose), and furthermore, cheaper solvents and solvent combinations may be employed, and still obtain transparent and lustrous films and filaments of acceptable tensile strength and water resistance. Of little technical but of great theoretical importance is the fact that benzylcellulose is insoluble in Schweitzer's reagent, thus enabling non-acted upon cellulose to be removed from a benzylating mixture by treatment with this cuprammonium solution.

The higher benzylated celluloses are soluble in benzene, toluene and xylene when a small proportion of alcohol is added—usually not over 15%, and upon evaporation of such a solution, the benzylated cellulose remains as a highly transparent film. The fact that in such a mixture there is present not over one-sixth of volatile liquid miscible with water, ensures little or no opalescence in the film from absorption of moisture during the progress of solvent evaporation, due to inducing the dew point at the surface of the solidifying solution. Di- and tri-chlorethylene, acetone-benzene (in the ratio of 3:5 to 5:3), methyl or ethyl lactate, benzyl alcohol, dimethyl, diethyl and dibutyl tartrates, form a range of solvents from the viewpoint of their boiling points and speed of evaporation, that covers about every technical requirement. Benzylcellulose swells in acetone, also in toluene, but does not dissolve. However, if two such solutions are mixed, the benzylcellulose may pass entirely into solution in the cold. Naturally, inasmuch as benzylcellulose is insoluble in water, the approach to the anhydrous condition of the solvents employed, exerts a

marked effect on the solvent power. This statement, however, has its limitations, as evidenced by the observation that a percentage ratio of acetone-toluene can be obtained in which benzylcellulose remains in the swollen condition but undissolvable, as shown by the filtration of a portion and evaporation to dryness. If into such a colloidal suspension of benzylcellulose in acetone-toluene, water be now sprayed until the water content is equivalent to about a 96% acetone of the acetone portion, the benzylcellulose will dissolve upon agitation, and from such a solution clear films are obtainable in which the tensile strength has not diminished.

As plasticizing and softening agents, their number is legion if one reads the patent literature or consults the Chapter on Solvents in this work. Glyceryldítolyl ether, the triphenyl-, tricresyl- and trinaphthyl-phosphates, dibutyl phthalate and dicresylin are examples of high boilers of proven efficacy. There has been no plasticizer discovered as yet insofar as we are aware, which bears the relation to benzylcellulose that camphor does to nitrocellulose. And the same may be said of the cellulose acetate art.

L. Clement and C. Riviere[1] report that by operating upon alkalicellulose with benzyl chloride at a definite temperature, a benzyl ether is produced which is *soluble* in acetone,—a product with which we are unacquainted. Their benzyl ether dissolves in cyclohexanone and cyclohexanol. Dibenzylcellulose is soluble in chloroform, especially anaesthetic chloroform which carries a small proportion of alcohol as a preservative, and in carbon tetrachloride. This is a sharp differentiation from the cellulose nitrates which are insoluble in both, and from the acetone-soluble (the technically useful) cellulose acetates[2].

1. Zts. ang. Chem. 1927, **40**, 1579; abst. C. A. 1928, **22**, 3293; I. E. C. (News Ed.) Jan. 10, 1928, 6; Chem. Zentr. 1929, I, 955.

2. T. Nakashima and I. Sakurada, Bull. Inst. Phys. Chem. Research, Tokyo, 1929, **8**, 272; Abstracts, 1929, **2**, 33; C. A. 1929, **23**, 3572; J. S. C. I. 1929, **48**, 684-A.

H. Dreyfus gives the benzylcellulose as prepared according to his patented directions[1], as soluble in acetone, methylethyl ketone, acetone oil, cyclohexanol, cyclohexanone, tetralin, benzene, toluene, xylene, ethyl propionate, ethyl acetate, ethyl lactate, ethyl butyrate, butyl propionate, ethyleneglycol monobutyl ether, butyl acetate, amyl acetate, ethylene dichloride, methylene chloride, tetrachlorethane, pentachlorethane, perchlorethylene, trichlorethylene, benzyl alcohol, glycol diacetate and monomethyl (or ethyl) ether of ethylene glycol. Insoluble in methyl, ethyl, propyl or butyl alcohols, but when these are mixed with the above solvents, dissolving mixtures result. The patentee does not state whether the list embraces solvents which merely have a dissolving action, or whether the benzylcellulose is entirely soluble therein.

Benzylcellulose is much less hygroscopic than cellulose acetate[2], and the higher benzylated ethers do not appreciably swell in water, but swell considerably, however, in 2-3% aqueous phenol or aniline, and are unaffected by 30% aqueous NaOH or 50% aqueous sulfuric acid at 25°.

III. *Plasticity.* The thermoplasticity of benzylcellulose is superior to both that of nitrocellulose or cellulose acetate in its pure condition. With the addition of plastic-inducing bodies, the properties of moldability are not equal to a camphor-nitrocellulose combination. Of course, the cellulose benzyl ethers are much less inflammable than is celluloid, and are also somewhat less inflammable than the cellulose acetates. Not as brittle as Galalith or Bakelite. At 110° it is sufficiently soft and pliable for molding purposes, and having a negligible contraction in passing from the softened to the hardened state, is especially valuable for those molding operations involving intricate detail in pattern. When softened by heat and/or plasticizing bodies

1. E. P. 313133; abst. C. A. 1930, **24**, 960; J. S. C. I. 1930, **49**, 726-B; Br. Plastics, 1930, **2**, 100. See G. Schneider, E. P. 309919; abst. C. A. 1930, **24**, 723.

2. L. Meunier and M. Gonfard, Compt. rend. 1932, **194**, 1839; abst. J. S. C. I. 1932, **51**, 725-A.

and allowed to harden by cooling, benzylcellulose forms transparent, lustrous and elastic compounds of excellent stability. In fact, the thermoplasticity and stability of this ether, and its workability under pressure at comparatively low temperatures, are its main technical advantages, and fabricated molding powders show no signs of deterioration after months of exposure to normal atmospheric changes. Even prolonged action of alkali solutions up to 20% strength, and relatively strong inorganic acids leaves the benzylcellulose composition unchanged. Marine weathering tests on shipboard show that benzylcellulose moldings, after several months exposure to saline atmosphere and extremes of climate remain substantially unaffected. Although benzylcellulose does not melt until about 160°, the softening temperature of 100-110° enables malaxation to be carried on successfully, especially if the softening point is reduced by the addition of plasticizing or flexilizing agents. Moldings free from volatile solvents require no extended period of storing before use. For straight molding, a pressure of a half ton per inch at 110-150°, if the pigment content is not unduly high, is usually sufficient for all commercial purposes. For injection molding, the normal injection and pressure equipment are used, no curing or subsequent hardening process being necessary.

These molding materials may be produced in a wide range of colors depending upon the nature and amount of dye, lake or pigment incorporated therein, and, as in the celluloid industry, the judicious blending of colors with transparent portions gives rise to imitation ivory, tortoise shell, onyx and similar effects. Unlike nitrocellulose, benzylcellulose is unaffected by sunlight, and does not discolor upon prolonged exposure to the atmosphere. There is practically no limit to the transparent, translucent and opaque effects producible by a blending of coloring matter by methods as used at the present time in the nitrocellulose thermoplastic art. There is no waste when using this molding material as the scrap is all capable of re-use. The flow-

able qualities of benzylcellulose are equal to that of celluloid. The non-inflammability coupled with a high stability and atmospheric permanence renders the working of benzylcellulose even at high temperatures and pressures devoid of danger.

Since benzylcellulose possesses many of the desirable chemical and electrical properties of ebonite without the limitation as to color range, nor with any attack on the molds as from the sulfur in ebonite or hard rubber materials, it should have particular appeal to that wide branch of the molding industry which has hitherto worked in ebonite and hard rubber compositions.

IV. *Viscosity.* The viscosity of a benzylcellulose may be modified within wide limits during the process of etherification as follows:

(a) Increase of ripening time over the normal period for alkalicellulose diminishes the viscosity of the benzylcellulose produced therefrom, usually with a corresponding lowering of tensile strength.

(b) Increase in the number of benzylations, increase in NaOH used, increase in temperature of etherification, all lower the viscosity of the finished ether.

(c) Prolonged washing out of soluble salts with water, especially hot water, tends to reduce the viscosity of the benzylcellulose formed in the usual process of production.

(d) The introduction of a non-solvent as benzene in the benzylating mixture tends to raise the viscosity of the benzylcellulose produced as compared to the same etherification in the absence of a diluent.

(e) Some cellulose benzyl ethers exhibit abnormal viscosities in selected solvents of solvent combinations. For instance, dibenzylcellulose shows abnormal behavior in *s*-tetrachlormethane, and methylcellulose (38% methoxyl) shows still more marked divergence from the Hagen-Poiseuille law in the same solvent. With cellulose nitrate the measurements of viscosity are particularly difficult of inter-

pretation, since mechanical treatment of the solution causes greater mobility[1].

The viscosity of benzylcellulose in solution may be attenuated by the addition of such basic agents as sodium or ammonium hydroxides[2], or by modifying the percentage of plastifying agents (tricresyl phosphate, diethyl phthalate, dibutyl tartrate) in respect to the volatile solvent portion (acetone, methylethyl ketone, benzene, chloroform[3]. A benzylcellulose of uniform low viscosity substantially free from degraded products may be produced by digesting at moderate temperatures with dilute HCl or oxalic acid at 25-50 lb. per sq. in. pressure, as exemplified in the two following examples: 100 parts benzylcellulose, having a viscosity in 10% solution of 1000 c.g.s., are heated in an autoclave with 8 times their weight of water containing 0.75% HCl at 50 lb. per sq. in. pressure for 0.5 hr. with stirring. The product is then washed, ground and dried at a low temperature. The viscosity has been reduced to 1-5 c.g.s. in 10% solution, and is particularly suitable for lacquer manufacture. In another example, 100 parts benzylcellulose of 2000 c.g.s. in 10% solution, are treated with 1000 parts water containing 1% oxalic acid for 20 min. at 50 lb. per sq. in. pressure, the product after washing being a white powder of viscosity of 80-100 c.g.s. in 10% solution[4].

Steam under pressure may be used instead of a dilute acid solution[5], a benzylcellulose reaction mass containing 5-40% (preferably 20%) benzyl chloride, being treated in an autoclave at 50 lb. per sq. in. pressure for 1 hr. The product is a creamy, spongy mass in the form of a soft paste, because of the thermoplasticity of the benzylcellulose

1. H. Staudinger and O. Schweitzer, Ber. 1930, **63**-B, 2137; abst. J. S. C. I. 1930, **49**, 1414-A.
2. Soc. Clement et Riviere. F. P. 675086; abst. C. A. 1930, **24**, 2882.
3. C. Dreyfus, F. P. 673029; abst. C. A. 1930, **24**, 2292; Kunst. 1931, **21**, 17.
4. Imperial Chemical Industries, Ltd., D. Traill and A. Levesley, E. P. 352999; abst. J. S. C. I. 1931, **50**, 1089-B. D. Traill, Can. P. 319056.
5. *Ibid.* E. P. 333902.

and the presence therein of benzyl alcohol, an excellent solvent for it. The mass hardens on cooling, and may be ground to a fine powder. It is soluble in benzene, toluene and xylene. Although the viscosity is reduced, the solutions are clear.

The above method of treatment may be modified depending upon the degree of completeness of benzylation, the degree of insolubility of that body and the amount of unacted-upon benzyl chloride remaining. Whereas in the benzylation of cellulose a large excess of benzyl chloride is used and final traces of the liquid difficult to remove, this excess of benzylating agent can be used to advantage by purifying the benzylcellulose reacting mass to a predetermined quantity of benzyl chloride, then treating with superheated steam. The undesirable benzyl chloride is then hydrolyzed to benzyl alcohol and the benzylcellulose becomes completely soluble, which facilitates the purification of the benzylcellulose.

One difficulty in operating with the above process is that the benzylcellulose, while it may be a soft, spongy mass while in the heated condition, is prone to solidify into a compact cake upon cooling, the toughness of the cake varying with the thermoplastic nature of the ether and the temperature and duration of the kiering treatment. Grinding difficulties are also apparent, especially where the benzylcellulose contains some plasticizing body as benzyl alcohol as a normal impurity. These difficulties in viscosity reduction are said to be non-existent, however, when the kiering operation is performed in the presence of a sufficient quantity of a water-soluble salt or mixture of salts, as sodium or potassium chlorides or citrates. It is preferable to use a salt which has about the same water solubility at raised as at ordinary temperature, the quantity of salt used being sufficient to give a highly concentrated or saturated solution at the maximum temperature reached during the kiering process. The benzylcellulose obtained is said to be

easily ground. The method of procedure is synopsized in the two following examples:

1. 100 parts benzylcellulose of viscosity 100 c.g.s. units in toluene-alcohol (80:20) of 10% solution, are kiered with 700 parts 0.75% oxalic acid solution and 300 parts sodium citrate for 45 min. The mass is washed free from acid and salts and dried. The viscosity in solution as before has dropped to 5 c.g.s. units.

2. 100 parts partially purified benzylcellulose reaction mass containing 5-15% benzyl chloride, and a portion of which when purified gives a viscosity of 25 c.g.s. units in toluene-alcohol 80:20, are heated with 1000 parts water and 500 parts commercial NaCl for 3 hrs. at 25 lb. per sq. in. pressure. The kiered product is a loosely cohering, friable mass, which is easily ground. When washed and dried, the viscosity is found to have dropped to the point suitable for lacquer manufacture[1].

A quantitative experiment has been recorded in treatment of cellulose ether for reducing the viscosity[2], in which 500 parts of the ether were dried at 95-100°, the viscosity 12% in xylene solution being about 30,000 centipoises at 25° when determined by the ball-fall method. The dry ethylcellulose is placed in a receptacle with stirring device while the charge is agitated with *dry* HCl gas, in total amount 0.3% on the weight of the cellulose ether, the temperature being maintained about 100° until the viscosity desired has been attained. The charge is then washed with water, then with dilute alkali, centrifugalized and dried.

Other volatile inorganic acids may be used instead of HCl, as hydrobromic or nitric, or an organic acid as formic, acetic, or acetic anhydride, sulfur dioxide, nitrogen tetroxide, acetyl chloride or thionyl chloride. Where substances are used which are acid anhydrides or acid forming, it is necessary to have a small amount of water, either in the

1. A. Levesley, F. Randall and Imperial Chemical Industries, Ltd., E. P. 356308.
2. Imperial Chemical Industries, Ltd., E. P. 313091.

charge of cellulose ether, or in the acid gas which is passed therein.

V. *Inflammability.* The rate of burning of benzylcellulose, by comparative experiments, both in film form of substantially identical cross sectional area, is about 10% slower than acetone-insoluble, chloroform-insoluble cellulose acetate, according to our experiments, and benzylcellulose acetate, at least 15% slower rate of burning than cellulose acetate.

Many compounds have been advocated and patented for diminishing the speed of burning of the aralkylcellulose. They may be roughly classified into:

(a) *Inorganic Salts.* A mixture of magnesium and ammonium sulfates with borax[1], or magnesium and ammonium chlorides with boric acid[2]; or[3], ammonium chloride, bromide, chromate, oxalate or sulfate, or alum, or sodium bichromate, sulfite, phosphate (Na_2H), or nitrite, are some of the inorganic fire-retardants which have been put forward. Ammonium bromide alone or with ammonium phosphate[4], cerium oxalate[5], antimony trichloride in ethyl acetate with urea added to saturation[6], magnesium silicofluoride[7], aluminum phosphate[8], magnesium chloride and boric acid in alcohol[9], and ammonium bromide, phosphate, sulfate or chloride[10].

(b) *Aromatic Phosphates.* Triphenyl phosphate[11]; tricresyl phosphate with calcium phosphate[12] or tartrate[13]; aromatic phosphates[14] with magnesium dihydrogen orthoan-

1. F. Vivas, U. S. P. 1839135. 2. *Ibid.* U. S. P. 1839136.
3. H. Dreyfus, F. P. 601297.
4. Le Film Ozaphane, E. P. 305653.
5. W. Lindsay, U. S. P. 1538862.
6. A. Arent, U. S. P. 1792457.
7. N. V., J. A. Carp's Garenfabr., Holl. P. 23648.
8. C. Dreyfus and H. Platt, U. S. P. 1837150, E. P. 296344.
9. F. Vivas, U. S. P. 1822254.
10. Soc. Ind. D'Applications Photographique, Swiss P. 138609.
11. A. Giebmanns, F. P. 670194.
12. W. Lindsay, U. S. P. 1493207, E. P. 206770.
13. *Ibid.* E. P. 233874. 14. *Ibid.* U. S. P. 1538860.

timonate; tricresyl phosphate with aluminum phosphate[1] or with magnesium carbonate[2], indicate the general trend of combinations which have been found most useful. The aromatic phosphates fulfill the double function of being softeners and plasticizing agents for benzylcellulose in addition to their combustibility-lowering effect.

(c) *Inorganic Esters.* As examples of these bodies may be mentioned the orthosilicates of glycol, glycerol, mannitol and glucose[3]; sodium oleate, palmitate or stearate[4]; magnesium oleate and zinc acetate[5]; cetyl palmitate and spermaceti[6]; vaseline[7] and paraffin[8] or beeswax[9] are indicative.

(d) *Halides in Organic Combination.* Many of these which have been proposed have dissolving and swelling power on the benzylcelluloses. Their chief drawback is in the possibility of slow liberation of halogen upon long exposure to air and light with a discoloration of the cellulose ether compound, and in some cases a diminution in tensile

1. W. Lindsay, U. S. P. 1538859.
2. C. Burke, U. S. P. 1633067, E. P. 289936.
3. L. Knorr and H. Weyland, D. R. P. 285285.
4. C. Duttonofer, E. P. 791, 1907; abst. C. A. 1907, **1**, 2506. Cf. E. P. 24782, 1904; abst. Meyer Jahr. Chem. 1905, **15**, 359; J. S. C. I. 1905, **24**, 105.
5. A. Wolkersdorfer, D. R. P. 74855; abst. Jahr. Chem. 1894, **47**, 1134; Ber. 1894, **27**, 815; Wag. Jahr. 1894, **40**, 749; Zts. ang. Chem. 1894, **7**, 472.
6. J. Lewin, E. P. 2149, 1880. R. Sjöberg, E. P. 2302, 1881; abst. Dingl. Joly. 1882, **246**, 184; Chem. Ind. 1882, **5**, 120; Jahr. Chem. 1882, **35**, 1411; Bull. Soc. Chim. 1882, **38**, 601; Ber. 1882, **15**, 266; Wag. Jahr. 1882, **28**, 404; Chem. Tech. Rep. 1883, **22**, I, 153; Proc. U. S. Nav. Inst. 1883, **9**, 751; Chem. News, 1885, **52**, 101.
7. Muencke, D. R. P. 690, 1877; abst. Wag. Jahr. 1878, **24**, 466; Chem. Ind. 1878, **1**, 127; Zts. Chem. Grossgew. 1878, **3**, 680; Poly. Notiz. 1878, **33**, 160; Chem. Zentr. 1878, **49**, 576; Dingl. Poly. 1878, **230**, 188.
8. Experiments conducted by the French Commission on Explosives, Mem. poudres, 1882-1883, **1**, 483; 1884-1889, **2**, 586, 605.
9. S. Mackie and C. Faure, E. P. 1830, 1873; abst. Chem. Ind. 1878, **1**, 205. Chem. News, 1874, **29**, 166; Dingl. Poly. 1874, **213**, 174; Ber. 1874, **6**, 741; Jahr. Chem. 1874, **27**, 1123. S. Mackie, C. Faure and G. Trench, E. P. 2062, 1874; abst. Ber. 1876, **9**, 205; Bayer Ind. Gewer. 1876, 141; Wag. Jahr. 1876, **22**, 480; Chem. Tech. Rep. 1876, **15**, 388; Zts. Chem. Grossgew. 1876, 1, 233.

strength. *iso*Propyl bromide[1], hexachlorethane (a solid)[2], ββ′-dichlorethyl ether[3], and brom-naphthalene or -anthracene[4] are examples. G. Schneider[5] has added the 6 compounds, acetyl-(or propionyl or butyryl)chlor(or brom)aniline; and C. Dreyfus[6] the 36 derivatives, trichlor(brom or iodo-phenyl(cresyl, xylenyl, naphthyl) formates, acetates or propionates. Benzyl bromide, benzal bromide and benzotribromide[7], all of powerful and disagreeable odor have been recommended by British Celanese, while A. Daly[8] has specified the following 10 compounds, acetyl-4-bromethyl acetanilid, acetyl-2.4(or 3.4)-dibromanilid, acetyl-2.4.5(or 2.4.6)-tribromanilid, acetyl-2.4.6-tribromanilid, acetyl-2.4.-6-tribrommethylanilid, diacetyl-3.4-dibrom-2-toluidide, diacetyl-1.3.6-tribrom-2-naphthalid, and benzyl-2.4.6-tribromanilid. All are soluble in ethyl alcohol. The prime requisite of all of the above named compounds is that they must be soluble in the dissolving menstruum of the particular cellulose ether with which they are to be incorporated, if transparent films are desired as the final product.

VI. *Stability.* The stability of benzylcelluloses, especially those ethers with two or more aralkyl groups per C_6 cellulose are more stable, especially under heat treatment and in the presence of alkaline solutions than are the inorganic or organic cellulose esters, and this relatively high stability is a function of the cellulose ethers, irrespective of the substituent groups. It is just becoming appreciated, that, although there is no acid radical to neutralize in the possible decomposition of benzylcellulose in particular, and the cellulose ethers in general, certain antacids as mono-, di- or tri-ammonium citrate[9], oxamide and oxamic

1. S. Carroll, U. S. P. 1813661.
2. W. Lindsay, U. S. P. 1630752.
3. *Ibid.* U. S. P. 1620977.
4. S. Carroll, U. S. P. 1763035.
5. Can. P. 317330. 6. U. S. P. 1838078.
7. C. Dreyfus, E. P. 313134; abst. C. A. 1930, **24**, 961; J. S. C. I. 1930, **49**, 1061-B.
8. E. P. 319073; abst. C. A. 1930, **24**, 2599.
9. F. Holmes, U. S. P. 875919; abst. C. A. 1908, **2**, 1499; Chem. Ztg. Rep. 1908, **32**, 208; Zts. Schiess. Spreng. 1908, **3**, 217.

acid[1], those substituted ureas in which the oxygen is replaced by an inorganic radical as thiourea and guanidine[2], an aniline salt as the chloride, nitrate, sulfate or oxalate[3], substituted anilines as chloraniline, bromaniline or nitraniline[4], the organic aliphatic anilids as formanilid, acetanilid[5]; the substituted toluidines as chlor-, brom-, and nitrotoluidine[6]; or the toluidine nitrates, chlorides or oxalates[7]; formtoluid, acettoluid, or the toluid of oxalic acid[8] or benzamide, dibenzamide and the amide of toluic acid (toluamide)[9] markedly increase the stability of benzylcellulose when incorporated therein in comparatively small amounts.

As an example, the I. G. Farbenindustrie[10] have patented the use for this purpose of certain substituted guanidines as triphenylguanidine, the introduction of as little as 0.5% based on the weight of cellulose ether present, increasing the stability by as much as five-fold. Stability may also be increased by the addition of non-volatile or difficultly evaporable thiazoles, either alone or in conjunction with inorganic bases as zinc oxide, lead oxide, lead carbonate or aluminum oxide to improve the ageing qualities. To increase the elasticity lowered by the addition of pig-

1. F. Holmes, U. S. P. 875920; abst. C. A. 1908, **2**, 1499; Chem. Ztg. Rep. 1908, **32**, 208; Zts. Schiess. Spreng. 1908, **3**, 217.
2. *Ibid.* U. S. P. 875921; abst. C. A. 1908, **2**, 1499; Chem. Ztg. Rep. 1908, **32**, 208; Zts. Schiess. Spreng. 1908, **3**, 217.
3. *Ibid.* U. S. P. 875923.
4. *Ibid.* U. S. P. 875922.
5. *Ibid.* U. S. P. 875924. Aust. P. 73001.
6. *Ibid.* U. S. P. 875925.
7. *Ibid.* U. S. P. 875926.
8. *Ibid.* U. S. P. 875927.
9. *Ibid.* U. S. P. 875928. In the method of manufacturing nitrostarch explosives as worked out by W. Snelling and W. Laws (U. S. P. 1329211, 1329212; abst. J. S. C. I. 1920, **39**, 249-A) nitrostarch is coated with a heavy mineral oil and then treated with an organic stabilizing agent soluble in the oil. W. Snelling (U. S. P. 1305946; abst. J. S. C. I. 1920, **39**, 282-A) has prepared a smokeless powder by mixing nitrostarch with an agent, e. g., liquid trinitrotoluene, which does not gelatinize the nitrostarch during the mixing process, and subsequently heating the mixture to 60°-90° C., to cause "colloidization." The ammonium nitrate explosive of W. Snelling (U. S. P. 1343063) contains ammonium nitrate in excess of 40% of the entire mixture, nitrostarch and a finely divided material of high covering power interspersed among the particles of the ammonium nitrate.
10. D. R. P. 538110.

ments as above[1], sulfoxides or disulfoxides, especially diphenylsulfoxide may be incorporated. The following two examples illustrate the working of the process:

1. 15 parts benzylcellulose are dissolved in 30 parts benzene, 35 toluene, 30 xylene, 10 alcohol and 3 methylglycol acetate, with addition of 0.4 parts mercaptobenzothiazole, the latter augmenting the stability by about fivefold.

2. Ethylcellulose 20 are dissolved in benzene 72, 8 alcohol, and 0.4-0.5 parts dehydrothiotoluidine. The latter may be replaced by a mixture of 0.3 dehydrothiotoluidine and 0.3 ethyl *p*-aminobenzoate.

It has been found that the stability of films and plastic masses of benzylcellulose may be considerably augmented by the addition thereto of non-volatile or difficultly volatile thiazoles, as indicated by the following illustration: 15 parts benzylcellulose are dissolved in 30 parts benzene, 35 of toluene, 30 of xylene, 10 of alcohol and 3 parts methylglycol acetate with the addition of 0.4 parts mercaptobenzothiazole or 0.3-0.4 parts 5-methylmercaptobenzothiazole. For the production of particular properties, plasticizers and other high boilers may be added, or for coating lacquers, pigments may be incorporated.

In a study of the effect of ultra-violet light on cellulose compounds[2], L. Clement, C. Riviere and A. Beck have found that irradiation of benzylcellulose in power form results in the formation of a high content of insoluble matter, the irradiation of benzylcellulose solution not diminishing its viscosity. However, ethylcellulose remains stable when irradiated, and its viscosity in solution is considerably reduced.

VII. *Dielectric Constant.* The dielectric constant of benzylcellulose is exceedingly low, which circumstance renders it highly suitable for the production of insulated materials, the impregnation of wires and cables, and the

1. L. Rosenthal, E. Messmer and R. Hebermehl, D. R. P. 537626.
2. Chim. et Ind. Spec. No. 702, March, 1932.

coating of batteries and other electrical equipment. Since it is unaffected by ozone or nascent oxygen, there appears to be a wide outlet for it indicated in the electrical trade, where rubber rapidly perishes. The maximum benzylated celluloses are preferable for this purpose, the electrical resistivity being as high as 2.7 x 10^{15} ohms/cm^3. The dielectric strength is of the same order as that of the phenol-formaldehyde condensates. The power loss, however, is much less, being of the order 0.8-1° at wave length of 300 meters—thus presenting decided advantages. The breakdown strength is 250-300 KV/cm., having the additional advantage of being impervious to moisture and non-tracking. These advantages are far from being purely academic.

The Pathe Cinema have reported these comparisons between comparable benzylcellulose and acetylcellulose films:

	Benzylcellulose	Acetylcellulose
Resistance to rupture, Kgm. per $cm.^2$	5-6	7-8
Percentage elongation before rupture	36-38	36-39
Number of folds before breaking	39-42	39-50

VIII. *Osmotic Pressure.* R. Herzog and H. Spurlin[1] have measured the osmotic pressure of 0.1 to 30% of a solution of benzylcellulose in methylglycol acetate at 18°, 30° and 50°, and find that in dilute solutions (up to about 1%), the osmotic pressure is a linear function of the concentration, whereas at concentrations greater than about 5%, it is proportional to the square of the concentration; extrapolation indicating a molecular weight of 29,000. The maximum of rise was reached at 18° approximately after 2 days, at 35° after 7 days, and at 50° after 6 hrs. The osmotic pressure is greater at 35° than at 18°, and the swelling pressure less at 35° than at 18°. With rise of temperature the osmotic pressure at low cencentrations increases, but the swelling pressure at high concentrations, i.e., in the swelling interval, falls. Freshly prepared solutions yield the same types of curves, but the absolute osmotic pressure is lower.

1. Zts. physikal. Chem. 1931, 239. See E. Büchner and P. Samwel, Akad. Amsterdam Versl. 1930, **33**, 749.

Comminuting Benzylcellulose. The preparation of corneous masses of benzylcellulose in a fine state of subdivision often presents difficulties due to the hardness of the benzylcellulose, or its incipient plasticity if traces of benzyl alcohol from the normal etherification happen to be present. The I. G. Farbenindustrie[1] have described a process applicable to ethylbenzyl-, ethyl-, ethylbutyl- and benzyl-cellulose in the dry state, in which the cellulose ether is passed between closely arranged friction rollers, and the rolled product then mixed with 1.2 parts of water while grinding in a ball mill for 48 hrs. In order to produce an emulsion of the benzylcellulose, 125 parts may be incorporated with 150 parts of 10% aqueous solution of methylcellulose, 100 parts of an emulsion of 50 parts dibutyl phthalate in 50 parts water which have been incorporated with 1.5 parts methylcellulose and 1.5 parts sodium butylnaphthalenesulfonate, and then homogenized, as by further grinding.

Benzylcellulose Applications. To increase the softness and flexibility of products made from benzylcellulose[2], *b*-naphtholamyl ether, a liquid insoluble in water and stable to light, has been patented. An excellent benzylcellulose solvent is chloretone (methaform) which when kneaded 30 parts with 70 of benzyl ether, forms a plastic which can be used for many of the purposes of celluloid[3]. Glyceryl formate, and glycol mono- and di-formates[4] have been advocated as solvents, and because the vinyl esters merely gel the benzyl ethers[5], or only dissolve them slowly, it has been found that these bodies in conjunction with volatile solvents as alcohol, produce moldable mixtures.

1. E. P. 330957; abst. C. A. 1930, **24**, 6013.
2. Farbenfabr. vorm. F. Bayer & Co., D. R. P. 307125; abst. J. S. C. I. 1920, **39**, 400-A.
3. H. Dreyfus, E. P. 205195; abst. C. A. 1924, **18**, 1199; J. S. C. I. 1923, **42**, 1172-A; Chem. Zentr. 1924, I, 716; Kunst. 1924, **14**, 91.
4. I. G. Farbenind., Swiss P. 127241; abst. C. A. 1929, **23**, 1190; Chem. Zentr. 1929, I, 120.
5. Celluloid Corp., E. P. 308657; abst. C. A. 1930, **24**, 499; J. S. C. I. 1930, **49**, 943-B; Brit. Plastics, 1930, **2**, #18, 278; Kunst. 1931, **21**, 16; Chem. Zentr. 1929, II, 814.

The speed of combustion of black gunpowder may be retarded by coating each grain, as in a tumbling barrel, with a film of benzylcellulose, the solvent being afterwards dissipated by exposure of the powder grains to the air[1]. In the moisture-proofing of paper articles such as shotgun cartridges[2], benzylcellulose is used in conjunction with such resins as copal, dissolved in benzene or toluene. In the manufacture of confectionery and sweetmeats[3], the plaques, bands, or like dropping material, are formed of, or provided with a coating of benzylcellulose, the latter being applied as a liquid to a base for backing, usually of paper. Cellulose ether emulsions[4], especially the "oil-in-water" type, are formed by dissolving benzylcellulose in a solvent less volatile than water, the volatility being sufficiently great so that the period of drying of the film is not unduly prolonged, when clear, flexible films result.

There have been patented as fire-retardants and inflammability-reducing chemicals for incorporation with the cellulose benzyl ethers, ammonium phosphate[5], and halogen substituted aromatic esters, such as trichlor (or brom or iodo) phenyl (cresyl or xylenyl) formates, acetates or propionates[6].

To produce transfers with a paper base and a composition containing benzylcellulose, there is added to the latter a resin and tritolyl phosphate as plasticizer, and this overprinted with a more readily fusible composition as rosin[7], or else the resinous material as cumar or ethyl

1. Imperial Chemical Industries, E. P. 300611; abst. J. S. C. I. 1929, **48**, 912-B.
2. C. Burke and F. Hahn, E. P. 315227; abst. C. A. 1930, **24**, 1741; Chem. Zentr. 1929, II, 3095. Can. P. 324113.
3. J. Jorgensen, E. P. 288758.
4. G. Davies, W. Jenkins and Imperial Chemical Industries, Ltd., Australia P. 23003, 1929.
5. Brit. Celanese, Ltd., E. P. 303516; addn. to E. P. 282723; abst. C. A. 1929, **23**, 4571; J. S. C. I. 1930, **49**, 553-B; Chem. Zentr. 1929, I, 2371.
6. C. Dreyfus, U. S. P. 1838078.
7. Kaumagraph Co., U. S. P. 1703675, 1718966. E. P. 333768; abst. C. A. 1931, **25**, 605.

abietate is combined with a high boiler such as ethyl lactate, or diethyleneglycolmonoethyl ether[1].

The stencil manufacturing process of A. Davis[2] involves the impregnation of Yoshino or Japanese cobweb paper with an ethyl acetate solution of benzylcellulose in 5% concentration, into 200 gms. of which solution 40 gms. castor oil, 40 gms. benzoylbutyl tartrate and 15 gms. halogenated hydrocarbon (as tetra- or hexa-chlornaphthalene) are added. The castor oil and benzoylbutyl tartrate readily mix with the benzyl ether solution, the halogenated hydrocarbon quickly dissolving in the mass. Solution is facilitated by warming. The mass is then poured into trays, and while still in the liquid condition, sheets of Japanese paper are drawn over the surface or floated thereon, but one side of the paper being coated. Excess of impregnating solution is removed by passing the sheets over a rod or wire. The sheets are now hung up in the air to solidify and permit the volatile components to dissipate. *p*-Chlorbenzylcellulose or phenylethylcellulose may replace the benzyl ether.

For the preparation of colloidal, bactericidal and emulsion preparations as a vehicle for medicaments[3], benzylcellulose has been recommended, 70 parts of a 5% solution dissolved in an oil as poppy seed, castor or olive, are thoroughly triturated in a mortar with 30 parts of an aqueous emulsion of an ethylcellulose or ethyl starch soluble in water. A salve-like emulsion results. An antiseptic mixture results by making a 5-10% solution of benzylcellulose or benzyl starch in a vegetable oil, and to 100 parts of this mixture is incorporated 10 parts *b*-naphthol, phenol or cresol.

1. W. Lawrence and Kaumagraph Co., E. P. 338611; abst. C. A. 1931, **25**, 2532.
2. U. S. P. 1771165; abst. C. A. 1930, **24**, 4598; J. S. C. I. 1931, **50**, 344-B.
3. L. Lilienfeld, U. S. P. 1444257; abst. C. A. 1923, **17**, 1310; J. S. C. I. 1923, **42**, 292-A; Chem. Zentr. 1923, IV, 436. D. R. P. 388369; abst. Chem. Zentr. 1924, I, 2450. Aust. P. 89859. Aust. P. 92914 addn. to 89859.

Then this solution is emulsified with 50-70 parts of a 5% methyl- or ethyl-cellulose soluble in water.

Compositions especially suitable for uniting sheets of glass are obtainable by combining benzylcellulose with diphenylol propane in the presence of 1-6% of water[1], or the benzylated cellulose may be admixed with a polymerized vinyl compound and acetin[2], then interposed between two sheets of glass and pressure applied while the sheets are in a heated condition. Reinforced webs, sheets or plates may be produced by combining benzylcellulose in solution with camphor or camphor substitutes, the solution being flowed into open-mesh metallic or other base, and the volatile portion allowed to evaporate[3].

In the protection of leather, skins, fabrics or other articles from unavoidable soiling, incident to handling during manufacture, they are temporarily coated by applying a thin film of cellulose benzyl ether, which film is removed when the article is ready for sale[4].

In the photographic art, benzylcellulose is finding several important uses. The Farbenfabriken vorm. F. Bayer & Co.[5] have described the formation of a photographic film of unusual clearness, flexibility and resistance to water, and, compared with nitrocellulose, has the advantage of non-flammability, and with acetylcellulose films in not being affected by alkaline treatments. The film may be made by dissolving 10 parts of the benzyl ether in benzene-alcohol (90:10), with addition of 1 part triphenyl phosphate. The viscous liquid obtained is poured out on a ground glass plate horizontally placed, and the solvent allowed to evaporate. The triphenyl phosphate may be replaced by *p*-toluol-

1. British Celanese, Ltd., E. P. 317443; abst. C. A. 1930, **24**, 2292.
2. W. Moss, U. S. P. 1831462.
3. H. Dreyfus, E. P. 173021; abst. Chim. et Ind. 1922, **8**, 1298.
4. Etabl. R. Schneider and A. Poelman, E. P. 344453; abst. J. S. C. I. 1931, **50**, 601-B.
5. Farbenfabr. vorm. F. Bayer & Co., D. R. P. 349868; abst. Chem. Zentr. 1922, II, 960. In this connection see D. R. P. 322586, E. P. 295578.

sulfamide, methyl *p*-toluenesulfonate, naphthalene, oxalic acid esters, tetrachlorethane or trichloracetanilid.

In a method of providing photographic raw film with visible reproducible inscriptions[1], by printing serial numbers or other indications on the back of the photographic support by means of a dye solution which penetrates into the interior of the support and dries in a few minutes, benzylcellulose has been patented. The inscriptions are thus made more insensitive to later treatment of the back of the film with liquids, especially the polishing operation. For applying the colloid (benzylcellulose), it is dissolved in a solvent which does not dissolve the dyestuff used in producing the colored impression. Benzylcellulose in a 1% solution of acetone and benzene fulfills these specifications and has proven satisfactory.

Where strips are produced composed of cellulose derivatives carrying mono-chromatic or multi-colored figuring[2], a 2% solution of nitro- or acetyl-cellulose and containing bronze powder, is usually sprayed on a traveling supporting surface through a stencil. Over this figuring when dry is applied continuously a 15% solution of cellulose benzyl ether colored with lampblack incorporated therein, a black film with sharply defined figurings of golden luster being obtained.

Five processes for the utilization of benzylcellulose in electrical insulation have been published, in one of which[3], benzylated cellulose is combined with bitumen, the plastic material being applied directly in a heated condition to the surface which is to be insulated. In another[4], the benzylcellulose is used in substantially fibrous form for heat and

1. I. G. Farbenindustrie, E. P. 295578; abst. C. A. 1929, **23**, 2113; J. S. C. I. 1929, **48**, 912-B; Chem. Zentr. 1929, I, 184.
2. *Ibid.* E. P. 288592; abst. J. S. C. I. 1929, **48**, 203-B; Chem. Zentr. 1928, II, 1154.
3. Siemens-Schuckertwerke G. m. b. H., E. P. 157119; abst. C. A. 1921, **15**, 1954; Chem. Zentr. 1921, II, 784; Kunst. 1923, **13**, 8. This patent is an addition to E. P. 156527; abst. C. A. 1921, **15**, 1772. Swiss P. 97643; abst. Chem. Zentr. 1923, IV, 424; Kunst. 1924, **14**, 90.
4. British Celanese, Ltd., E. P. 315280; abst. C. A. 1930, **24**, 1685.

sound insulation. In producing insulating materials[1], benzylcellulose plasticized with 20-30% by weight of triaryl or trialkyl phosphate with ethyl or butyl phthalate or tartrate is advocated.

Resinous products have been described obtained by the condensation of halogenated coal tar hydrocarbons containing side chains or their equivalents, as benzyl chloride, benzal chloride, benzyl alcohol, xylyl chloride, *p*-xylylidene dichloride on the one hand, with naphthalene derivatives as methylnaphthalene, phenanthrene, anthracene, benzene, toluene or xylene[2]. As an example, the condensation product from equal amounts of xylyl chloride and naphthalene, and benzylcellulose[3] may be used as a lacquer or enamel in the ratio of about 40-50 of the former to 60-50 of the latter, the two being warmed together with stirring until a homogeneous mass results, which may then be thinned to any desired degree by the addition of volatile solvents (benzene).

The lacquer evolved by W. Moss and B. White[4] comprises benzylcellulose, ester gum, pigment and diethyl phthalate dissolved in a solvent mixture of ethyl acetate, acetone, benzene, toluene and xylene. Compositions suitable as lacquers and varnish ingredients[5] are obtained by heating ethyl- or benzyl-cellulose with resins and/or oils to 280-300°. Thus, ester gum 1, linseed oil 2, benzylcellulose 1 may be heated to 280° until the latter has completely dissolved in the resin-oil mixture. After cooling, the composition may be dispersed in benzine or benzene, or linseed oil varnish.

1. Non-Inflammable Film Co., Ltd., and V. Yarsley, E. P. 355654; abst. J. S. C. I. 1931, **50**, 1016-B.
2. Farbenfabr. vorm. F. Bayer & Co., D. R. P. 301713; abst. J. S. C. I. 1921, **40**, 210-A; D. R. P. 302521; abst. J. S. C. I. 1921, **40**, 708-A.
3. *Ibid.* D. R. P. 336476; abst. Kunst. 1921, **11**, 190; Chem. Zentr. 1921, IV, 148; J. S. C. I. 1921, **40**, 577-A; Ann. Rep. S. C. I. 1921, **6**, 139.
4. U. S. P. 1815444. W. Moss, B. White and C. Dreyfus, Can. P. 302649; abst. C. A. 1930, **24**, 4647. Compare E. P. 313134.
5. British Celanese, Ltd., W. Whitehead and C. Dreyfus, E. P. 318630. K. Burgemeister, D. R. P. 523300; abst. C. A. 1931, **25**, 3502.

A solution formed of synthetic resins[1] obtained by causing a phenol, fatty acid and formaldehyde to react[2], is added to a solution of benzylcellulose of 5-10% total solids; or[3], the lacquer may comprise an oxyn as linoxyn, combined with benzylcellulose in a harmonious solvent mixture. For the protection of metal surfaces against corrosion[4], a solution of benzylcellulose in alcohol containing the metallic salt of an organic acid of high molecular weight has been patented, such as copper naphthenate, ferric stearate, copper oleate, lead naphthenate, ferric laurate or ferric resinate. An illustrative formula is benzylcellulose 15, copper naphthenate 5 (or ferric stearate 2), triphenyl phosphate 6-9, benzene 50, xylene 50, and alcohol 10.

Resins suitable for combination with benzylcellulose for use in films or as lacquers[5] are made by condensing toluenesulfonamide with formaldehyde or other aldehyde, usually with a small proportion of urea, in the presence of heat and absence of moisture, and incorporating with this condensate, various proportions of cellulose benzyl ether, depending upon the effect desired in the finished preparation. Thin bands may be formed by combining into a continuous layer a film in which is incorporated powdered magnesia or lithopone to enhance its affinity for dyestuffs[6], and the other layer of benzylcellulose, the two layers being joined

1. Such as those produced by the processes described in E. P. 293453, 324025; abst. C. A. 1929, **23**, 1763; 1930, **24**, 338.

2. Bakelite Corp., E. P. 342286; abst. C. A. 1931, **25**, 4421. Cites E. P. 293452; abst. C. A. 1929, **23**, 1763. E. P. 324025; abst. C. A. 1930, **24**, 3387.

3. I. G. Farbenindustrie, E. P. 307361; abst. C. A. 1929, **23**, 5338; J. S. C. I. 1930, **49**, 780-B; Brit. Plastics, 1930, **2**, #17, 101; Chem. Zentr. 1929, II. 100. F. P. 670762; abst. C. A. 1930, **24**, 1996. G. Knoeffler and I. G. Farbenindustrie, D. R. P. 542889. Benzylcellulose solution 2 kilos, containing 150 gms. benzylcellulose, are mixed with 75 gms. tricresyl phosphate, 700 gms. acetone, 75 gms. amyl acetate and 700 gms. of a 20% solution of linoxyn dissolved in amyl acetate.

4. I. G. Farbenind., E. P. 323525; abst. J. S. C. I. 1930, **49**, 204-B.

5. British Celanese, Ltd., W. Moss and B. White, E. P. 317456.

6. Chem. Fabr. von Heyden, A. G., E. P. 337501; abst. C. A. 1931, **25**, 2311.

by means of a small proportion of solvent aided by heat and pressure.

Lacquer coatings, films and artificial filaments are stabilized against "ageing"[1] by adding to butyl- or benzylcellulose substituted guanidines or aralkylated organic bases as triphenylguanidine, biguanides, *b*-naphthylbiguanide, benzyl- or dibenzyl-aniline, carbazole or *N*-ethylcarbazole. It is claimed that a film made from benzylcellulose 20, naphthylbiguanide 0.4-0.5 lasts approximately five times as long as the same benzylcellulose film free from nitrogenous base. Coating compositions containing benzylcellulose[2] with suitable plasticizers are caused to adhere more tenaciously to a wooden or metallic surface by the interposition of a nitrocellulose lacquer or layer, the latter being preferably thicker than the former.

Sheets similar to tissue paper and intended for wrapping purposes[3] may be prepared by floating on water a thin solution of benzylcellulose, using preferably solvents which are miscible with the water, and upon absorption of solvent, the cellulose ether pellicle is pulled from the aqueous surface and dried. Lacquers are prepared by combining a diphenylolcycloparaffin (as diphenylol-cyclohexane) with benzylcellulose[4], together with suitable plasticizers and volatile solvents. Materials simulating celluloid but of relatively low flammability[5] are obtained by incorporating with benzylcellulose, aromatic acylated amines such as acetyl-4-brommethylanilide, acetyl-2.4- (or 3.4) dibromanilide, acetyl-2.4.6- (or 2.4.5-)tribromanilide, diacetyl-2.4.6-tribrommethylanilide, diacetyl-3.5-dibrom-2-toluide, acetyl-1.3.6-tribrom-2-naphthalide and benzoyl-2.4.6-

1. I. G. Farbenindustrie, E. P. 342288; abst. C. A. 1931, **25**, 4725; abst. J. S. C. I. 1931, **50**, 404-B; Brit. Plas. 1931, **3**, #26, 44.
2. Brit. Celanese, Ltd., E. P. 298608; abst. C. A. 1929, **23**, 3098; J. S. C. I. 1930, **49**, 431-B; Brit. Plastics, 1930, **2**, #13, 52.
3. C. Olsen, U. S. P. 1458592; abst. C. A. 1923, **17**, 2645.
4. British Celanese, Ltd., E. P. 342429; abst. C. A. 1931, **25**, 4421; Brit. Plastics, 1931, **2**, #25, 40.
5. H. Dreyfus, F. P. 675745; abst. C. A. 1930, **24**, 2881. Cites F. P. 498726 and Addn. 21381 to F. P. 498726.

tribromanilide, the prepared portion being 100 of cellulose ester to 7 of the brom-derivatives. Similarly[1], plasticizers for the benzylcelluloses, dissolved in a mixture of acetone and diacetone alcohol are the unsymmetrical diarylethanes, as diphenylethane, ditolylethane, dixylylethane and dinitrodiphenylethane. Chloretone[2] has also been brought forward as a valuable cellulose benzyl ether plasticizing body, dissolved in acetone.

As combined fire-retardants and plasticizers for benzylcellulose, aromatic phosphoric esters as the phosphates of diphenylmethyl, diphenylethyl, phenyldimethyl, phenyldiethyl, dicresylmethyl, dicresylethyl, cresyldimethyl, and cresyldiethyl have received patent protection[3], being all soluble in acetone and softened by a temperature under the decomposition point of the cellulose ether. They are alleged to be superior to mixtures of triphenyl phosphate and tricresyl phosphate.

By treating solvent naphtha with sulfuric acid, a highly viscous oil with blue fluorescence is obtained, which distills *in vacuo* at 150-300°, contains polymerized coumarone, and constitutes an excellent plasticizing agent for benzylcellulose or benzyl starch[4], especially useful in the production of celluloids, artificial leather and insulating compositions[5], formulas for each being given. Moldable benzylcellulose

1. E. I. DuPont de Nemours & Co., E. P. 312604; abst. C. A. 1930, **24**, 961; J. S. C. I. 1930, **49**, 780-B.

2. H. Dreyfus, U. S. P. 1661169; abst. C. A. 1928, **22**, 1473; J. S. C. I. 1928, **47**, 295-B; Plastics, 1928, **4**, 688; Kunst. 1929, **19**, 162. E. P. 205195; abst. C. A. 1924, **18**, 1199; J. S. C. I. 1923, **42**, 1172-A; Kunst. 1924, **14**, 91; Chem. Zentr. 1924, I, 716.

3. Pathe Cinema, F. P. 606969; abst. J. S. C. I. 1927, **46**, 552-B; Chem. Zentr. 1927, I, 1091; Kunst. 1926, **16**, 207.

4. L. Lilienfeld, U. S. P. 1625415; abst. C. A. 1927, **21**, 2054; J. S. C. I. 1927, **46**, 518-B; Chem. Zentr. 1927, II, 362. E. P. 163271; abst. C. A. 1922, **16**, 141; J. S. C. I. 1922, **41**, 50-A; Chem. Zentr. 1922, II, 543.

5. *Ibid.* U. S. P. 1625416; abst. C. A. 1927, **21**, 2054; J. S. C. I. 1927, **46**, 519-B; Plastics, 1927, **3**, 608. E. P. 171661; abst. C. A. 1922, **16**, 1301; J. S. C. I. 1922, **41**, 53-A; Chem. Zentr. 1922, II, 544; Kunst. 1923, **13**, 9. F. P. 535132; abst. Caout. et Gutta. 1922, **19**, 11495; Chem. Zentr. 1922, IV, 274. D. R. P. 504226; abst. C. A. 1930, **24**, 5444. Can. P. 249773; abst. Chem. Zentr. 1926, I, 2757. Dan. P. 29621. Aust. P. 91680.

compositions are also obtainable by combining with certain oils which are prepared by the action of acetylene in the presence of aluminum chloride upon high-boiling coal tar fractions[1]. The insulating composition of Siemens-Schuckertwerke[2] is a benzylcellulose varnish in which is incorporated methylhexalin and/or paracoumarone. Other plasticizing bodies for the benzyl ethers which have been advocated[3] are butyl combinations as sodium butylnaphthalenesulfonate, butyl stearate, monobutyl phthalate and dibutyl phthalate.

In the delustering of yarns or fabrics composed of or containing cellulose benzyl ethers[4], varying degrees of resistance to the delustering action may be induced by differential application to the fabric of the delustering agent, or by knitting into the fabric two yarns, one of which is more susceptible or resistant to delustering than the other. If steam is used to produce the subdued effect, a solvent or swelling agent in a size is applied locally as in a pattern, and the fabric then submitted to steam.

Resins obtained by condensing acylated polyhydric alcohols (glycerol, sorbitol, pentaerythritol), in which at least one free hydroxyl group is retained, with polybasic carboxylic acids (phthalic, succinic, maleic, diglycollic, salicylacetic, chlorphthalic, abietic, linoleic, ricinoleic, naphthenic, lauric), are incorporated with cellulose ethers

1. L. Lilienfeld, U. S. P. 1563204; abst. C. A. 1926, **20**, 503; J. S. C. I. 1926, **45**, 483-B; Chem. Zentr. 1926, I, 1709. E. P. 149317; abst. C. A. 1921, **15**, 434; Chem. Zentr. 1921, I, 52; J. S. C. I. 1921, **40**, 840-A; Rev. de Chim. Ind. 1921, **30**, 280. E. P. 149319; abst. C. A. 1921, **15**, 419; J. S. C. I. 1922, **41**, 95-A; Chem. Zentr. 1921, I, 44. F. P. 521000; abst. Chim. et Ind. 1922, **7**, 762; Chem. Zentr. 1922, IV, 964. Aust. P. 90010; abst. Kunst. 1923, **13**, 45; Chem. Zentr. 1923, II, 1066. Dan. P. 29621. Ital. P. 210536. Nor. P. 37755. Swed. P. 54449. See his U. S. P. 1625416; E. P. 171661; F. P. 535132; D. R. P. 504226.

2. F. P. 417392 and Addn. 16144; Aust. P. 54719; E. P. 149319; D. R. P. 246443, 336476; Swiss P. 97643.

3. I. G. Farbenindustrie, F. P. 685162. See E. P. 330957; abst. Nitrocellulose, 1931, **2**, 104.

4. C. Dreyfus and W. Whitehead, U. S. P. 1838663. H. Dreyfus, F. P. 37906 Addn. to F. P. 686644; abst. C. A. 1932, **26**, 318.

See p. 197, n. 5.

(ethyl-, ethylbutyl- or benzyl-cellulose) in organic solvent, an example being benzylcellulose with the resin from glycerol, colophony, palmitic acid, and maleic acid. Highly valuable plastic products are said to result[1].

A method for the manufacture of an enamel has been patented by C. Dreyfus[2], comprising benzylcellulose combined with a synthetic resin in the presence of a volatile solvent, whereas the method of the British Celanese[3] is to combine the benzylcellulose with an artificial resin formed by the condensation of xylenesulfonamide with an aldehyde (formaldehyde, paraformaldehyde, acetaldehyde), ethyl lactate and diethyl phthalate being added. They are especially indicated as adhesives in the attachment of plastic sheets to glass. H. Dreyfus[4] combines with cellulose benzyl ethers for the preparation of lacquers and varnishes, resins of the coumarone series, the phthalic anhydride-glyceryl resins and the polymerized lactic acid resins. Celluloid substitutes result of high strength and thermoplasticity[5], by combining benzylcellulose with a synthetic resin produced from acetone and furfural, a volatile solvent as ethyl acetate or lactate, or benzyl alcohol being used as a diluent; or[6] a synthetic resin obtained by the condensation

1. I. G. Farbenindustrie, E. P. 330895; abst. J. S. C. I. 1930, **49**, 958-B. See E. P. 303915, 320041. F. P. 687119; abst. C. A. 1931, **25**, 833. G. Schultz, Farbstofftabellen, 1923, No. 73. F. P. 685163; abst. C. A. 1930, **24**, 163. Belg. P. 366433.
2. Can. P. 302649.
3. E. P. 315808; abst. C. A. 1930, **24**, 1754.
4. E. P. 313133; abst. C. A. 1930, **24**, 960; J. S. C. I. 1930, **49**, 726-B; Brit. Plastics, 1930, **2**, #17, 100. See G. Schneider, E. P. 309913; abst. C. A. 1930, **24**, 723. The following two examples indicate the preferred combinations, all being parts by weight; (1) benzylcellulose 30, synthetic resin 46, pigment 15, diethyl phthalate 10, are dissolved in a solvent mixture containing ethyl acetate 420, acetone 210, benzene, toluene and xylene 70 each. Or, (2) benzylcellulose 4, synthetic resin 5, diphenylol propane 1, pigment 2, ethyl acetate 60, acetone 20. The diphenylol propane acts as a plastifier and softening agent, while the acetone and ethyl acetate constitute the volatile solvent portion. The synthetic resin is preferably one of the phenol-formaldehyde or phenol-furfural type.
5. British Celanese, Ltd., E. P. 307289; abst. J. S. C. I. 1930, **49**, 469-B; Chem. Zentr. 1929, I, 3152.
6. *Ibid.* E. P. 307290; abst. J. S. C. I. 1930, **49**, 469-B.

of furfuraldehyde and either an aromatic amine as aniline, or a phenol in the presence of an alkaline catalyst may be combined with the benzyl ether in the presence of volatile solvents.

In the manufacture of a molding powder of benzylcellulose base[1], suitable plasticizers and softeners claimed are triacetin, *p*-toluenesulfonamide, xylene-alkylsulfonamide, diethyl phthalate, mannol, resorcinol diacetate or nitrobenzene, with the addition of urea or urea derivatives as antacids and stabilizers. In producing pattern effects on yarns or fabrics having or composed of benzylcellulose[2], the pattern is composed of the same material but in slowly evaporating solvents, which is caused to adhere to, or be imprinted on, the fabric aided by heat and pressure to fully develop the plastic effect of the mixture. The plastic material of W. Hengstmann[3] is composed of a mixture of benzylcellulose, natural or artificial resin and an ester of an aliphatic dibasic acid. Thus, the cellulose ether is dissolved in a mixture of benzene, ethyl acetate and acetone, the solution mixed with a solution of resin in benzene and a small quantity of adipic ester added. The mixture is then pressed into blocks or plates under high pressure at about 60° and allowed to dry and harden. Sulfur or sulfur compounds may be added to the mixture, which is then vulcanized during molding by heating to 160°.

A pleasing decorative effect may be induced on plastic sheets of benzylcellulose[4] by uniting one or more colored or decorative cloths made of threads of cellulose material which is plastic under heat, being applied to the original sheet so that the structure of the cloth disappears complete-

1. American Cellulose & Chemical Mfg. Co., E. P. 249600. Can. P. 269482. F. P. 607465.
2. British Celanese, Ltd., W. Dickie and J. Rooney, E. P. 248832.
3. F. P. 691728; abst. C. A. 1931, **25**, 1345. D. R. P. 499676; abst. C. A. 1931, **25**, 568.
4. Soc. des Usines Chim. Rhone-Poulenc, E. P. 305189; abst. C. A. 1929, **23**, 4819; Chem. Zentr. 1929, II, 238. F. P. 648152; abst. C. A. 1929, **23**, 2793. D. R. P. 530121.

ly upon application of pressure. The Pathe Cinema benzylcellulose plasticizer is composed of triphenyl phosphate 15, tricresyl phosphate 12[1]. The artificial horn of F. Schmidt[2] is prepared by mixing benzylcellulose 30, alcohol 20 and a small amount of water, a second mixture being prepared from commercial casein 60, water 10 and alcohol 5, and these two mixtures then combined by kneading to form a homogeneous product.

Floor or wall coverings may be formed of cellulose benzyl ether plasticized by gelatinizing agents as tricresyl phosphate or tolyl phosphate and mixed with linoxyn and coloring matter, being applied to jute or other coarse fabric[3].

Another method for the production of floor coverings has received patent protection[4], in which the disadvantages of slow drying and poor surface resistance to oil paints is overcome by the use of benzylcellulose. The paint or enamel used as a covering for linoleum and similar floor coverings, in a preferred form comprises benzylcellulose 6, linseed oil 7, glyceryldítolyl ether 3, ethyl lactate 4, glyceryl diethyl ether 4, blown castor oil 6, solvent naphtha 20 and pigment 50. Glyceryldítolyl ether is the plasticizer, ethyl lactate a medium boiling solvent, glyceryldiethyl ether a high boiling solvent, and blown castor oil a softener.

The non-chalking composition of G. Ensminger[5] comprises a pigmented lacquer in which the tendency to disintegrate under the influence of the elements and thus leave minute particles of the pigments exposed on the surface is minimized by the use of "leaded zinc oxide" (zinc oxide containing a proportion of lead sulfate), as indicated by the

1. F. P. 643884; abst. C. A. 1929, **23**, 1749; Chem. Zentr. 1929, I, 2602.
2. U. S. P. 1811972; abst. C. A. 1931, **25**, 4983. E. P. 230025; abst. Chem. Zentr. 1925, II, 624. Swiss P. 113925.
3. H. Boernstein and N.-V. Nederlandsche Linoleumfabriek, E. P. 306140; abst. C. A. 1929, **23**, 5023; J. S. C. I. 1930, **49**, 420-B; Br. Plastics, 1930, **2**, #13, 53; Chem. Zentr. 1929, II, 112. D. R. P. 535139; abst. C. A. 1932, **26**, 1143.
4. Imperial Chemical Industries, Ltd., F. Walker and A. Hetherington, E. P. 360815.
5. U. S. P. 1860532; abst. C. A. 1932, **26**, 3943.

following example: benzylcellulose 9.9, dammar resin 2.6, dibutyl phthalate 1.7, chrome green 0.8, leaded zinc oxide 4.6, bone black 2.1, monoethyl-ethyleneglycol acetate 3.6, butyl acetate 3.8, ethyl acetate 30.1, toluene 27.7, amyl alcohol 3.1. Monoethylinbenzoyl benzoate may also be used as plasticizer.

A process has been described for the manufacture of floor coverings in which benzylcellulose is the base material, thereby omitting oxidation products of drying oils, such as linoxyn. The benzylcellulose is plasticized and then mixed with coloring substances and fillers in an unmoistened or unmelted state. The mass so obtained is pressed into the form of a flat, homogeneous layer with or without fabric by heated rollers or presses. The following two examples indicate the scope of the process:

1. 20 parts benzylcellulose are gelatinized with 27 parts tricresyl phosphate, 40 parts wood meal, 20 parts fillers and 15 parts color added, and the mass kneaded until uniform.

2. 15 parts linoleum cement (a mixture of oxidized oils and resins) are mixed with 32 parts "benzylcellulose-gelatinate," 40 parts wood meal, 20 parts fillers and 15 parts color, and incorporated by kneading or mixing.

Artificial masses are producible by incorporating benzylcellulose with viscous or solid polymerization products of alkylene oxides as ethylene or propylene oxides, as indicated by the following illustration[1]: 5 parts benzylcellulose are dissolved with the addition of 1.75 parts of a polymerization product of ethylene oxide melting at 52°, in a mixture of benzene and toluene 40 each, butyl acetate 9, ethyl alcohol 6.25, an exceptionally satisfactory wood lacquer being obtained. An odorless dyestuff material has been described[2], comprising 5 parts benzylcellulose in which has been dissolved by heat, 50 parts octadecadien-(9.11)acid (1) triglyceride.

1. I. G. Farbenindustrie, E. P. 352042.
2. J. Scheiber, D. R. P. 544697; Addn. D. R. P. 522486.

As a cellulose derivative thermoplastic composition, H. Dreyfus[1] has described a mixture of 70 parts ethyl- or benzyl-cellulose and 30 parts chloretone; or[2] 60 parts benzylcellulose or benzylstarch soluble in benzene, are mixed with 30-40 parts camphor and dissolved in 200 parts benzene or chloroform, being then kneaded in a vacuum kneading machine for 2 hrs. at 60°. Subsequently about half of the volatile solvent is evaporated, and the mass calendered (rolled out), dried, heated and pressed.

In the preparation of coatings[3], aqueous dispersions of finely divided cellulose derivatives and aqueous emulsions of solvents, softening and gelatinizing agents may be incorporated together to produce special technical effects. The following example is explanatory: An aqueous dispersion is obtained by intimately mixing 100 parts 40% aqueous paste of benzylcellulose which contains 5% methylcellulose, 10 parts of a pigment dyestuff as Lithol Fast Scarlet (Schultz-Julius No. 73), and an emulsion of 20 parts dibutyl phthalate in about 0.75 part methylcellulose, 0.75 part sodium butylnaphthalenesulfonate and 20 parts water, and this is applied with a paint brush onto wood, metal or brickwork in the usual manner. After drying, an elastic, non-bending coating is obtained. Onto this coating if desired, a solution of nitrocellulose, esterified colophony, triphenyl phosphate, butyl alcohol and acetate, may be sprayed or painted.

The plastic composition of W. Moss and B. White[4] is formed by dissolving benzylcellulose in a suitable combination of volatile solvent and plastifiant, to which synthetic resins and "effect materials" are added. Especially useful in dental technique[5] is claimed for a product of benzylcel-

1. E. P. 205195.
2. L. Lilienfeld, U. S. P. 1858019; abst. C. A. 1932, **26**, 3919.
3. I. G. Farbenindustrie, E. P. 330897.
4. E. P. 313133; abst. C. A. 1930, **24**, 960; J. S. C. I. 1930, **49**, 726-B; Br. Plastics, 1930, **2**, #17, 100. See G. Schneider, E. P. 309913; abst. C. A. 1930, **24**, 723.
5. Soc. Anon. Des Laboratories "Odont-Email," F. P. 683418; abst. C. A. 1930, **24**, 4597.

lulose 100, triphenyl phosphate 5, tritolyl phosphate 5, crystallizable benzene 360, and 98% alcohol 40.

To increase the resistance of artificial filaments to water—one of the drawbacks in the artificial silk industry—E. Berl[1] mixes an acetone solution of acetylcellulose with an acetone solution of benzylcellulose, and extrudes this solution into filament form, the dry method of spinning being preferable. H. Dreyfus[2] in benzylcellulose filament formation, where the filaments are of tubular formation, dissolves in a solvent mixture containing at least two dissimilar solvents, the spinning temperature being *below* the boiling point of the higher boiling component. Solvents are so selected that the variation in their respective boiling points may be adjusted to give the desired voluminosity to the issuing filament.

In the wet spinning of benzylcellulose solutions[3], it is recommended to maintain the solution above that of the spinning bath, so that more concentrated solutions may be spun, and hence smaller jet apertures used. Coagulation is effected in a non-solvent liquid as castor oil or hydrocarbon oils, that is partially miscible with the solvent in the spinning solution. In another method of spinning cellulose benzyl ether solutions[4], the spinning liquid is extruded through orifices at the outlet of which the solution is received into a coagulating bath, the nature of the solvent being such, or the coagulation bath being so adjusted, that a definite proportion of the solvent remains. The threads are then heated, and obtained in a transparent or translucent, brilliant state.

Artificial filaments may be formed from a solution of benzylcellulose by combining therewith an artificial resin obtained by the condensation of formal-glycerol and a hy-

1. U. S. P. 1484004; abst. C. A. 1924, **18**, 1198; J. S. C. I. 1924, **43**, 415-B; Kunst. 1925, **15**, 163. D. R. P. 385962; abst. Chem. Zentr. 1924, I, 1127. Faser. 1924, **6**, 20.

2. E. P. 317098.

3. British Celanese, Ltd., E. P. 341148; abst. C. A. 1931, **25**, 5029.

4. C. Dreyfus, F. P. 697814; abst. C. A. 1931, **25**, 3168.

droxyaromatic alcohol (hydroxybenzyl alcohol, hydroxytolyl alcohol, hydroxyxylyl alcohol)[1], in the presence of a high boiler as diphenylolpropane. Benzylcellulose with *m*-xylylethane ether or benzylcresyl ether is dissolved in a mixture of alcohol and toluene, and extruded through capillaries for artificial filament formation. C. Palmer and W. Whitehead[2] have devised a process and described an apparatus for the production of benzylcellulose filaments, which involves the winding and twisting of the filaments as a simple and economical operation, and including a cap-spinning device.

If it is desired to impart to benzylcellulose fibers or fabrics waterproof or gasproof properties[3], they are first woven, then, with or without the addition of a plasticizing agent, compacted by means of combined heat and pressure, or[4], the fibers may be applied very gently to soften and spread the individual filaments and thus partially cover the otherwise voids between filatures. Crepe fabrics are producible, as by the C. Dreyfus process[5], by weaving together benzylcellulose filaments with degummed natural silk yarn, then subjecting the fabric to a creping bath. Aluminum lactate is suitable[6].

In the operation of producing openwork fabric of predetermined design[7], benzylcellulose yarn is treated with a mineral acidic carbonizing promoting compound, and the fabric then subjected to a carbonizing temperature. Filaments, yarns, strips, knitted tubes, and filament aggregates may be formed into strips and tapes of flattened cross-sec-

1. G. Seymour, U. S. P. 1828449.
2. E. P. 198023; abst. J. S. C. I. 1923, **42**, 765-A.
3. British Celanese, Ltd., T. Woodman and W. Dickie, E. P. 249946; abst. C. A. 1927, **21**, 1019; J. S. C. I. 1926, **45**, 532-B; Ann. Rep. S. C. I. 1926, **11**, 131.
4. C. Dreyfus, E. P. 248147; abst. Chem. Zentr. 1926, II, 2855.
5. U. S. P. 1813530; abst. C. A. 1931, **25**, 5301.
6. H. Jaboulay, F. P. 740951.
7. C. Dreyfus, R. Dort and H. Platt, U. S. P. 1834339.

tion[1] by submitting the benzylcellulose textile, with or without the addition of plasticizing bodies, to combined heat and pressure, at temperatures below the melting point of the cellulose benzyl ether. Twisted or untwisted warps, or woven or knitted narrow strips of fabrics may be similarly treated.

In the loading of yarns or threads of cellulose benzyl ether[2], a soluble salt of tin, zinc, aluminum, bismuth or tungsten is employed in conjunction with a following bath of tannin, soluble phosphate or silicate, or[3], a loading metal and a thiocyanate may be used, the thiocyanate not exceeding in weight the metal.

In dyeing cellulose ethers and esters[4], in spite of the water-repellent properties of fibers, films and other materials consisting of benzylcellulose, and although the hydroxyl groups in the cellulose molecule suffer steric hindrance by reason of the etherifying groups present, such materials may be dyed in the normal manner by means of direct cotton and also acid dyestuffs (in a neutral bath), such as Nigrosine B, Alizarine Astrol B, Azo Yellow 3 G, Rocelline and Orange II, the fastness of the resulting shades being improved, when necessary, by an after treatment of the dyed material with solutions containing copper or chromium[5].

1. H. Dreyfus, E. P. 341034; abst. C. A. 1931, **25**, 4720; Silk J. 1931, **7**, #84, 53. F. P. 702209, 702210; abst. C. A. 1931, **25**, 4125. Compare E. P. 248147, 249946, 328312. See also F. P. 700876, 701269; abst. C. A. 1931, **25**, 3833.

2. British Celanese, Ltd., H. Dreyfus and G. Ellis, E. P. 285941; abst. C. A. 1929, **23**, 290; J. S. C. I. 1928, **47**, 330-B; Silk J. 1928, **5**, #49, 78; Chem. Zentr. 1928, II, 204. Can. P. 276516, Belg. P. 344890.

3. H. Dreyfus, E. P. 281084; abst. C. A. 1928, **22**, 3528; J. S. C. I. 1928, **47**, 227-B; Chem. Zentr. 1928, I, 1732. F. P. 634165. Tin thiocyanate (F. P. 642331) has also been specified.

4. H. Dreyfus, E. P. 196952; abst. C. A. 1923, **17**, 3794; J. S. C. I. 1923, **42**, 713-A; J. Text. Inst. 1923, **14**, 204-A; J. Soc. Dyers, 1923, **39**, 291; Chem. Zentr. 1923, IV, 619; Faserstoffe, 1924, **6**, 10. F. P. 558917; Chem. Zentr. 1924, I, 1109.

5. *Ibid.* E. P. 196953; abst. C. A. 1923, **17**, 3794; J. S. C. I. 1923, **42**, 713-A; J. Text. Inst. 1923, **14**, 204-A; J. Soc. Dyers, 1923, **39**, 291; Faserstoffe, 1924, **6**, 10; Chem. Zentr. 1923, IV, 619.

According to H. Meyer[1], washable paint material colors, in which the dyestuff is converted into solid form with water-insoluble binding agents, and then thinned with solvents before use, are obtained by proceeding according to the following illustrative example: Nitrocellulose and benzylcellulose each 10, plasticizer 5, dye 20, this being incorporated in a mixture of benzylcellulose 10 and solvent naphtha 100. As binding agent, Albertol resin or celluloid may be used, and ethyl alcohol, or acetone as solvent.

For the formation of flexible flooring and wall coverings benzylcellulose has been patented as in the process of H. Boernstein[2], being superior to the nitrocellulose already used for this purpose on account of its greater stability, diminished inflammability and solubility in a wider range of inexpensive solvents. The cellulose benzyl ether is mixed with a gelatinizing agent as tricresyl phosphate and in the presence of oxidation drying oils, the mass then pressed into homogeneous layers by hot-rolling, with or without a fabric. For instance, 20 parts benzylcellulose are gelatinized with 27 of tricresyl phosphate, mixed with 40 of wood flour, 20 of filler and 15 of dye. The mixture is then rolled or kneaded to a fine powder, and hot pressed onto jute. Or, 15 of linoleum cement (a mixture of oxidized oils and resins) is mixed with 32 of gelatinized benzylcellulose, 40 of wood flour, 20 of filler and 15 of dye, and worked up into plastic form, then spread on a receptive surface.

Bearing in mind that the usual cellulose-containing filters show rapid wear and deterioration, especially when used for filtering concentrated alkali solutions as in mercerizing and alkalicellulose production, the fibers swelling and coalescing, and thereby impeding passage of liquid therethrough, the I. G. Farbenindustrie[3] obviate these difficulties by preparing a filter of benzylcellulose, either in the fibrous condition, or by weaving benzylcellulose fila-

1. Deka-Textilfarben A. G., D. R. P. 535167.
2. H. Boernstein and N. V. Nederlandsche Linoleumfabriek, D. R. P. 535139.
3. D. R. P. 535337.

ments into fabric form, and using this as a filter cloth. Both acids and alkalis exert but little effect on such a filter, and although the initial cost is comparatively high, increased period of usefulness is said to more than compensate.

In the preparation of a film resistant to ageing[1], the use of substituted guanidines is recommended, as by incorporating with benzyl cellulose ether 20, tricresyl phosphate 2, and to this is added 0.4-0.5 of *b*-naphthylbiguanid dissolved in benzene 75, and alcohol 5. The films obtained are said to show a stability about five times as long, especially towards ultraviolet light, as compared with the same formula with the naphthyl compound not present.

Benzylcellulose may be colored by incorporation with chromium or copper compounds of dyes[2], particularly *o*-hydroxyazo dyes, examples being chromium salt added to diazotized 5-nitro-2-amino-1-oxybenzene and 1-phenyl-3-methyl-5-pyrazolon, pure red being formed. Or[3], 1-*b*-hydroxyethylaminoanthraquinone sulfate or other suitable ester of an anthraquinonylamine alcohol may be employed. Dyed effects on benzylated cellulose are also producible by the use of azo compounds containing one or more amino groups substituted by one or more aliphatic side chains, each containing one or more hydroxyl groups, but no carboxyl group[4], such as a dye from picramic acid and dihydroxypropylaniline. A suitable dyestuff also, is one containing a urethane residue as 4.4'-dinitrodiphenylurethane[5],

1. I. G. Farbenindustrie, L. Rosenthal, E. Messmer and R. Hebermehl, D. R. P. 538110.

2. I. G. Farbenindustrie, Akt.-Ges., W. Mueller, K. Holzach and H. Krzikalla, D. R. P. 517491; abst. C. A. 1931, **25**, 2304. Cites D. R. P. 337993.

3. H. Olpin, U. S. P. 1688553; abst. C. A. 1929, **23**, 289; J. S. C. I. 1928, **47**, 926-B. E. P. 285641; abst. J. S. C. I. 1928, **47**, 364-B.

4. H. Dreyfus, U. S. P. 1735961; abst. C. A. 1930, **24**, 972; J. S. C. I. 1930, **49**, 54-B. E. P. 292180; abst. C. A. 1929, **23**, 1513; J. S. C. I. 1928, **47**, 639-B; Silk J. 1928, **5**, #52, 80; Chem. Zentr. 1928, II, 1943.

5. *Ibid.* U. S. P. 1735960; abst. C. A. 1930, **24**, 972; J. S. C. I. 1930, **49**, 54-B. E. P. 292452; abst. C. A. 1929, **23**, 1513; Silk J. 1929, **5**, #52, 80; Chem. Zentr. 1928, II, 1944.

or a thiourethane obtained by heating 1-acetylaminoanthraquinone 4-isothiocyanate with ethyl alcohol or alcoholic KOH[1].

Materials composed of or containing benzylcellulose are rendered more resistant to hot treatments such as ironing and given a good affinity for dyes[2], by treating them with alkaline tin solutions as sodium or potassium stannate. In mordanting benzylated cellulose yarn[3], treatment with sodium, potassium, ammonium, iron, aluminum or chromium thiocyanate may be used, the amount required being governed by the depth of shade desired. The use of a quantity of thiocyanate in excess of the equivalent of the mordanting metal (iron, chrome, aluminum) improves the absorption of the mordant by the material.

According to an invention of British Celanese, Ltd.[4], plastic sheets of benzylcellulose and having a thickness of 0.005-0.03 inch may be formed by first coating the surface of a film casting apparatus with the cellulose ether in a solvent mixture comprising a low, medium and high boiling solvent, and thereafter evaporating off the solvent portion. By *low* boiling solvent is one boiling below 100° as acetone, benzene, ethylene dichloride, ethyl acetate, methylene chloride, methyl or ethyl alcohol, chloroform; by *medium* boiling are comprehended solvents boiling 100-125°, and by *high* boiling those which boil 125-225°. Examples of such

1. H. Dreyfus, U.S.P. 1735963; abst. J.S.C.I. 1930, **49**, 54-B. E. P. 291816; abst. C. A. 1929, **23**, 1287; J. S. C. I. 1928, **47**, 639-B. F. P. addn. 32948 to F. P. 627072; abst. C. A. 1929, **23**, 1287; Chem. Zentr. 1928, II, 392. Can. P. 285799. Patent cites E. P. 291118, 285968, 285969.

2. British Celanese, Ltd., and G. Ellis, E. P. 302775; abst. C. A. 1929, **23**, 4353; J. S. C. I. 1929, **48**, 169-B; Silk J. 1929, **5**, #59, 72; Chem. Zentr. 1929, I, 2718.

3. G. Ellis, U. S. P. 1757519; abst. J. S. C. I. 1930, **49**, 555-B. E. P. 280698; abst. C. A. 1928, **22**, 3305; J. S. C. I. 1928, **47**, 86-B; Silk J. 1928, **4**, #47, 68; Chem. Zentr. 1928, I, 1096. F. P. 644565; abst. C. A. 1929, **23**, 1759. H. Dreyfus, Can. P. 285978; abst. Chem. Zentr. 1932, I, 2242. Can. P. 287598; abst. Chem. Zentr. 1932, I, 2646. (Before the mordanting the goods are treated with swelling agents, e. g. with aqueous solutions of alkali thiocyanates; then they are mordanted and dyed with a mordant dye.)

4. British Celanese, Ltd., E. P. 348099, Addn. to 347648.

medium and high boiling solvents are ethyl lactate, ethyl oxybutyrate, diacetone alcohol, benzyl alcohol, ethyleneglycol monomethyl ether, tetrachlorethane, butyl alcohol, acetate and propionate, amyl acetate and amyl alcohol. An illustrative formula is as follows: Benzylcellulose 6, ester gum 1, diethyl phthalate 1, ethyl acetate 12, benzene 4, xylene 4.

In coating compositions, benzylcellulose apparently has a wide field on account of its relative stability and less liability of discoloration on ageing, the latter property being of particular importance in the preparation of clear or unpigmented lacquers for use as coatings for wood, metal or electric light bulbs. The non-inflammability, solubility in cheap solvents and low hygroscopicity are also important[1]. The scope of the method is shown in the following three examples:

I. Benzylcellulose 12, of 1 c.g.s. viscosity, and 2.4 of tricresyl phosphate are dissolved in a mixture of ethyl lactate 6, industrial spirits 12.9 and toluene 51.7. The clear benzylcellulose base thus obtained is pigmented with 15 parts color base prepared by grinding together chrome yellow 9, dammar 3, industrial spirits 1 and toluene 3.

II. This is an example of a clear benzylcellulose lacquer, and may be used as a bronzing liquid by thinning down further with volatile solvent. Benzylcellulose 15, of viscosity 0.5 c.g.s. units and 5 of clear ester gum are dissolved in a solvent mixture containing castor oil 2, dibutyl phthalate 1, tetrachlorethane and ethyleneglycol methyl ether 7 each, industrial spirits and xylene 15 each, and toluol 30.

III. Example of a pigment enamel. Benzylcellulose 18, viscosity 0.2 c.g.s. units, are dissolved in a solvent mixture containing ethyl lactate 4.5, alcohol and xylene 11.6 each, toluene 54.3, to form a benzylcellulose base. 5.7 parts of this base are incorporated in a Werner-Pfleiderer mixer with white pigment 15 till a coherent gelatinous mass is

1. Imperial Chemical Industries, Ltd., D. Traill and A. Levesley, E. P. 357123.

obtained and the pigment properly dispersed. The paste is now thinned with 61 parts benzylcellulose base, 2.4 parts tricresyl phosphate are added, and finally 2 parts dammar dissolved and added thereto a mixture of alcohol 1.9, toluene 2 and ethylene chlorhydrin 10. The incorporation is continued until a perfectly homogeneous mass results.

Softeners of the acetal type have been proposed as benzylcellulose plastifying agents on account of their relatively low vapor pressure, compatibility with both alkyl and aralkylcelluloses and excellent stability. A typical formula would be benzylcellulose 10, acetal of the ethylether of diethylene glycol 2, toluene-alcohol (1:1) 88. Such a composition is said to give a satisfactory film which is clear and flexible[1].

From a study of the solubility of benzylcellulose in several solvents and thinners[2], the following composition for a dope, which was stable for at least a year, was found to be suitable for the undercoating of airplane wing fabric: benzene 40, alcohol 10, toluene 20, xylene 10, acetone 20, benzyl alcohol 1, and benzylcellulose 10. Plasticizers may be added, and pigments are recommended for better results. With this dope, straining of the fabric is said to be less, the tautening effect, however, being less with benzylcellulose than with ethylcellulose.

In the coagulation of cellulose ethers and esters for the production of filaments, films and plastic masses, nitrates of the alkali and alkaline earth metals, especially ammonium, magnesium, calcium and zinc nitrates, are recommended[3], dissolved in an equal amount of water. For instance, to coagulate a 10% benzylcellulose in 70% acetone, 15% benzine and 15% methylglycol acetate, 120 gms. calcium nitrate crystals (containing 4 mol. water) are used, dissolved in 100 gms. water.

1. E. I. du Pont de Nemours & Co., E. P. 318980.
2. T. Araki and T. Nagamote, J. S. C. I., Japan, 1932, **35**, 68; abst. C. A. 1932, **26**, 3374. He claims benzylcellulose dissolves best in benzene containing 1% ethyl alcohol.
3. L. Clement and C. Riviere, F. P. 711668.

In the production of attractive fabrics by means of coating compositions, L. Lilienfeld[1] superposes upon a soft fabric as satin or sateen a unitary or plurality of coatings of a cellulose ether. In an example cited to exemplify the process, cotton sateen is coated with an 8% solution of benzylcellulose in pure pyridine and dried at 40°. Or 10 parts benzylcellulose may be dissolved in 90 parts pyridine whereupon 10 parts of 2-oxytrimethylene-1.3-sulfide[2] are added to the solution. Cotton sateen is then coated with this solution.

In the treatment of yarns, fabrics or films for loading purposes where composed of ethyl- or benzyl-cellulose[3], it has been found that the usual weighting agents for natural silk (tin, zinc, aluminum, bismuth, tungsten, and antimony tannate, phosphate or silicate) may be used, provided the materials are created initially or during the stage of loading with ureoid bases (urea, urethanes, thiourea, thiourethanes, guanidine or their alkyl or aryl substitution products, and including diethyldiphenylurea and monomethylurea. Thus, a cellulose derivative in woven or knitted form is soaked 0.5 hr. in a cold 2% solution of monomethylurea. The fabric is removed, drained, and steeped in a stannic chloride solution of 40° Tw. for 0.5 hr., then rinsed and either thoroughly washed with water containing a calcium salt in solution or given a sodium phosphate treatment.

In the manufacture of lacquers and priming compositions[4], resins made by condensing acylated polyhydric alcohols, in which at least one free hydroxyl group is retained, with polybasic carboxylic acids, are incorporated with cellulose ethers in organic solvents. Examples are: ethylcellulose with the resin from phthalic acid and glycerol mono- or di-linoleate or ricinoleate or colophony glyceride

1. E. P. 357190.
2. L. Lilienfeld, E. P. 25246, 1911. These thio derivatives of glycerol are prepared by treating *a*- or *b*-dichlorhydrin with an alkali sulfide in aqueous or alcoholic solution. Dihalogen hydrins, mono-, epi- and epidi-halogenhydrins may be likewise treated.
3. H. Dreyfus, U. S. P. 1867658.
4. I. G. Farbenindustrie, E. P. 330895.

or *b*-hydroxyethyl linoleate; benzylcellulose with the resin from glycerol, colophony, palmitic acid and maleic acid.

Mixed Benzylcellulose Ethers. Combinations of benzylcellulose with the alkylcelluloses as methyl and ethylcellulose offer alluring industrial possibilities, not the physical admixture of an alkyl and aralkyl ether, but combinations of the two groups in the same cellulose aggregate. Whereas the lower methyl and ethylcelluloses are limited in their technical usefulness by virtue of the fact that they either dissolve or swell in water, the addition thereto of a relatively small proportion of benzylcellulose (in some cases not exceeding 1%) changes a water-soluble methylcellulose (say) into an ether practically unaffected by moisture, either hot or cold, which is susceptible to important industrial exploitation. The ratio of percentage composition of alkyl in combination with cellulose before incipient benzylation has been effected; ratio of benzyl to alkyl, effect of benzylating a double (methylethyl) alkylated cellulose, and the optimum conditions for alkyl and subsequent aralkyl etherification constitute a virgin field as yet but superficially touched and offering practically limitless potentialities.

Methylbenzylcellulose. Ethylbenzylcellulose. The methylbenzyl ether may be made by the process of G. Balle[1], comprising etherifying alkalicellulose with a mixture of methyl halide and benzyl halide in the presence of neutral salts, or in accordance with the directions of H. Dreyfus[2],

1. D. R. P. 494917; abst. C. A. 1930, **24**, 3646. See D. R. P. 492062; abst. C. A. 1930, **24**, 2599. F. P. 669256; abst. C. A. 1930, **24**, 1740. E. P. 305946; abst. C. A. 1929, **23**, 5040. An alkalicellulose is prepared in the usual way by immersing cellulose in NaOH solution and pressing until the mass contains 1 mol. cellulose per mol. NaOH, corresponding to about a 50% NaOH dipping, and containing about 66% cellulose, 17% NaOH and 17% water. This is mixed with 1-3 times the weight of magnesium chloride to alkalicellulose, then 0.5 mol. each benzyl chloride and methyl chloride with constant agitation at 60-80°. After the etherifying agent has disappeared, 1 mol. powdered NaOH is added and again a mixture of 0.5 mol. each methyl and benzyl chlorides is allowed to react at 80-120°.

2. U. S. P. 1451331; abst. C. A. 1923, **17**, 2505; J. S. C. I. 1927, **46**, 447-A; E. P. 164377; abst. C. A. 1922, **16**, 494; Chem. Met. Eng. 1921, **25**, 714; J. S. C. I. 1921, **40**, 540-A; Chem. Tech. Uebers. 1921, **45**, 327. Belg. P. 290448. E. P. 164375; abst. J. S.

in which the mixed ether is prepared by first acting upon modified cellulose with methyl sulfate or ethyl sulfate, then with benzyl chloride. The I. G. Farbenindustrie[1] first alkylate with either methyl chloride or ethyl chloride or both, then aralkylate with benzyl chloride, producing either a methylethyl-, methyl-, or ethyl-benzylcellulose. The latter contain 24.7% methoxyl and 8% benzyl in cellulose combination. When alkalicellulose is treated simultaneously with a mixture of ethyl and benzyl chlorides, an ethylbenzylcellulose results, being a monoethylcellulose containing 1% benzyl, and this may be acetylated by treatment with acetic acid, acetic anhydride and a small proportion of catalyst to an ethylbenzylcellulose acetate. Likewise methyl or ethyl chlorides with brombenzyl chloride gives rise to methyl- or ethyl-brombenzylcellulose, which has likewise been acetylated to the corresponding methyl- and ethyl-brombenzyl cellulose acetates.

H. Dreyfus has described a process for methylbenzylcellulose formation[2], whereby the alkalicellulose is partially alkylated with methyl sulfate, and the etherification then completed with benzyl chloride, or the partial benzylation may precede the methylation.

The I. G. Farbenindustrie, through their chemists, have evolved three processes for the production of alkyl-aralkylcelluloses. In the method of G. Balle and K. Ost[3], cellulose

C. I. 1921, **40**, 540-A. In an example, 1 mol. cellulose is impregnated with 4 mols. NaOH in an equal weight of water, the mass then kneaded with 2 mols. benzyl chloride and afterwards with 1 mol., the temperature in the first stage being 50-100°, and in the second, 50° down to room temperature. 6 mols. NaOH are then added, and a further 3 mols. benzyl chloride, and subsequently 2 mols. diethyl sulfate, temperatures being as before. Finally 6 mols. NaOH and 3 mols. ethyl sulfate are incorporated.

1. . G. Farbenind. A. G. and E. Teupel, D. R. P. 521721; abst. C. A. 1931, **25**, 3481. U. S. P. 1833270. Can. P. 293163.

2. E. P. 164375; abst. C. A. 1922, **16**, 495; J. S. C. I. 1921, **40**, 540-A; Ann. Rep. S. C. I. 1921, **6**, 138; Chim. et Ind. 1922, 8, 654; Chem. Tech. Uebers. 1921, **45**, 327. U. S. P. 1451330; abst. C. A. 1923, **17**, 2505; J. S. C. I. 1923, **42**, 447-A; Chem. Zentr. 1924, I, 2759. F. P. 530891; abst. Chem. Zentr. 1922, II, 899. F. P. Addn. 24082 to F. P. 530891. Australian P. 2543, 1921.

3. D. R. P. 522054; abst. C. A. 1931, **25**, 3167. U. S. P. 1867050.

ethers insensitive to water are made by treating an alkalized cellulose with excess of alkylating agent containing up to 2 mols. of an aralkyl halide for each 10-30 mols. of alkylating agent, the etherification being carried out at such temperatures, and, if necessary at such pressures, that a hydrolysis of the excess alkylating agent used is avoided. The hydrolysis temperatures of the various alkylating agents under different pressures vary according to the nature of the alkylating agent used. As an example, 900 parts by weight of wood cellulose in the form of pasteboard are soaked 2 hrs. in 50% NaOH solution at 30°, then pressed to a content of 3-6 mols. alkali per mol. original cellulose. The mass is disintegrated, allowed to stand a short (indefinite expression) time at 20° for ripening. The alkalicellulose thus obtained is heated in a pressure vessel with a mixture of 5460 parts ethyl chloride and 762 parts benzyl chloride (equivalent to 1 mol. cellulose, 14 mol. ethyl chloride, 1 mol. benzyl chloride), at 110-120° and at the pressure corresponding to this temperature of the etherifying mixture for 6-7 hrs. After removal of excess ethyl chloride, the reaction product is freed from excess alkali and NaCl by washing with water, and some excess benzyl chloride and benzyl alcohol by extraction with a suitable organic solvent which is a non-solvent of the cellulose ether, and dried. The ethylbenzylcellulose obtained is soluble in alcohol-benzene 1:1 to a clear solution, and resistant to water, even ice water.

The utilization of ethylbenzylcellulose as a delustering agent in artificial filament formation has been put forward by W. Schieber, H. Pfannenstiel and H. Mahn[1], especially applicable to the treatment also of textiles of regenerated cellulose as by the nitrocellulose, viscose and copper ammonia rayon processes. The textile or filament is coated

1. I. G. Farbenindustrie, A. G., W. Schieber, H. Pfannenstiel and H. Mahn, D. R. P. 518194; abst. C. A. 1931, **25**, 2577. I. G. Farbenindustrie, A. G., G. Poetzsch and H. Jaeger, D. R. P. 518197; abst. C. A. 1931, **25**, 2576. I. G. Farbenindustrie, A. G., K. Sponsel and G. Balle, D. R. P. 518241; Addn. to D. R. P. 516751; abst. C. A. 1931, **25**, 3481.

with a 0.2% benzylcellulose dissolved in acetone and containing 40% water, which is applied to the filament or textile, the skeins or fabric being wet with this solution, centrifuged and dried. The skeins are said to be well dulled after drying, the degree of dullness being regulated by the amount of ethylbenzylcellulose in solution, and the ratio of precipitant (water) to solvent (acetone). Variation in dulling effect is also producible by varying the boiling point of the solvent portion.

In the preparation of color bleaching-out layers, either gelatin or nitrocellulose has heretofore been almost exclusively used as a binding agent. B. Wendt and H. Bincer[1] have found that by combining ethylbenzylcellulose with nitrocellulose obviated the disadvantages formerly existing, which are that there has heretofore been no satisfactory fixing process for the reason that for the usual class of sensitizers of the class of the thiosinamines there existed no satisfactory solvent, in which the binding was capable of swelling, but in which the dye was insoluble. When there is selected, in order to bring about a proper fixation, a binding agent as the cellulose ethers, which has the property of swelling in liquids, in which the dyes are insoluble but in which the sensitizers dissolve, the preparation of an otherwise practically usable layer suffers in that, on drying the poured layers, the dyes precipitate out so that later on, soiled appearing pictures are obtained. These objections are obviated, according to the patentees, by using a bleaching-out layer prepared from a mixture of ethylbenzylcellulose 70, nitrocellulose 30, and sensitized with diethylthiosinamine. The layer can be fixed with a mixture of benzine and anisol, 3:1.

H. Dreyfus has evolved a process for ethylbenzylcellulose formation[2], and its combination with plasticizing

1. D. R. P. 498028; abst. C. A. 1930, **24**, 4721. E. P. 341151.
2. U. S. P. 1451331; abst. C. A. 1923, **17**, 2505; J. S. C. I. 1927, **46**, 447-A; E. P. 164377; abst. C. A. 1922, **16**, 494; Chem. Met. Eng. 1921, **25**, 714; J. S. C. I. 1921, **40**, 540-A; Chem. Tech. Uebers. 1921, **45**, 327. Belg. P. 290448. E. P. 164374, 164375; abst. J. S. C. I. 1921, **40**, 540-A.

bodies for film, lacquer and filament production. In the first process cellulose or a conversion product of cellulose insoluble in alkalis is treated with 50% caustic soda solution in the ratio of 4 mols. NaOH to 1 mol. cellulose, which is first kneaded with 2 mols. benzyl chloride and afterwards with 1 mol. ethyl sulfate. The reaction with benzyl chloride is executed at 50-100°, that with ethyl sulfate at 50° or lower. After 2-4 hrs. 6 mols. NaOH in powdered form are further added and the mass malaxated with 3 mols. benzyl chloride at 50-150° and afterwards with another 2 mols. ethyl sulfate at about 50°. Finally 6 mols. NaOH and 3 mols. ethyl sulfate are added and the etherification is considered completed.

Alkylated sulfonamides of high boiling point have been described as plasticizing agents for cellulose derivatives, xylene monomethyl (or ethyl) sulfonamide being examples[1]; also[2] toluene-*o*-monomethyl (or monoethyl) sulfonamide; and including benzene monomethyl (or methylethyl) sulfonamide, *o*-, and *p*-toluene dimethyl (or methylethyl or diethyl) sulfonamide[3], including xylene dimethyl (or diethyl or methylethyl) sulfonamide. It has now been found that by combining the above sulfonamides with mixed cellulose ethers as methylbenzyl-, chlorethyl-, nitrobenzyl-, or methoxybenzyl-cellulose, excellent plastic masses for films or celluloids may be prepared. H. Dreyfus[4] has also described benzylchlorbenzylcellulose, obtained by benzylating with benzyl chloride to a partial cellulose etherification, then completing the aralkylation by the use of chlorbenzyl

1. H. Dreyfus, E. P. 132283; abst. C. A. 1920, **14**, 346; J. S. C. I. 1919, **38**, 896-A; Chim. et Ind. 1920, **4**, 798; Kunst. 1920, **10**, 79; 1921, **11**, 61; 1923, **13**, 7.

2. H. Dreyfus, E. P. 133353; abst. J. S. C. I. 1920, **39**, 14-A; Chim. et Ind. 1921, **6**, 512; Kunst. 1920, **10**, 80, 198; 1923, **13**, 7.

3. H. Dreyfus, E. P. 154334; abst. C. A. 1921, **15**, 1075; J. S. C. I. 1921, **40**, 42-A; J. Soc. Dyers Col. 1921, **37**, 56; Chem. Zentr. 1921, II, 575.

4. E. P. 164385; abst. J. S. C. I. 1921, **40**, 540-A; Ann. Rep. S. C. I. 1921, **6**, 139; Chim. et Ind. 1922, **8**, 1081; Chem. Zentr. 1921, IV, 883. U. S. P. 1454960; abst. C. A. 1923, **17**, 2362; J. S. C. I. 1923, **42**, 600-A; Chem. Zentr. 1923, IV, 1018.

chloride. These ethers may also be plasticized by various sulfonamide derivatives[1].

Nitrobenzylcellulose. Aminobenzylcellulose. In the formation of diazotizable fibers, it has been proposed to superficially esterify cotton fibers with nitrobenzoyl chloride thus forming a cellulose nitrobenzoate, or with nitrated aromatic sulfonic acid chlorides, whereupon the ester is converted by reduction into a cellulose ester of an aromatic aminocarboxylic acid or aminosulfonic acid[2]. Another process is based on the superficial conversion of cotton into a cellulose nitrobenzyl ether (nitrobenzylcellulose) by heating the cellulose with nitrobenzylphenyldimethylammonium chloride (nitroleucotrope), this cellulose ether being subsequently reduced to the diazotizable aminobenzylcellulose[3].

Leucotrope (benzylphenyldimethylammonium chloride) is a reagent capable of readily producing benzylcelluloses. The nitro-leucotropes do not appear to have been previously used as benzylating agents, only *p*-nitrobenzylphenylammonium chloride having been described[4]. *m*-Nitrobenzylphenyldimethylammonium chloride may be prepared from *m*-nitrobenzyl chloride and dimethylaniline; m. pt. 144°.

When cotton is boiled with 1-2% solution of nitro-leucotrope to which slightly more than the quantity of sodium carbonate has been added, a nitrobenzylcellulose forms, in amount depending upon the time of boiling, and the proportion of cotton to solution. For 1 gm. cotton, 100 cc. of 1% nitro-leucotrope solution is required and boiling continued for 10 min., after which the cotton is washed and reduced with hydrosulfite solution at 60-70°. The product

1. H. Dreyfus, E. P. 164375; abst. C. A. 1922, **16**, 495; J. S. C. I. 1921, **40**, 540-A; Ann. Rep. S. C. I. 1921, **6**, 138; Chim. et Ind. 1922, **8**, 654; Chem. Tech. Uebers. 1921, **45**, 327. U. S. P. 1451330; abst. C. A. 1923, **17**, 2505; J. S. C. I. 1923, **42**, 447-A; Chem. Zentr. 1924, I, 2759. F. P. 530891; abst. Chem. Zentr. 1922, II, 899. F. P. Addn. 24082 to F. P. 530891. Australian P. 2543, 1921.

2. P. Karrer and W. Wehrli, Dissertation, 1926, Zurich.

3. D. Peacock, J. Soc. Dyers Col. 1926, **42**, 53; abst. C. A. 1926, **20**, 1325; J. S. C. I. 1926, **45**, 270-B; Chem. Zentr. 1926, I, 3102.

4. Wedekind, Ann. 1899, **307**, 287.

is then diazotized in the usual manner with a nitrous acid solution at 5-7°, washed, then immersed in a solution of the desired component. Coupling with *b*-naphthol produces a rose shade; with H acid, violet; with R salt, rose; with Schaffer's acid, red; with chromotropic acid, red violet; with *m*-phenylenediamine, orange brown; with J acid, red; with phenyl J, red; with carbonyl J, orange red. The shades produced by *p*- and *m*-nitro-leucotrope were indistinguishable. The distinctive feature of these dyeings is their fastness to washing, although they possess the usual fugitiveness to light of azo colors.

According to C. Graenacher[1], diazotizable cellulose fibers may be prepared by converting superficially, cellulose into nitrobenzylcellulose, or partially acetylated fibers into nitrobenzylcellulose acetate, by treating them, after bringing into a reactive condition with nitrated benzyl halides in the presence of an agent which binds acid, other than a caustic alkali, the reaction being conducted at 100°, and the liberated hydrogen halide neutralized by alkali earth hydroxide or carbonate present in the mass. The nitrobenzyl chloride may be used undiluted, or in the form of a solution in an indifferent solvent or a suspension in water.

In an improvement of the above process[2], the nitrobenzyl chloride may be substituted by a homologue as nitroxylyl chloride, forming nitroxylylcellulose; or there may be substituted a chlornitrobenzene derivative (other than an *o*-dinitro-compound) containing halogen in *o*- or *p*-position to the nitro-group, as *o*- and *p*-nitrochlorbenzene, 1-chlor-2.4-dinitrobenzene, forming nitrochlorphenylcellulose and chlordinitrophenylcellulose respectively. Excellent diazotizable fibers are produced in this manner. For example, cotton in the form of mercerized yarn is swollen by immersion for several hours in 10% NaOH solution, the alkali carefully washed out (a tedious operation), and the fibers

1. E. P. 346385; abst. J. S. C. I. 1931, **50**, 672-B; Textile Mfr. 1931, **58**, 306; Chem. Zentr. 1931, II, 1933.
2. C. Graenacher, E. P. 347117; Addn. E. P. 346385.

in moist condition treated at 90-95° for several hours in the presence of lithium carbonate, with fused 1-chlor-2.4-dinitrobenzene. After this operation the cotton is washed and treated with a reducing agent.

The preparation of aminomethylbenzylcellulose and acetamidobenzylcellulose has been described[1]. Other suitable nitrogen-containing aralkylating agents which have been proposed are *o*-, *m*- and *p*-nitrobenzyl chloride, 2.4-dinitrobenzyl chloride, *p*-nitrophenylethyl chloride, 2-nitro-1.4-dichlormethylbenzene, 2-chlormethylbenzylamine, *o*-chlorpropylaniline, 3-acetaminobenzyl chloride, leading to the formation of such bodies as nitrobenzylcellulose, dinitrobenzylcellulose, nitrophenylethylcellulose, etc. The general method of procedure is indicated in the following examples:

1. 162 parts cotton or purified wood pulp are treated with 320 parts 50% NaOH solution, kneaded for 2 hrs., and then added 300-400 parts 2-chlormethylbenzylamine, the addition being made gradually, and the whole maintained at 50-75°. After 4 hrs. a further 160 parts powdered NaOH are worked into the mass, together with 450 parts of the aminoaralkylating agent. After this addition, the temperature may be allowed to rise up to 100°. The product is soluble in acetic acid.

2. *p-Nitrobenzylcellulose. p-Aminobenzylcellulose.* Alkalicellulose prepared as above, using 162 parts cellulose is gradually incorporated with 350-450 parts *p*-nitrobenzyl chloride, and the whole maintained at 50-75°. After 4 hrs. a further 160 parts powdered NaOH are worked in, together with 500 parts of the nitroaralkylating agent. The temperature is then allowed to rise to 100° and maintained until completion of the etherification. Both ethers are soluble in acetic acid.

The nitrobenzylated fibers thus obtained yield on treatment with a reducing agent, as sodium hydrosulfide or sodium hydrosulfite, aminobenzylated fibers which in appearance and color scarcely differ from the parent material.

1. H. Dreyfus, E. P. 344420.

The fibers are diazotizable by means of nitrous acid, and azo-dyestuffs can be developed on them by means of various coupling components.

In the formation of nitrogen-containing aralkyl cellulose esters[1], compounds have been described using as etherifying agents, nitrobenzyl chloride, *p*-nitrophenylethyl chloride, 2-nitro-1.4-dichlormethylbenzene, 2-chlormethylbenzylamine, *o*-chlorpropylaniline and 3-acetaminobenzyl chloride, resulting in the production of nitrobenzylcellulose, nitrophenylethylcellulose, nitrodimethylcellulose, chlormethylbenzylcellulose, and acetaminobenzylcellulose as examples. These ethers are stable, soluble in acetic acid and other solvents, are plasticizable, and have affinity for acid dyestuffs.

Benzylcellulose Esters. Combinations of partially benzylated cellulose with acid radicals, whereby many of the advantages of the ester and ether separately may be combined with a minimizing of the drawbacks, is a field that has been very superfiially explored up to the present time, and offers important possible technical advantages. Combinations of cellulose benzyl ethers with cellulose esters may be either by physical admixture of ester and ether, or by introducing both alkyl, aralkyl or aryl groups in the cellulose and then esterifying.

I. *Physically Prepared Benzylcellulose Esters.* Films and threads having a dull or mat surface are prepared, according to L. Clement and C. Riviere who have patented a process for so-doing[2], by dissolving separately acetylcellulose in acetone, and benzylcellulose in a mixture of acetone, benzene and methyl and ethyl alcohol, combining the two solutions in varying proportions, and soaking the film or threads in this solution. During the evaporative process, the cellulose compound is incipiently gelatinized or precipitated, inducing the subdued effect desired.

1. H. Dreyfus, E. P. 345989; abst. J. S. C. I. 1931, **50**, 626-B; Silk J. 1931, **8**, #87, 54.
2. F. P. 700477; abst. C. A. 1931, **25**, 3834.

Because denitrated nitrocellulose and acetylcellulose are weak in the wetted state and because the cellulose ethers are said to dye with difficulty, E. Berl[1] combines solutions of both by means of harmonious dissolvants, an especially meritorious combination being acetylcellulose with benzylcellulose, whereby decreased susceptibility to moisture and better dyeing is said to result.

II. *Chemically Combined Benzylcellulose Esters.* The general method of procedure in preparing these acyl ethers is to partially benzylate cellulose (the usual method) and then esterify with the respective acid. The converse of etherifying a cellulose carboxylate does not react as smoothly.

Benzylcellulose Nitrate may be prepared, as by the method of British Celanese[2] by preliminarily treating cellulose with nitric acid, but in the subsequent formation of alkalicellulose prior to benzylation, there must be a considerable saponification of the nitric groups. Alternately, benzylcellulose is first prepared, and this nitrated in an esterifying mixture containing 7-70% (some range) of nitric acid. It is claimed that the solubility of benzylcellulose is increased by forming a benzylcellulose nitrate.

Ethylbenzylcellulose Formate may be formed by treating 200 gms. ethylbenzylcellulose containing 1.6 mol. ethoxyl and 0.5 mol. benzoxyl ($C_6H_5CH_2OH$) per mol. C_6 cellulose with 600 gms. 90% formic acid at 20°, when a limpid solution results after having been stirred for 10 hrs. This is poured into agitated water, the ethylbenzylcellulose ester washed to neutrality and dried. The product dissolves in methylene chloride but is insoluble in water[3].

1. U. S. P. 1484004; abst. C. A. 1924, **18**, 1198; J. S. C. I. 1924, **43**, 415-B; Kunst. 1925, **15**, 163. D. R. P. 385962; abst. Chem. Zentr. 1924, I, 1127; Faser. 1924, **6**, 20.

2. E. P. 319691; abst. C. A. 1930, **24**, 2599; Cellulose, 1930, **1**, 150; Silk J. and Rayon World, 1930, **6**, 68. See C. Dreyfus, E. P. 308322, 308587.

3. G. Balle, H. Lange and K. Ost, U. S. P. 1823847; abst. C. A. 1932, **26**, 152. E. P. 347651; abst. C. A. 1932, **26**, 2862; Silk J. 1931, **8**, #89, 54.

Ethylbenzylcellulose Acetate. This ether-ester may be prepared by acetylating with acetic anhydride in the presence of acetic acid as solvent and a small quantity of catalyst[1], a cellulose ether containing 0.5-1.5 alkyl groups and 1-2% benzyl (C_6 molecule). In the actual preparation, 100 of cellulose are soaked in 30% NaOH solution, pressed to 2.5 times the weight of the original cellulose taken, mixed with 100 of ethyl chloride and 14 of benzyl chloride (0.2 mol.), and heated for 3 hrs. at 110°. The reaction product is washed free from salts and alkali by means of water and dried. 115 parts of a monoethylcellulose containing about 1% benzyl are obtained. To 100 parts of this, 160 of acetic anhydride, 500 of acetic acid and 1 of sulfuric acid are added, and acetylation is effected at slow heating for 2 hrs. in a suitable apparatus. Thereupon the ether-acetate is precipitated directly with water without hydrolyzing, and washed free from acid.

Benzylcellulose Linoleate is an example of benzylcellulose ester of a higher fatty acid. This ether-ester may be prepared, for instance[2], by introducing 20 parts benzylcellulose (46% benzyl) with stirring, into 80 parts linoleic acid, heating to 100° with the addition of 0.1-0.3 of boric acid. Heating is continued for 9 hrs. with continuous stirring in an atmosphere of nitrogen at 130-150°. The benzylcellulose soon passes into solution, and after completion of the esterification a homogeneous mass is obtained, from which free linoleic acid is removed by extraction with benzine, in which benzylcellulose linoleate is insoluble. This product is a tough, semi-solid, which on addition of driers dissolves in a mixture of glycol monoethyl ether and xylene. This solution is said to be an excellent lacquer, the coatings of which dry very quickly in the air to a tough, elastic film,

1. I. G. Farbenindustrie, Akt. Ges., and E. Teupel, D. R. P. 521721; abst. C. A. 1931, **25**, 3481. E. Teupel, U. S. P. 1833270. E. P. 331903; abst. C. A. 1930, **25**, 204; J. S. C. I. 1930, **49**, 900-B; Br. Plastics, 1930, **2**, 230.

2. I. G. Farbenindustrie, Akt. Ges., E. P. 334897; abst. Br. Plastics, 1931, **2**, 317; J. S. C. I. 1930, **49**, 1146-B. F. P. 695323; abst. C. A. 1931, **25**, 2866.

which is no longer soluble in benzene, and exhibits a high resistivity to alkalis and dilute acids. Benzylcellulose benzoate, salicylate, phenylacetate, undecylate, laurate, palmitate, stearate, oleate, and abietate[1] have been described, and may be produced by the general method above outlined.

Benzylcellulose Sulfonate. Alkalicellulose reacts with *o*- or *p*-sulfobenzyl chloride to give a water-soluble sulfobenzyl ether, which may be isolated as sparingly soluble calcium or barium salt, or by performing the reaction in alcohol and evaporating the alcohol. The products are uninflammable and textiles may be fireproofed by impregnation with the aqueous solution and precipitation of the calcium, barium or aluminum salt within the fiber. By causing cellulose to react in the presence of an alkaline reagent with an arylhalidesulfonic acid or salt[2], benzylcellulose sulfonate, aluminum benzylsulfonate, sodium benzyl-chloride-sulfonate, sodium benzyl-chloride-*p*-sulfonate and sodium xylylchloride-sulfonate may be prepared. The following 3 examples illustrate the method of procedure, the parts being by weight:

I. Alkalicellulose 18 is kneaded 2 hrs. with 20% alcoholic NaOH 100 parts, and sodium benzyl-chloride-*o*-sulfonate 22.8 in alcohol 100 added, the mixture again kneaded 8 hrs. at 50-60°, whereupon the alcohol is removed by evaporation. The residue forms a whitish mass readily soluble in water, sparingly soluble in alcohol, and almost insoluble in acetone and benzene.

II. Alkalicellulose 36, and 20% aqueous NaOH solution 200, are boiled together for 2 hrs., and the mass then kneaded at 50-60° with 92 parts sodium benzyl-chloride-*p*-sulfonate until the product is entirely soluble in water. Properties nearly the same as in Ex. I.

1. I. G. Farbenind., E. P. 330957; abst. C. A. 1930, **24**, 6013; J.S.C.I. 1930, **49**, 814-B. Cf. Schultz, Farbstofftabellen, 1923, No. 173.

2. *Ibid.* E. P. 277317; abst. J. S. C. I. 1928, **47**, 853-B; Chem. Zentr. 1928, I, 445. U. S. P. 1682382; abst. J. S. C. I. 1929, **48**, 14-B. F. P. 640687.

III. Alkalicellulose, air dry, 18, is soaked in 100 of 20% alcoholic NaOH, and to this mass with stirring, are added 48.2 of sodium xylyl-chloride-sulfonate in 100 of alcohol. The mass is then kneaded until it becomes soluble in water.

By treatment of alkalicellulose with sodium 1'-chlor-1-methylbenzenesulfonate or sodium 1'-chlor-1.3-dimethylbenzenesulfonate, water insoluble cellulose ethers result of the benzylcellulose sulfonate type, applicable for the formation of filaments and films[1].

When alkalicellulose is treated with a mixture of carbon bisulfide and aralkyl halide[2], there is produced a change in the cellulose accompanied by a considerable increase in the weight of the fiber, but the products are insoluble in water and preserve the appearance of the cellulose. However, they have a high capacity for undergoing reactions with organic bases as diethylethylenediamine, piperazine and piperidine, whereby further products are obtainable which exhibit a fundamental change in the dyeing properties of the cellulose. For example, a solution of 100 parts benzyl chloride in 600 parts carbon bisulfide is caused to act on alkalicellulose for 1-4 hrs. in the cold, when a bright yellow product, smelling of garlic, is formed, which is then rinsed in cold and in warm water. This material without drying, is warmed 1-2 hrs. on the water bath with 10% aqueous solution of diethylethylenediamine until the yellow color changes to a gray-white. The dyeing properties will be found to be greatly enhanced.

It has been found that cellulose may be benzoylated at low temperature with resulting slight degradation of the cellulose[3] by conducting the reaction in the presence of ethylene chloride, which acts as a solvent for the cellulose benzoate produced, at temperatures as low as 80°. The reaction is preferably conducted in the presence of pyridine, benzoyl chloride being used as etherifying agent. The com-

1. I. G. Farbenind., Aust. P. 117056. See E. P. 164375.
2. Society of Chemical Industry, E. P. 341237.
3. C. Webber and C. Staud, U. S. P. 1880559.

ponents are heated together under 100° for 18-24 hrs. After the cellulose has been benzoylated to the desired extent, the mass may be poured into hot water which volatilizes the ethylene chloride and precipitates the benzylcellulose.

The method may be carried out specifically as follows: Cotton 2 parts is placed in a suitable container equipped with reflux condenser and 11.5 parts benzoyl chloride, 8 parts pyridine and 20 parts ethylene chloride. The container is steam-heated for 18-24 hrs. until the acylated cellulose has passed into solution. The benzylcellulose is then precipitated with water, washed with ethyl alcohol or other pyridine solvent, and dried at a low temperature.

Other Aryl and Aralkyl Celluloses. With the exception of benzylcellulose and ethylbenzylcellulose, little is known of these bodies. The Farbenfabriken vorm. F. Bayer & Co.[1] have described xylylcellulose as being useful for making celluloid-like plastics and varnishes, while the manufacture of phenylethylcellulose from a patentability viewpoint has been covered by H. Dreyfus[2], and its use in stencil manufacture has been set forth by A. Davis[3]. For benzylcellulose phenyl (or tolyl)urethanes, see the Topic "Cellulose Urethanes."

1. D. R. P. 384007; abst. Chem. Zentr. 1924, I, 268.
2. U. S. P. 1451330, 1451331, 1454960.
3. U. S. P. 1771165; abst. C. A. 1930, **24**, 4598.

CHAPTER X

MIXED CELLULOSE ETHERS

Mixed Cellulose Ethers. The mixed ethers of cellulose divide themselves into the two classes of (1) physical admixtures, and chemical mixtures, i.e., ethers produced at one operation by the use of a mixture of alkylating agents of different reacting groups as a mixture of methyl and ethyl sulfates, or etherification in a two-step process in which a portion of the replaceable hydroxyls in cellulose has been either substituted by one or more groups, and this incompletely etherified cellulose further substituted by alkyl, aralkyl or aryl.

1. *Physically Mixed Cellulose Ethers.* In order to nullify the well known solubility in water of some of the methylcelluloses and the lower ethylated celluloses, especially in water at 20° or lower, and to diminish their tendency to swelling when in the moist state, it is proposed to mix methylcellulose with a small proportion (about 2%) of water-insoluble (highly ethylated) ethylcellulose, either alone or with the addition of rubber latex, or with later alone. The method of procedure is to incorporate the ethylcellulose with the methyl ether by a thorough kneading until the formation of the colloidal solution is complete, films prepared therefrom being undissolvable by water after drying[1].

2. *Chemically Combined Mixed Cellulose Ethers.* In a process patented by the I. G. Farbenindustrie[2], mixed ethers of cellulose or starch are formed by reacting on the carbohydrate in the presence of alkali metal hydroxide, in a mixture comprising a methyl or ethyl halide, and an alkyl compound of which the alkyl group contains three

1. I. G. Farbenind., E. P. 252176; abst. C. A. 1927, **21**, 1548; J. S. C. I. 1928, **47**, 154-B; Chem. Zentr. 1927, I, 1091; Kunst. 1929, **19**, 90.

2. E. P. 326865. F. P. 684330. D. R. P. 522171.

or more C atoms as propyl, butyl or amyl chlorides, to produce methyl (or ethyl) with propyl (butyl or amyl) cellulose, the simplest member being methylpropylcellulose. These mixed ethers, it is claimed, show an unusually low sensitivity to water and great strength especially in film form, notwithstanding the fact that a relatively low degree of alkylation is produced. Thus, for example, whereas films from methylethylcellulose exhibit a high capacity for stretching under the action of water, ethylbutylcellulose films have a very low water-stretching capacity, and ethylamylcellulose still less.

On account of easier and less expensive purification, these ethers are said to possess a technical advantage over the aralkyl-alkyl ethers of cellulose such as ethylbenzylcellulose (see pp. 190, 236, 237, 241, 278, 282, 286, 287, 290).

They may be prepared as by the three following illustrative examples:

1. *Ethylbutylcellulose.* An alkalicellulose comprising cotton 40 to 120 of 50% NaOH solution is heated to about 120° with ethyl chloride 60 and butyl chloride 120, excess of chlorides distilled off and the crude product washed with water. The mixed cellulose ether is soluble in alcohol-benzene, a film produced therefrom possessing the relatively low water expansion of 0.5%. Instead of the above indicated proportions, there may be used 40 of cellulose prepared from pine wood by the sulfite process, 160 of 50% NaOH solution, 80-100 of ethyl chloride and 60 of butyl chloride.

2. *Ethylpropylcellulose.* Cellulose 10, and 50 of 50% NaOH solution are mixed with ethyl chloride and propyl chloride 20 each, excess of alkyl chloride removed by distillation and the crude product washed with water. The ether obtained has an ethoxyl content of 33% and a propoxyl content of 12%, and is soluble in a mixture of alcohol-benzene (1:9). The tearing strength amounts to 10 kgm., the extensibility to 25%, and the water expansion to 0.6%.

3. *Ethylbutylcellulose.* Cellulose as in (2), 10 parts, 50% NaOH solution 60 parts, is heated to about 120° with a mixture of ethyl and butyl chlorides 20 parts each, excess of alkylating agent distilled off, and after washing, a cellulose ether is obtained of 14% butoxyl and ethoxyl 32%, the tearing strength of which is 10-11 kgm., extensibility 25% and water expansion 0.5%.

G. Young[1] has described mixed cellulose ethers as methylethylcellulose, obtained by reacting upon alkalized cellulose with a mixture of methyl and ethyl chlorides, differing in the fact that the products formed are insoluble in methyl or ethyl alcohols and in benzine. The process of L. Lilienfeld[2] is not fundamentally different.

By the etherification of alkalicellulose with mixtures of halogen alkyls[3] by the addition of ethylene oxide or its homologues, a shortening of the reaction time ensues, a lowering of the reaction temperature is possible, and all simple and substituted, saturated and unsaturated halogen alkyls may be used in varying mixed proportions. In addition to the use of ethylene oxide *per se* as reaction accelerators and second etherification components, all compounds which show the ethylene group can be used, and the reaction carried out in the presence of diluents as chlorbenzene. For further acceleration of etherification, catalysts as dimethylaniline may be added.

Inasmuch as the etherification as the result of employment of ethylene oxide, may be carried on under mild conditions as to temperature and pressure, films and other products obtained from these oxyalkylcelluloses are distinguished by their favorable mechanical qualities, especially noticeable in their stretching and folding tests. The process is exemplified in the following four examples:

1. U. S. P. 1504178. E. P. 184825. F. P. 555279.
2. E. P. 6035, 1913. U. S. P. 1188376.
3. I. G. Farbenind., D. R. P. 527616; abst. C. A. 1931, **25**, 5288. Swed. P. 72244. F. P. 686598; abst. C. A. 1931, **25**, 592. E. P. 345028; abst. J. S. C. I. 1931, **50**, 672-B. U. S. P. 1877856.

1. *Benzyloxyethylcellulose.* Hydroxyethylbenzylcellulose. One mol. alkalicellulose is mixed with 6 mol. benzyl chloride and 1 mol. ethylene oxide in an autoclave heated to 50°, the mixture rising to about 120° by means of the liberated heat of reaction. After the course of the reaction is complete, the mixture is re-heated and held at slightly over 100° for 2-3 hrs. As soon as a mass free from fibers is obtained, it is cooled, kneaded with ethyl alcohol and extracted. After removal of excess benzyl chloride the mass is washed with water to dissolve the alkali present and the NaCl formed. The resulting benzyloxyethylcellulose is soluble in chloroform, diethylene oxide and benzene; insoluble in benzine, methyl or ethyl alcohols and ether.

2. *Benzyloxybutylcellulose,* Hydroxybutylbenzylcellulose. Alkalicellulose 1 mol. is worked up with 6 mols. benzyl chloride and 1.5 mols. butylene oxide according to Ex. 1. There is obtained a benzyloxybutylcellulose of solubility as in Ex. 1.

3. *Propyloxyethylcellulose,* Propylhydroxyethylcellulose. Alkalicellulose 1 mol. is warmed in an autoclave with 3 mols. ethylene oxide and 20 mols. propyl chloride at 50°, whereupon the liberated heat of reaction raises the mass to about 120°. After 5-7 hrs. a fiber-free mass results, which is heated on a water-bath in order to recover excess propyl chloride. After the NaCl is formed and excess alkali has been washed out with water, the reaction product is dried. There is obtained a propyloxyethylcellulose soluble in benzene.

4. *Chlorbenzyloxyethylcellulose.* Alkalicellulose 12 is worked up with 25 of 2-chlorbenzyl chloride and 1.25 of ethylene oxide according to Ex. 1, there being obtained 5.5 of a chlorbenzyloxyethylcellulose.

H. Dreyfus[1] has described the production of benzylchlorbenzylcellulose by the use of a mixture of benzyl chloride and chlorbenzyl chloride; C. Graenacher[2] a nitroben-

1. U. S. P. 1451330.
2. E. P. 346385; abst. J. S. C. I. 1931, **50**, 672-B.

zylcellulose; and B. Wendt and H. Bincer[1] a physical mixture of cellulose nitrate and ethylbenzylcellulose by methods basically analogous to those above.

By the introduction of only 0.5-2% benzylcellulose in a 0.5-1.5 alkyl, ethylcellulose[2], it is claimed that swelling power and solubility in water of the ethylcellulose is counteracted, it being immaterial whether the benzyl ether is produced together with the alkyl ether of cellulose in a single process in which benzyl chloride is added to an alkylating mixture, or whether it is only caused to react after the cellulose alkyl ether has been formed.

The amount of benzyl chloride added is about 0.2 molecular proportion calculated on a C_6 cellulose, and taking into consideration the saponification of benzyl chloride to benzyl alcohol when using the above molecular proportion, this results in the formation of a mixed ether of about 1% benzyl content. Nitrobenzyl chloride may be used, forming an ethylnitrobenzylcellulose, and all these ethers may be esterified, especially acetated. The following example is illustrative:

Cotton or wood pulp 100 is soaked with 30% NaOH solution, pressed to 2.5 times the original weight of the cellulose, mixed with ethyl chloride 100 and benzyl chloride 14, and heated for 3 hrs. at 110°. The reaction product is washed free from salts and alkalis and dried. Yield 115 of a monoethylcellulose containing 1% benzyl. To 100 parts of this, 160 of acetic anhydride and 500 of acetic acid are added with 1 part sulfuric acid, and acetylation carried on at 30° for 2 hrs. Thereupon the ether-acetate is precipitated directly with water without hydrolyzing, and washed free from acid. The ethylbenzylcellulose acetate obtained, being a monoethyl-1.5-acetylcellulose containing about 1% benzyl, is soluble in acetone, ethyl acetate, and chlorinated hydrocarbons, and possesses excellent stability to water.

1. D. R. P. 498028.
2. I. G. Farbenind., E. P. 331903; abst. C. A. 1931, **25**, 214.

The H. Dreyfus process for mixed cellulose ether manufacture[1] is indicated by the following example:

Cellulose or a near conversion product of it not soluble in alkali is impregnated with 50% NaOH solution, so that about 4 molecular equivalents of NaOH are contained in it, relative to one molecular weight of cellulose (C_6 basis). The latter is then kneaded with 2 mols. benzyl chloride and afterwards with one mol. ethyl sulfate. The reaction with benzyl chloride takes place at 50-100° and with ethyl sulfate at 50° or lower. After 2-4 hrs. 6 molecular equivalents of NaOH in the form of powder are added, and the mass kneaded with a further 3 mols. benzyl chloride at between 50-150°, and afterwards with another 2 mols. ethyl sulfate at 50° or lower. Finally 3 mols. powdered NaOH and another 3 mols. diethyl sulfate are added. The ethylbenzylcellulose formed is said to be freely soluble in organic liquids and substantially unaffected with water.

Ethylbutylcellulose may be prepared by treating 10 parts cotton paper with 20 parts 50% NaOH solution to which 10.5 of powdered NaOH are added and the mass thoroughly incorporated[2]. A mixture of 20 ethyl chloride and 30 butyl chloride by weight is then slowly added, the mass being in a horizontal pressure vessel with stirring arrangement. Heat for 2-3 hrs. at 110° and then at 140° for the same length of time. Then the secondary products are distilled off, the crude product washed and dried. The ethylbutylcellulose formed is soluble in benzene-alcohol 1:1. In the above formula and method of procedure, if the alkylating agent is 14 methyl chloride, 16 ethyl chloride and 24 butyl chloride, methylethylbutylcellulose results, of approximately monomethyl-monoethyl-monobutyl, being about the same proportion of entering alkyl of each. If the alkylating agent be 14 methyl chloride, 16 ethyl chloride, 21 propyl chloride, then a methylethylpropylcellulose is formed. Likewise 16 ethyl chloride, 21 propyl chloride and 26 butyl

1. U. S. P. 1451331. E. P. 164375. Belg. P. 290448. See also E. P. 164374, 164377.
2. I. G. Farbenind., E. P. 346426.

chloride give rise to ethylpropylbutylcellulose. All these mixed ethers in their pure state are soluble in an equal volume of benzene-alcohol, and toluene-alcohol, in the latter, to a lower solubility degree.

The I. G. Farbenindustrie have described mixed cellulose ethers[1], obtained by etherifying at ordinary or increased pressure with 10-30 mols. alkylant and 2 mols. aralkylant, as specifically indicated in the following examples:

1. *Ethylbenzylcellulose.* 900 parts wood pulp in sheet form are treated with 50% NaOH solution at 30° (comprising 3-6 mol. alkali to 1 mol. cellulose), pressed, aged for a short time at 20°, and then etherified with a mixture of 5460 of ethyl chloride and 762 parts benzyl chloride (14 mol. ethyl to 1 mol. benzyl) at 110-120° for 6-7 hrs. The reaction product is then washed with water to remove excess of alkali and sodium chloride and dried. The diethylmonobenzylcellulose formed is soluble in aliphatic hydrocarbons.

2. *Methylbenzylcellulose.* 960 parts cotton linters in sheet form are treated with 55% NaOH solution 2 hrs. at 40-45°, excess alkali removed by vacuum until the weight has been reduced to 2700 parts. It is then placed in an autoclave with 6000 parts methyl chloride and 1500 parts benzyl chloride and heated at 70-80° for 3-4 hrs. Excess of alkylant is then washed out with water, the cellulose ether being unaffected by water.

3. *Ethylbenzylcellulose.* 960 parts wood pulp in sheets are treated 2 hrs. at 45-55° with 60% NaOH solution, pressed to 2500-2600 parts, and allowed to age at 20-22°. The alkalicellulose is then mixed with 5500 parts ethyl chloride and 1200 parts benzyl chloride and heated under pressure 4 hrs. at 110-120°. The mixed cellulose ether is soluble in alcohol-benzene 1:1 to a clear solution resistant to water.

1. Aust. P. 126586.

4. *Methylxylylcellulose.* 163 parts wood pulp sheets are treated with 2000 parts 6% lithium hydroxide solution (which is unduly expensive), and reduced to 400-500 parts by vacuum distillation. The lithium cellulose is then etherified with a mixture of 1540 parts methyl sulfate and 140 parts *p*-xylyl chloride at 50-80°. The methyl-*p*-xylylcellulose is insoluble in water.

By reacting upon alkalicellulose with an alkyl halide of the group consisting of saturated, unsaturated, substituted or unsubstituted alkyl halides in the presence of an alkylene oxide and a diluent, alkylhydroxyalkylcelluloses as methylhydroxypropylcellulose are formed[1], soluble in chloroform, diethylene dioxide and benzene, insoluble in benzine, methyl alcohol, ethyl alcohol and water.

Mixed cellulose ethers are also obtainable through simultaneous action of an excess of alkylating and arylating agent upon alkalicellulose at elevated temperatures and pressures, methylphenyl-, ethylphenyl-, methylxylyl-, ethylxylyl-, propylphenyl-, propylxylyl-cellulose resulting. Mixtures, which for every 10-30 mols.[2] alkylating agent contain up to 2 mols. of an aralkylhalogenide are used, the temperature being so regulated that a hydrolysis of the excess of alkylating agent is avoided.

M. Hartmann[3] has described cellulose derivatives formed by causing such halogen-alkylamines as contain a halogen atom capable of being exchanged, to react with such cellulose compounds as are capable of reaction with compounds containing exchangeable halogen atoms. As halogen alkylamines may be used chlorethyldiethylamine, chlorethylethylaniline as free base, or their hydrochlorides. Reacting compounds may be used in various proportions. Into 1 mol. $C_6H_{10}O_5$, 1-3 mols. of the chloramine ester may be introduced, so that for instance, 1 OH group

1. I. G. Farbenindustrie, M. Hagedorn and E. Rossbach, Can. P. 304221.
2. I. G. Farbenindustrie, Aust. P. 126586; abst. Chem. Zentr. 1932, I, 2790.
3. U. S. P. 1777970. F. P. 680956. See F. P. 486575, 687301, 689557. Swiss P. 141556, 142175, 144227.

of the cellulose corresponds with 1 mol. of chloralkylamine. However, it is possible to go below the molecular ratio 1:1. By the action of a small proportion of chloralkylamine there is obtained a basic cellulose derivative which has little tendency to swell, whereas by a stronger reaction, products result which swell more readily.

These basic cellulose ethers show, as compared with cellulose, an essential variation in properties. For example, they may be quickly and intensely dyed with acid dyestuffs, and also show an enhanced affinity for other classes of dyestuffs. These ethers may also be used as parent material for further treatment, as by etherification with ethyl chloride, or by formylation or acetylation, forming so-called ether-oxides or ether-esters.

The latitude of the process is indicated by the following examples:

1. *Diethylaminoethylcellulose.* 15 parts loose cotton are converted into alkalicellulose, and after pressing, subjected to the action of 18 parts chlorethyldiethylamine hydrochloride. By the excess of alkali the organic base is liberated, the goods are kneaded for 8 hrs. and then washed. The cellulose ether may be purified by solution in Schweitzer's reagent and re-precipitation.

2. *Diethylaminoethylcellulose Acetate.* 1 part diethylaminocellulose is heated with 2 parts glacial acetic acid and 4 parts acetic anhydride in the presence of zinc chloride until the fibrous material has passed into solution. The product is then precipitated by the addition of water and washed until neutral.

3. *Diethylaminomethylcellulose.* A bath is prepared containing 1 part chlorethyldiethylamine dissolved in 10 parts water, 2 parts of 10% solution of the quaternary methyl sulfate of mono-oleyldiethylethylenediamine, and 40 parts milk of lime of 5% strength, whereupon 10 parts cellulose acetate silk are allowed to rotate in this solution for 1 hr. at ordinary temperature. The acetate silk thus

treated has its luster preserved and is quickely colored with acid dyestuffs.

4. A solution containing 1 part chlorethylpiperidino hydrochloride in 10 parts water is mixed with 5 parts 10% NaOH solution, and 10 parts viscose rayon immersed in the solution for 1 hr.

The I. G. Farbenindustrie[1] prepare hydroxyalkylcellulose and esters therefrom in the following manner:

1. An oxyethylcellulose having two of the three cellulose OH groups etherified, and obtained by the action on mercerized cellulose at 250° of ethylene oxide is acetylated with a mixture of acetic anhydride, acetic acid and a small quantity of sulfuric acid, the reaction being accompanied by a considerable evolution of heat. The hydroxyethylcellulose acetate is colorless and amorphous, soluble in acetone, cyclohexanone, alcohol at the boiling point, and mixtures of alcohol and benzene. Insoluble in water, benzene and ligroin. Films obtained by evaporation to dryness are said to be much more flexible than cellulose acetate films, that is, the introduction of the oxyethyl-group in cellulose acetate materially increases the flexibility of films made therefrom. Oxyethylcellulose phthalate or succinate may be prepared in a similar manner. These latter two dissolve in benzene-alcohol or cyclohexanone.

The above patent also describes the preparation of mixed esters of sorbitol as the formo-(or aceto- or benzo-)-oxalate, -maleate, -succinate or -phthalate.

It has also been found in the preparation of mixed ethers of carbohydrates[2] that action of alkylene oxides upon alkalicellulose takes place in a surprisingly easy manner also in an acid medium. For the accomplishment of this reaction, inorganic as well as organic acids or their functional derivatives may be used, such as acid halides, acid anhydrides, acid amides and acid esters. The acid concentration must be kept sufficiently low so as to prevent

1. F. P. 652383. See F. P. 700880, and Addn. 40124 thereto.
2. I. G. Farbenindustrie, D. R. P. 542867.

the alkylene oxides from being converted with water into glycols. Suitable are $N/5$ sulfuric acid or $N/5$ hydrochloric acid. At these acid concentrations and with careful cooling, the conversion of the alkylene oxides with water may be repressed in favor of the etherification of the cellulose. In this way oxyalkylcellulose of low degree of etherification results, and which may be readily acetylated or otherwise esterified.

The oxyalkylation under certain circumstances may be kept so low that oxyalkyl-rests in the cellulose may be detected only by qualitative methods. The methods are illustrated as follows:

1. 100 gms. linters are soaked with 500 cc. $N/10$ sulfuric acid and carefully mixed with a solution of 100 gms. ethylene oxide in 500 cc. acetone in a glass flask in a mixing apparatus, the temperature being maintained at 20-25° meanwhile. After 24 hrs. the highest degree of oxyethylation attainable under these circumstances is achieved, and the reaction product purified by washing and subsequently boiling with water, then dried. The oxyethylcellulose obtained may be acetylated in the usual manner to oxyethylcellulose acetate without any previous treatment, on account of a diminished sensitiveness to water.

2. 100 gms. linters are kneaded with 400 gms. glacial acetic acid and 3 gms. sulfuric acid for 1 hr. By repeated washing with benzene, petroleum ether, ether or dichlormethane (methylene chloride) the excess glacial acetic acid is removed, while the sulfuric acid remains absorbed on the fibers. Then a solution of 75 gms. ethylene oxide in 300 cc. benzene is added, and the reaction temperature kept at 20° by careful cooling. After 2-3 hrs. the etherification is substantially completed, but the reaction mixture is left to stand for 10 hrs. After acetylation, a primary acetone-soluble oxyethylcellulose acetate is formed.

O. Ernst, K. Sponsel and G. Balle[1] prepare cellulose ethers by a continuous process by continually steeping a

1. U. S. P. 1863745.

roll of cellulose weighing 100 kgm. at 55° in a 60% NaOH solution, squeezing out excess of alkali until the weight is reduced to 250 kgm. and then wound up on a winding trestle together with a wire netting cloth. It is to be remembered that alkalicellulose in this condition has little tensile strength. The roll thus obtained is then placed in an etherifying vessel and methylated or ethylated in the usual manner for 8 hrs. at 70° under 5 atms. pressure. The product is washed with hot water and dried. Observe that the alkalicellulose is not subjected to an ageing treatment. The cellulose ether obtained dissolves in alcohol-benzene 1:1 to a clear, viscous solution, likewise in ice-cold water.

If it is desired to reduce the viscosity of the formed cellulose ether, it is treated with an acid gas as HCl at 25° until the desired reduction in viscosity has been attained[1]. The acid and the cellulose ether solution should be devoid of moisture.

Cellulose ether-esters may also be prepared from wood pulp[2], as synopsized as follows:

1. 100 gms. bleached sulfite wood pulp are steeped in an excess of 17.5% NaOH solution, pressed to 2.5-3 times the original weight of the cellulose, then disintegrated for about 2 hrs. at 15-20°. From 50-60 parts ethyl sulfate are then added, and the whole mixed for 1 hr. The mass is then kept 204 days at 15-20°, preferably in an inert atmosphere as nitrogen. This intermediate product formed is an ethylcellulose containing about 5% ethoxyl. The product is next introduced into a mixture of 225 parts acetic anhydride, 500 parts acetic acid and 2.5 parts sulfuric acid for each 100 parts cellulose ether. Acetylation proceeds smoothly at 18-20°, yielding a viscous solution from which the ethylcellulose acetate may be precipitated at once by the addition of water, or the solubility may be modified by partial hydration before precipitation, in a manner analogous to the transformation of chloroform-soluble, acetone-

1. E. Reid, U. S. P. 1864554.
2. W. Glover and Courtaulds, Ltd., E. P. 268552.

insoluble cellulose acetate into the chloroform-insoluble, acetone-soluble modification by a diminution of the acetyl percentage.

If a cellulose ether be heated with an organic acid, some of the organic acid groups will combine with the cellulose ether to form a mixed ether-ester[1], the reaction being quite similar to the simple esterification reaction that takes place on heating alcohol with an acid. The method of operating is indicated by the following explicit examples:

1. *Ethylcellulose Acetate.* 10 parts ethylcellulose are dissolved in 100 parts glacial acetic acid, and after digesting at 100° for 41 hrs. in a container fitted with reflux condensation, there is produced an ethylcellulose acetate containing 7.3% acetyl, soluble in ethylene chloride, 1.4-dioxane, benzene-alcohol, ethylene chloride-alcohol, chloroform-alcohol, or even in alcohol or benzene alone.

2. *Ethylcellulose Lactate.* 20 parts ethylcellulose are digested with 85% lactic acid and 75 parts 1.4-dioxane, the reacting mixture being then heated to 100° for 90 hrs. The ethylcellulose lactate formed contains 4.7% lactyl.

Methyl-, ethyl- or benzyl-cellulose may be prepared by the G. Miles method[2] by treating 100 parts cellulose in the form of alkalicellulose with 7 molecular proportions of etherifiant, with the addition of sufficient caustic soda to maintain an alkaline reaction. Etherification proceeds for 9 hrs. at 40-45°. If ethyl sulfate is used as ethylating agent, the ethylcellulose formed contains no cold water soluble cellulose ethers.

Cellulose varnishes have been described[3], especially suitable for coating surfaces, in which methyl- or ethylcellulose esters of the higher fatty acids as ethylcellulose laurate, methylcellulose myristate or methyl- or ethyl-cellulose palmitate are used.

1. C. Webber and C. Staud, U. S. P. 1880558.
2. U. S. P. 1864546.
3. I. G. Farbenindustrie, E. P. 317987; abst. J. S. C. I. 1929, **48**, 863-B.

Cellulose Methylene Ether. Methylenecellulose. Methylene ethers of carbohydrates have been known for some time, especially these and acetone derivatives of sugars. E. Fischer[1] in 1895, and B. Tollens[2] in 1899, isolated a methylene glucose by allowing formalin with HCl to remain in contact with glucose for a considerable period. Many attempts have been made to condense cellulose and starch with formaldehyde in the presence of an alkali. E. Blumer[3] allowed a mixture of 5° Be. NaOH and formaldehyde to act upon starch for some hours, then heated for a short time and washed until odorless, then with acetic acid and finally dried, while H. Karplus[4] sought to increase the water-resisting properties of cellulose by submission to formaldehyde vapors at 90°. While the formaldehyde may temporarily alter the physical characteristics of the cellulose, no stable condensation product of formaldehyde with cellulose is formed.

F. Beltzer[5] has given a summation of the action of formaldehyde upon starch, and A. Classen[6], X. Eschalier[7]

1. Ber. 1895, **28**, 2496; abst. J. C. S. 1896, **70**, i, 4.
2. Ber. 1899, **32**, 2585; abst. J. C. S. 1900, **78**, i, 15.
3. D. R. P. 179590; abst. Papier Ztg. 1907, **32**, 309, 398; Chem. Ztg. 1907, **31**, 85; C. A. 1907, **1**, 1507; J. S. C. I. 1907, **26**, 1066; Chem. Zentr. 1907, I, 383; Wag. Jahr. 1906, **52**, II, 79; Zts. ang. Chem. 1907, **20**, 1246; Jahr. Chem. 1905-08, II, 948.
4. E. P. 234618.
5. Eighth Intl. Cong. Appl. Chem. 1912, **7**, 7; abst. C. A. 1912, **6**, 3185; 1913, **7**, 551; J. S. C. I. 1912, **31**, 868; Kunst. 1912, **2**, 442; Wag. Jahr. 1912, **58**, II, 445; Zts. ang. Chem. 1913, **26**, II, 303.
6. D. R. P. 92259, 1896; abst. Chem. Zentr. 1897, II, 456; Chem. Ztg. 1897, **21**, 539; Jahr. Chem. 1897, **50**, 1516; 1898, **51**, 1242; Wag. Jahr. 1897, **43**, 623. D. R. P. 94628, 1896; abst. Chem. Zentr. 1898, I, 295; Chem. Ztg. 1897, **21**, 1004. D. R. P. 99378, 1899; abst. Chem. Zentr. 1899, I, 160; Chem. Ztg. 1898, **22**, 963; Jahr. Chem. 1898, **51**, 124; Wag. Jahr. 1898, **44**, 559. D. R. P. 94282, 1896; abst. Chem. Zentr. 1898, I, 229; Chem. Ztg. 1897, **21**, 963; Jahr. Chem. 1897, **50**, 1645; Wag. Jahr. 1897, **43**, 623; Friedlaender, 1900-1902, **6**, 1129. E. P. 1144, 1897; abst. J. S. C. I. 1897, **16**, 459. The combination of formaldehyde with starch has been called "amyloform," while that with dextrin has been named "dextroform." For additional data on amyloform and glutols, see A. Classen, Therap. Monatsh. 1897, **11**, 33; Muench. med. Wochschr. **44**, 307; abst. Chem. Zentr. 1897, I, 395, 939. C. Schleich, Therap. Monatsh. 1897, **11**, 97; abst. Chem. Zentr. 1897, I, 715. A. Gottstein, Therap. Monatsh. 1897, **11**, 95; abst. Chem. Zentr. 1897, I, 715.
7. U. S. P. 995852. E. P. 25647, 1906; abst. J. S. C. I. 1907,

and E. Bloch-Pimentel[1] processes for the fixation of formaldehyde with carbohydrates chemically in an alkaline medium. According to H. Maggi and G. Woker[2], the dialysate from a mixture of starch and formaldehyde has properties of dextrin and the simpler carbohydrates, whereas V. Syniewsky[3] found that potato starch left for two months in contact with 40% formalin gave a mobile, opalescent fluid which should be regarded as a definite compound. F. Wood[4] repeating the work of Eschalier in 1920, found that two distinct stages occurred in the reaction, the fibers soon losing their solubility in cuprammonium hydroxide but adsorbed a large quantity of copper solution preferentially, while in the later stage when the moisture content became small, the fibers were quite inert to copper solution. C. Cross and E. Bevan[5] "generally verified" Eschalier, and found 0.2-0.3% formaldehyde fixed by the cellulosic fiber—a negligible quantity, while W. Bruckhaus[6] increased the strength of rayon by treatment with formaldehyde in the presence of alum and lactic acid. F. Beltzer regarded Eschalier's product as a formal of cellulose (a methylene ether).

26, 1292. F. P. 374724, 1st addn. 8122, 1907; 2nd addn. 9904, 1908; 3rd addn. 9905, 1908; 4th addn. 10760, 1909; abst. J. S. C. I. 1907, **26**, 821, 1292; 1908, **27**, 157; 1909, **28**, 362, 1121.

1. U. S. P. 1044434, 1912; 1234720, 1917; abst. C. A. 1913, **7**, 221; 1917, **11**, 2611. E. P. 7893, 1912; abst. C. A. 1913, **7**, 3227.

2. Ber. 1918, **51**, 790; abst. J. C. S. 1918, **114**, i, 375; C. A. 1918, **12**, 700. Cf. G. Woker, J. S. C. I. 1916, **35**, 1268. M. Jacoby, Ber. 1919, **52**, 558; abst. J. S. C. I. 1919, **38**, 508-A. W. v. Kaufman and A. Lewite, Ber. 1919, **52**, 616; abst. J. S. C. I. 1919, **38**, 508-A. W. Biedermann, Fermentforsch. 1916, i, 474. J. Wohlgemuth, Biochem. Zts. 1919, **94**, 213.

3. Ann. 1902, **324**, 201; abst. J. C. S. 1903, **84**, i, 68; Chem. Zentr. 1902, II, 1248. Bull. Acad. Sci. Cracow, 1902, 435; abst. J. S. C. I. 1902, **21**, 1341; Chem. Zentr. 1902, II, 986; Jahr. Chem. 1902, **55**, 1039.

4. J. S. C. I. 1931, **50**, 411-T; abst. C. A. 1932, **26**, 1254. See F. Wood, J. S. C. I. 1930, **49**, 1079-C. & I.; Chem. Age. (London) 1930, **23**, 548; abst. Nitrocellulose, 1931, **2**, 102. (See p. 253, n. 1.)

5. J. S. C. I. 1908, **27**, 1187.

6. Kunstseide, 1926, **8**, 115; abst. C. A. 1927, **21**, 648; J. S. C. I. 1926, **45**, 659-B. Kunstseide, 1926, **8**, 319; abst. C. A. 1927, **21**, 6531. Oest. Chem. Ztg. 1926, **29**, 156; abst. C. A. 1926, **20**, 3818; Rayon, 1926, **3**, #11, 20. See D. R. P. 348149, 365668.

M. Samec and S. Ferjancic[1] examined sulfuric acid-formaldehyde mixtures (60-75% sulfuric acid, 5-10% formalin) from the viewpoint of cellulose hydrolysis, and demonstrated that formaldehyde hastened the process. Apparently the only known compound containing a hydroxymethyl compound of cellulose is the compound described by H. Buston and S. Schryver[2], of formula $OH.CH_2.CH(OH).O.CH_2.OH$,—being a three C atom carbohydrate obtained from cabbage leaves—the molecule, notwithstanding its smallness, being unusually stable. Formaldehyde-treated cellulose possesses deeper dyeing properties, and has been applied as a test for mercerization by H. Mannell[3], as a measure of the greater activity of mercerized cellulose compared with normal cellulose. The amounts of formaldehyde fixed (indicative of the extent of conversion into methylene ether) are in the ratio of about 1.4 to 1[4].

F. Wood (loc. cit.) immersed cellulose containing increasing amounts of water in a mixture of HCl and paraform in an inert solvent, and found that when a saturated aqueous HCl solution supersaturated with paraform was present in small amount, there was formed a dye- and water-resisting cellulose ether. F. Wood and E. Butterworth[5] showed that small amounts of paraform induce no swelling, while larger amounts do so. L. Meunier and R. Guyot[6] in examining the Eschalier process have measured the diminution in swelling by means of the centrifuge method[7], and J. Blanksma[8] published in 1929 experiments carried out in 1908 on the action of heat on starch and cellulose with trioxymethylene in sealed tubes.

1. Kolloid Chem. Beih. 1921, **14**, 209; abst. C. A. 1922, **16**, 1011.
2. Biochem. J. 1923, **17**, 470; abst. C. A. 1924, **18**, 1003.
3. J. Text. Inst. 1926, **17**, 247-T.
4. A. Urquhart and A. Williams, J. Text. Inst. 1925, **16**, 155; abst. C. A. 1925, **19**, 2749.
5. J. S. C. I. 1927, **46**, 375-T.
6. Compt. rend. 1929, **188**, 506; abst. Rev. gen. Colloides, 1929, **7**, 53.
7. H. Coward and L. Spencer, J. Text. Inst. 1923, **14**, 28-T; abst. C. A. 1923, **17**, 1553.
8. Rec. trav. chim. 1929, **48**, 561.

To prepare methylene ethers of cellulose, methylene derivatives as methylenating agents similar to methyl sulfate as methylating agent were employed, these including chlormethyl alcohol, monochlormethyl ether, dichlormethyl ether, methylene sulfate, methylene disulfate, dichlordimethyl sulfate, chlormethoxysulfonyl chloride and chlordimethyl sulfate. It was found that methylene compounds containing no oxygen atom are insufficiently reactive to be utilized at convenient temperatures, methylene sulfate and dichlormethyl ether possessing the drawback of being easily hydrolyzed. Monochlordimethyl sulfate, first described by J. Houben and H. Arnold[1] was found to give a mixed cellulose methylmethylene ether when applied to alkalicellulose, the etherifying agent reacting as an equimolecular mixture of dichlormethyl sulfate and methyl sulfate.

Dichlordimethyl sulfate and chlormethoxysulfonyl chloride[2] with alkalicellulose gave an ether of 17.2% maximum methylene oxide content[3], 10 to 15 treatments being necessary to obtain the result. Cellulose methylene ether (methylenecellulose) thus obtained has a fibrous structure, is insoluble in cuprammonium hydroxide and all solvents tried, stable to boiling with $N/1$ NaOH solution, but quantitatively hydrolyzed with $N/1$ mineral acids. The formula deduced is $C_6H_7O_2(OH)(O_2CH_2)$ in which there is still one free hydroxyl group. The isolation of cellulose monomethylene opens up the possibility of investigation of reactions of the third hydroxyl group in the molecule and the production of definite mono-substituted derivatives of cellulose.

La Soie Artificielle[4] have described a product formed

1. Ber. 1907, **40**, 4306. As a result of his investigations of the action of formaldehyde upon starch, M. Schenk, Helv. Chim. Acta, 1913, **14**, 520; abst. C. A. 1932, **26**, 296, concludes that formaldehyde, as in methylal formation with methyl alcohol, etherifies the cellulose with the formation of hydroxymethylcellulose.

2. K. Fuchs and E. Katscher, Ber. 1927, **60**B, 2288; abst. C. A. 1928, **22**, 382. See D. R. P. 505687.

3. F. Wood, Nature, 1929, **124**, 762; abst. C. A. 1930, **24**, 1214.

4. E. P. 9196, 1915; abst. C. A. 1916, **11**, 3159. F. P. 477655; Swiss P. 74231; abst. J. S. C. I. 1916, **35**, 597. X. Eschalier, E. P. 25647, 1906; abst. J. S. C. I. 1907, **26**, 1292. F. P. 374724; abst. J. S. C. I. 1907, **26**, 821; Mon. Sci. 1908, **69**, 29.

by the action of trioxymethylene upon cellulose, the latter being treated with formaldehyde and ferric chloride, desiccated, and then heated. The reaction takes place in the second phase. Coincidental to the formaldehyde treatment may be added formic, acetic or butyric acids—perhaps resulting in a partial esterification effect—, the final product being a transparent mass, unaffected by water.

Alkyl Lignin. Wood Ethers. Our knowledge of etherified lignins and the woods in general, rests primarily upon the investigations of E. Heuser and co-workers, H. Urban, A. v. Wacek and those whose researches have culminated in the issuance of patented processes for the manufacture of these ethers from wood and wood products.

From several reactions of lignin, it appears that it contains hydroxyl groups, and P. Klason[1] has sought to determine the number, particularly in the calcium lignonesulfonates obtained from sulfite liquor, by the action of *p*-brombenzyl chloride, and later with methyl sulfate[2]. E. Heuser and C. Skiöldebrand[3] introduced 34.6% methoxyl into the lignin molecule by means of alkaline methyl sulfate, the lignin being obtained by the method of the R. Willstaetter and L. Zechmeister method[4] of hydrolyzing the cellulose with 42% HCl, from which they calculated 4 OH groups for the lignin. It has been established[5] that it is unnecessary to dissolve completely the lignin in alkali solution, only possible by the use of a large excess of NaOH combined with pressure.

In the method of E. Heuser, R. Schmitt and L. Gunkel, 5 gms. lignin prepared by the action of 500 cc. HCl (density 1.2) upon 50 gms. fat-free sawdust gave a lignin yield of

1. Papierfabr. 1910, **8**, 1285; abst. J. S. C. I. 1911, **30**, 79; C. A. 1911, **5**, 3155. Schriften des Ver. der Zellstoff und Papierchemie, 1911, 2.
2. Ber. 1920, **53**, 1868; abst. C. A. 1921, **15**, 860.
3. Zts. ang. Chem. 1919, **32**, 44; abst. J. S. C. I. 1919, **38**, 215-A.
4. Ber. 1913, **46**, 2401; abst. C. A. 1913, **7**, 3412.
5. E. Heuser, R. Schmitt and L. Gunkel, Cellulosechemie, 1921, **2**, 81; abst. C. A. 1922, **16**, 490; J. C. S. 1922, **122**, 325. Papierfabrik. 1921, **19**, 81; abst. Chim. et Ind. 1922, **8**, 141.

27.4-28.2%, the methyl-lignin averaging 14.65% methoxyl; but when *suspended* in 10% NaOH and treated at 60° with 30 gms. methyl sulfate, gave 98% of methyl-lignin with a methoxyl content of 20.65% gradually rising to a maximum of 26.29% upon repeated methylations. They also methylated methyl-free lignin with methyl sulfate at 60-70°, obtaining a black mass of 100% lignin etherified, and found that the lignin, for purposes of methylation, must, under no circumstances, be *dissolved* in alkali.

The lignin used by H. Urban as the basis of his investigation was obtained from finely ground fir wood containing 4.7% methoxyl and submitted to treatment by the Willstaetter and Zechmeister above mentioned. On methylation of this lignin (best at ordinary temperature) the methoxyl content rapidly rose to a maximum value of 32% cellulose, under similar conditions methylating to a maximum of 44.5%, and wood to 40.9% methoxyl respectively. From this maximum methylated lignin, on treatment with a mixture of phosphoric and hydrochloric acids, a methyllignin of about 25% methoxyl was obtained, which could be further methylated to 32% methoxyl. Potash fusion of this compound yielded 14% protocatechuic acid, and on hydrolysis was reduced to a 24% methoxyl content. The separation of lignin from cellulose in methylated wood by solution of the cellulose portion in chloroform is unsatisfactory. Wood may be converted into an acetyl compound, soluble in chloroform, but of low viscosity, if treated with chlorine in the usual acetylating mixture.

According to A. v. Wacek[1], the methylation of beech wood flour gives a product of 39-39.4% methoxyl as maximum ether content, and does not swell and hardly dissolves in solvents of lignin and methylcellulose. If, after cold hydrolysis with 17% HCl, it is refluxed with alcohol, 70-77% dissolves, and the residue forms a swollen, gelatinous

1. Ber. 1928, **61**B, 1604; abst. C. A. 1928, **22**, 4808; Can. Pulp and Paper Mag. 1929, 187; J. S. C. I. 1928, **47**, 1227-A; Chem. Zentr. 1928, II, 2644.

mass[1]. Water precipitates from the alcohol about 28%, the rest remaining in solution and partly separating on heating in white flocks which redissolve on cooling. From the fact that the water-precipitated portion contains 36-38% methoxyl, which is higher than the value for an exhaustively methylated isolated lignin, it appears that methylcellulose also is present. These methoxyl values correspond to trimethylcellulose mixed with 41-18.8% of dimethylcellulose. As this trimethylcellulose does not dissolve before hydrolysis, it may be concluded that this portion, at least, of the cellulose is not combined through its three OH groups in the wood, and even if it is assumed that cellulose is not uniformly united in wood, it follows that a part of it does not involve the linking of one or more of its three hydroxyls.

It is known that methylbeech wood is decomposed by hydrolysis into an acetone soluble and acetone insoluble portion, and that the latter, which is 61-63% of the beechwood, gives on extraction with water and then chloroform, cellulose ethers which, from their methoxyl content, appear to consist primarily of tri- with some di-methylcellulose. If the water-soluble portion, which appears to be of the highest purity, is degraded with methyl alcoholic-HCl under pressure, 2.3.6-trimethylglucose results[2].

In the preparation of alkyl ethers in general, and ethylbenzylcellulose specifically from wood cellulose[3], 900

1. A. v. Wacek, Ber. 1930, **63**B, 282; abst. C. A. 1930, **24**, 2878.
2. H. Suida and H. Titsch, Ber. 1928, **61**B, 1599; abst. C. A. 1928, **22**, 4807.
3. It is to be borne in mind, that in general, these cellulose ethers of 1.5-2.5 alkyl molecules per molecule of cellulose, are most appropriate for technical purposes because they possess greater tensile strength, elasticity and other desirable properties, but are unstable towards water, especially at low temperatures, either swelling or passing into solution in water as the temperature diminishes. On the other hand, where the alkyl content is above 2.5 molecules, the swelling and solubility in water diminishes, and the physical constants and mechanical features are correspondingly improved. This process endeavors to combine the desirable properties of high tensile strength and elasticity with insolubility in water at all normal temperatures, primarily by the introduction of a relatively small proportion of benzyl group in conjunction with the ethyl. The finished ester should correspond in composition to about 2 mols. ethyl to slightly more than 1 mol. benzyl, that is, to a diethyl-*half*benzylcellulose.

of lignocellulose in the form of pasteboard are soaked for 2 hrs. in 50% NaOH solution at 30°, then pressed until the alkali content amounts to 3-6 mols. calculated upon one mol. cellulose, the mass being then disintegrated and allowed to ripen at 20° for 4-40 hrs. In actual practice, the ripening period should exceed 35 hrs. at the above temperature, and the alkalicellulose should be protected from the carbon dioxide of the air. The alkalicellulose is then heated for 6-7 hrs. in an autoclave containing 5460 of ethyl chloride and 762 of benzyl chloride, equivalent to 1 mol. cellulose, 14 mols. ethyl chloride and 1 mol. benzyl chloride, the temperature being kept between 110-120°. Excess of ethyl chloride is then distilled off, and alkali and sodium chloride removed by washing with water, followed by removal of benzyl chloride by means of suitable organic solvents, the product then being dried. The mixed ester obtained is soluble without residue in alcohol-benzene 1:1, and stable towards water, even ice water[1].

In another process, the entire wood substance is etherified[2] (i.e. the lignin and pentosans in addition to the cellulose), the esters so produced being separable into fractions by suitable solvents, so that highly viscous portions are obtained of enhanced technical value. The wood employed may be either mechanical wood pulp, sawdust or wood shavings, but should be previously deresinified. The process is exemplified by an example, 1 part of pine wood sawdust, for instance, being mixed with 4 parts 50% NaOH and heated with 3 parts ethyl chloride under pressure for 6 hrs. at 100°. Ethyl chloride is removed by partially removing the pressure, and the ethyl ether washed with water until free from salt. The product obtained is a light, granular substance, insoluble in water, soluble about 70% in alcohol-

1. I. G. Farbenindustrie, Akt. Ges., E. P. 305946; abst. C. A. 1930, **24**, 5040; J. S. C. I. 1930, **49**, 414-B; Chem. Zentr. 1929, II, 111. F. P. 669256; abst. C. A. 1930, **24**, 1740. D. R. P. 492062; abst. C. A. 1930, **24**, 2599.

2. *Ibid.* E. P. 325512; abst. C. A. 1930, **24**, 4157; J. S. C. I. 1930, **49**, 414-B.

benzene (1 to 1-3), and dissolves completely in methylene chloride, phenol, benzyl alcohol when hot, becoming plastic at around 200°. Substituting etherifying agents, there may be produced methyl esters which swell strongly and partially dissolve in water, and benzyl ethers which are more readily fusible and highly stable to water. It must be borne in mind, that when operating upon sawdust, it should be ground to an impalpable powder before etherifying, and the moisture content should be 2% or lower, i.e. in the bone-dry condition. If one part of beechwood sawdust is treated as above indicated[1], a wood ether of about 45% ethoxyl is obtained which is substantially soluble to a viscous solution in alcohol-benzene, partly in acetone, carbon tetrachloride or ether, and softens at about 170°.

In a modification of the above process, if 1 part of pine wood sawdust is treated with 8 parts 30% NaOH solution and warmed with 3 of benzyl chloride for 3 hrs. at 100°, and the reaction mass freed from benzal chloride, benzyl ether, alcohols and aldehydes and washed with water until neutral, the yield of benzylcellulose amounts to 150%. It is a coarse, hard, granular material, odorless, melting about 120°, and but partly soluble in benzene. Based on the assumption of 100% benzyl chloride being used, and a maximum esterification period, the ether formed is about a 2.4-benzylcellulose.

In order to augment the solubility of wood ethers[2] without materially diminishing the yield, 100 of pine wood in the form of sawdust are intimately commingled with 300 of 50% aqueous NaOH, then 300 of ethyl chloride added, and the mixture heated under pressure for about 6 hrs. at 100°. After removal of ethyl chloride by distillation, and salts by washing, the solubility of the ethyl ether obtained may be increased, especially in an alcohol-benzene mixture, by proceeding in one of the five following ways:—

1. I. G. Farbenindustrie, Akt. Ges., and E. Teupel, D. R. P. 528359; abst. C. A. 1931, **25**, 4707.
2. I. G. Farbenindustrie, Akt. Ges., E. P. 330011; abst. J. S. C. I. 1930, **49**, 807-B.

1. 100 parts of the wood ether (about 55% soluble in alcohol-benzene 1:4) are covered with 300 parts of 1% chlorine dioxide aqueous solution and left for 3 days with frequent agitation. The mixture is then filtered and washed with water to neutrality. The yield amounts to 100% and is completely soluble to a clear solution in alcohol-benzene (1 to 1-9), the viscosity being somewhat reduced as the result of the treatment.

2. As in (1) above, but with the addition of 10 parts calcium carbonate, the HCl evolved being fixed as chloride, and CO_2 escaping. The wood ether is freed from remaining calcium carbonate by addition of excess of HCl, then washed until neutral. The ether is completely soluble in 1-9 of benzene with 1 of either alcohol, methylene chloride, chloroform or pyridine.

3. 100 of the wood ether are allowed to swell in 300 of 50% acetic acid, and into the mixture are introduced 300 of chlorine dioxide, the mixture being allowed to stand a day with frequent agitation. The wood ether is then washed to neutrality and dried.

4. 100 of wood ether are suspended in 1000 water, and 5 of chloric acid and 0.1 of sodium vanadate added. The mass is electrolyzed with a 4 volt current of 5 amps. per sq. decimeter, the chlorine dioxide formed being almost immediately consumed by the wood ether. The electrolysis is interrupated when the degree of solubility desired has been obtained.

5. 100 wood, 1000 water has added thereto 5 of potassium chlorate, 2 of concentrated sulfuric acid and 3.5 of vanadium sulfate. The chloric acid liberated is reduced by the vanadium to chlorine dioxide.

A process has been evolved for the treatment of different kinds of straw, such as rye, wheat, barley, or oat, or fibers as bamboo or esparto, in which a purified cellulose is claimed to be obtained, together with a relatively smaller portion of etherified lignin, no prior alkali treatment of the

cellulose being required[1]. The process, which appears unduly expensive, is exemplified by the following examples:—

1. 100 of chopped barley straw are added to 1000 ethyl alcohol containing 20% HCl gas, and the mixture allowed to stand at room temperature for several days with frequent agitation. After filtering and washing the residue with alcohol, a cellulose still containing 4% lignin is obtained in 40% yield. The alcoholic solution, containing ethyl lignin, is freed from alcohol by distillation, and the lignin ether precipitated by dilute acid and washed to neutrality.

2. The HCl gas in (1) above may be replaced by 20 of ethyl bromide, the mixture being heated at 150° for 2 hrs. at a pressure rising to 11-12 atms. After filtering the alcoholic solution from the precipitate of cellulose, the alcoholic portion is precipitated as above, and the ethylated lignin recovered.

3. Esparto 100, benzyl alcohol 1000, HCl (sp. gr. 1.19) 2.5 are heated to about 150° for about 8 hrs. in an autoclave. After filtering and washing out the benzyl alcohol by means of ethyl alcohol, about 45 of cellulose are obtained. The solution, containing benzyl alcohol, is neutralized and vacuum-distilled off, the residue being poured into water, precipitating benzyl lignin as a brown powder.

Glycol-lignin Ethers. Lignin has been isolated as a compound to which the term "glycol-lignin" has been applied by treating lignin at 100° with glycol containing a trace (0.05%) dry HCl as catalyst, and H. Hibbert and L. Marion[2] as well as W. Kuester and R. Daur[3], have prepared nitrated and nitroacetylated lignins therefrom. Nitrated glycol-lignin has been methylated with methyl iodide and dry silver oxide at 50°, and obtained as a light-brown, amorphous powder, insoluble in alkalis. Yield 40% on the nitrated lignin. Methylated glycol-lignin has also

1. K. Ott and H. Schuessler, U. S. P. 1806703.
2. Can. J. Research, 1930, **2**, 364; abst. J. S. C. I. 1930, **49**, 1275-A.
3. Cellulosechemie. 1930, **11**, 4.

been nitrated[1]. Dinitrophenyl glycol-lignin has been prepared, the methylated compound obtained by methylating with methyl sulfate and 50% KOH[2], being a light-brown powder, insoluble in NaOH, alcohol or glacial acetic acid. A methoxymethyl glycol-lignin is known, obtained by the interaction of chlordimethyl ether with the sodium salt of glycol-lignin. It is insoluble in toluene, ether and dilute sodium hydroxide solution. Glycerol chlorhydrin-lignin has likewise been described[3], and may be readily methylated by methyl sulfate and KOH[4], methoxyl 23.2%. Methylglycol-lignin obtained by dissolving glycol-lignin is 1% aqueous KOH, and treating with a mixture of 45% KOH and methyl sulfate, is a grayish, amorphous powder, soluble in alcohol and acetone, but insoluble in ether, chloroform and benzene. It is also insoluble in sodium hydroxide and sodium carbonate solutions. By the use of ethyleneglycol monoethyl ether on lignin, a glycol-ether-lignin results, which has also been transformed into the methyl derivative—methylglycol-ether-lignin—which dissolves in moist acetone and alcohol, but is insoluble in benzene, chloroform and ether. The methoxyl content is 27.45%.

W. Fuchs and R. Daur[5] have prepared methylglycol-lignin ("methylin") in 70% yield, by extraction of pine wood sawdust with methyl glycollic hydrochloric acid. When fused with KOH, protocatechuic acid results in good yield, both substitution and addition resulting upon treatment with bromine in carbon tetrachloride. When heated with *b*-naphthol in presence of HCl, it yields dinaphthapyran.

By repeated treatment of pine wood with diazomethane

1. H. Hibbert and L. Marion, Can. J. Research, 1930, **3**, 130; abst. J. S. C. I. 1930, **49**, 1418-A.
2. *Ibid.* Can. J. Research, 1931, **5**, 302.
3. H. Hibbert and J. Phillips, Can. J. Research, 1930, **3**, 65; abst. C. A. 1930, **24**, 5757; J. S. C. I. 1930, **49**, 1275-A.
4. W. Haworth, J. C. S. 1915, **107**, 8; Proc. Chem. Soc. 1914, **30**, 293; abst. C. A. 1915, **9**, 1034; J. S. C. I. 1915, **34**, 241; Bull. Soc. Chim. 1915, (4), **18**, 300; Chem. Zentr. 1915, I, 881; Meyer Jahr. Chem. 1915, **15**, 109.
5. Cellulosechemie, 1931, **12**, 103; abst. J. S. C. I. 1931, **50**, 718-A; C. A. 1931, **25**, 5761.

in diethyl ether, W. Fuchs and O. Horn[1] obtained a preparation with 15.8% methoxyl. The sawdust so treated shows an unchanged woody structure, is almost colorless, and gives no lignin reactions. It appears that the cellulose portion of the wood is probably present as monomethylcellulose (17.6% methoxyl) but when isolated with chlorine or chlorine oxide (yield 56%) the product contains but 7.8% methoxyl. Cotton and filter paper may be methylated with diazomethane in ether more readily than the cellulose in wood, and glucose upon the same treatment does not etherify. Hydrolysis of the methylated wood with HCl gives a very light lignin, showing a faint, but unmistakable double refraction. It contains 19.7% methoxyl, while the lignin prepared by another method[2] contains 15.4% methoxyl. Predicated on the assumption that at least one free OH group is methylated by diazomethane, this would indicate a minimum molecular weight of around 800 for the lignin in wood. Methylation of wood for 48 hrs. gave a lignin of 18% methoxyl, and Willstaetter lignin after 8 days, a product with 20.9% methoxyl, showing that lignin contains an OH group which may be methylated with diazomethane, but there is little difference between genuine and isolated lignin.

The relative cheapness of wood and ligneous products and their wide-spread occurrence, gives a technical interest to compounds such as the above described, as possible solvents, plastifying bodies or ingredients for lacquers, coating compounds and celluloid substitutes. Chemists are meticulously going over Beilstein page-by-page in a search for a product, for instance, which in the cellulose ester and cellulose ether industry, is the analogue of camphor in its deportment with the nitrated celluloses. The initial cost of preparation is practically immaterial provided the properties desired are obtainable, for the reason that factory production methods are usually but a fraction of the cost

1. Ber. 1929, **62**B, 1691; abst. C. A. 1930, **24**, 236. See Ungar. Diss. Zürich, 1914.

2. L. Kalb, T. Lieser, R. Hahn, F. Nevely and H. Koch, Ber. 1928, **61**B, 1007; abst. C. A. 1928, **22**, 2925.

of small scale preparation formulas, and therein the value of their enumeration lies.

Lignin reacts rapidly with gaseous nitrogen dioxide and, after a short period, the initial absorption is succeeded by evolution of nitric oxide due to a secondary oxidation. With methyl-lignin[1] only the initial rapid absorption is observed. The absorption spectra of the alkyl-lignins, lignsulfonic acids and the alkali lignins have been measured by the method of Victor Henri, the general similarity of the spectra of the different substances pointing to the fact that they have a common residue. However, there is a distinct difference between the spectra of derivatives of lignin from conifers and deciduous trees[2].

R. Herzog and A. Hillmer[3] have made absorption spectra measurements of lignin and alkylated lignins in hexane, water, ethyl alcohol and ethyl ether. The following values for γ_{max} (in $m\mu$) and log E_{max}, respectively, were obtained as follows: Alkali lignin from pine 280, 4.33; from rye straw, 276, 4.31; jute, 275, 3.99; linden, 274, 4.30; primary ethyl-lignin from beech, 275, 3.73; glycol-lignin from spruce, 282, 4.29; pectin-lignin from flax, 279, 4.28.

From a "black lye" prepared with pure NaOH, B. Holmberg and T. Wintzell[4] obtained with sulfuric, hydrochloric, and acetic acids or with CO_2, apparently identical precipitates separated by alcohol into two chief fractions, an insoluble *a*-lignin, and soluble *lambda*-lignin, gray- yellow to yellow-brown, amorphous powders, easily forming colloidal solutions, and containing 3-4 methoxyl groups. Upon methylation in the cold with methyl sulfate and alkali, the

1. K. Freudenberg and W. Dürr, Ber. 1930, **63**B, 2713; abst. C. A. 1931, **25**, 1497; J. S. C. I. 1931, **50**, 74-A; Zts. ang. Chem. 1929, **42**, 618.
2. E. Hägglund and F. Klingstedt, Zts. physik. Chem. 1931, **152**A, 295; abst. C. A. 1931, **25**, 2053. See Svensk Kem. Tid. 1929, **41**, 185; abst. C. A. 1930, **24**, 1578. V. Henri and P. Steiner, Compt. rend. 1922, **175**, 421; abst. C. A. 1922, **16**, 4140.
3. Ber. 1931, **64**B, 1288; abst. C. A. 1931, **25**, 4277.
4. Ber. 1921, **54**B, 2417; abst. C. A. 1922, **16**, 1245.

a-methyl-lignin gave 23.41% methoxyl, and the other, 23.16%.

Lignin obtained from flax has likewise been both acetylated and methylated. By means of methyl sulfate three methoxyl groups have been introduced under very mild conditions, the ether obtained being insoluble in alkalis and extremely difficult to hydrolyze[1]. Soluble in glacial acetic acid and in acetone, slightly soluble in water. When purified by precipitation from acetone solution, the methoxyl content was 25.6%. By acetation of methyl-lignin, less than one acetyl group is introduced, although acetyl-lignin is readily prepared.

Lignin prepared according to the method of A. Friedrich and J. Diwald[2], when shaken with NaOH and methyl sulfate, gave a methyl-lignin, yellow-brown powder, decomposing at 110°, methoxyl 25.2%. A benzyl-lignin, light yellow, has also been prepared.

A. Friedrich and E. Pelikan[3] have studied lignin through the bromine absorption capacity. Lignin alkylated with methyl sulfate (about 25% methoxyl) takes up 32.1% bromine. In the alkylation of the brominated product (38.7% Br) in alkaline solution with methyl sulfate, or in acetone solution with diazomethane, the bromine content drops only to 27-28%, indicating nearly the same degree of alkylation as with the original lignin.

Methylation of Ligninsulfonic Acid. The calcium salt of ligninsulfonic acid has been methylated by P. Klason[4]. From an original methoxyl content of 12.87%, the methylated product rose to 19.7% methoxyl. E. Heuser and S. Samuelsen[5] likewise have methylated ligninsulfonic acid (10 parts) with 10% NaOH solution (200) and methyl sulfate (65). The methylated product was insoluble

1. W. Powell and H. Whittaker, J. C. S. 1924, **126**, 359.
2. Monats. 1925, **46**, 31; abst. C. A. 1926, **20**, 1598.
3. Biochem. Zts. 1931, **239**, 461; abst. Chem. Zentr. 1932, I, 2458.
4. Ber. 1920, **53**, 1864; abst. C. A. 1921, **15**, 860.
5. Cellulosechemie, 1922, **3**, 78; abst. C. A. 1922, **16**, 3754.

in the reaction mixture, and upon the fifth methylation, gave 25.43% methoxyl, the ash content meanwhile rising from 1.20% to 5.06%, notwithstanding careful washing. Yield of methylated product, over 80% of theory. The methylated acid (methyl-ligninsulfonic acid) was light yellow, becoming darker on standing, insoluble in petroleum ether and mineral acids; traces soluble in alcohol only when freshly prepared.

H. Urban[1] has described combinations of toluenesulfochloride with lignin, in which the moist lignin is incorporated with 10 times its weight of 8% NaOH solution and then treated with 10 parts *p*-toluenesulfochloride in a pressure tube, being heated with stirring at 75-80°. NaOH solution is then further slowly added until the odor of the toluenesulfochloride disappears. The material is then filtered by suction, washed with acetone, then with water and dried at 100° in a vacuum. It forms a light brown powder in which 2 to 3 toluenesulfo-groups have entered the cellulose molecule. As in the methylation of cellulose, it appears that 2 of the 3 OH groups are readily attacked, in general, but 2 toluenesulfo-radicals being introduced into the cellulose molecule in the formation of cellulose *p*-toluene-sulfochloride.

Triphenylmethylcellulose. In conjunction with an examination of ethers of triphenylcarbinol[2], B. Helferich and H. Koester have prepared carbohydrate ethers of triphenylmethyl[3]. If starch or cellulose is heated—the latter best after re-precipitation,—as from a xanthate solution using pyridine and triphenylchlormethane, then of the three hydroxyls, one is etherified by triphenylcarbinol. If a large excess of triphenylchlormethane or a prolonged reaction

1. Cellulosechemie, 1926, **7**, 73; abst. J. S. C. I. 1926, **45**, 531-B.
2. B. Helferich, P. Speidel and W. Toeldte, Ber. 1923, **56B**, 766; abst. C. A. 1923, **17**, 2574. The triphenylmethyl-groups are readily split off from the compound by means of chloroform containing HCl, in the form of triphenylmethyl chloride, and by means of aqueous HCl as a carbinol, the cellulose being regenerated.
3. Ber. 1924, **57B**, 587; abst. C. A. 1924, **18**, 2873; J. C. S. 1924, **126**, i, 500; Chem. Zentr. 1924, I, 2104.

time be used, one hydroxyl appears to be the maximum etherified. This is somewhat analogous to glycerol, where but two of the three hydroxyls are etherified by triphenylcarbinol.

With starch and cellulose, this ether formation with triphenylcarbinol is extraordinarily sensitive to acids, merely shaking the chloroform solution of the ether with chloroform containing HCl, being sufficient to split off the triphenyl group in a few seconds as chloride, or in the presence of water as carbinol. The polysaccharide recovered appears to give the same values on analysis as the starting material.

Triphenylmethylcellulose swells in various organic solvents at room temperature, dissolving slowly but completely and uniformly in pyridine, chloroform and bromoform to viscous, colloidal solutions. In these solutions the free hydroxyls are susceptible to various reactions. Heating in pyridine and acetic anhydride esterifies about one hydroxyl, treatment of the solution with chloracetic chloride substitutes about 1.5 hydroxyls per one glucose rest, a triphenylmethylcellulose acetate being formed. Hydroxyl determinations according to the methods of L. Tschugaeff[1] and T. Zerewitinoff[2] give values indicating approximately two free hydroxyls per glucose component. These cellulose etheresters are amorphous and retain a small proportion of impurity (solvent and ash) very tenaciously.

Triphenylmethylcellulose may be prepared by heating filter paper or cotton in a mixture of pyridine and triphenylchlormethane at 120° with continuous agitation, the cellulose slowly passing into solution. If a cellulose hydrate be used instead of a normal cellulose, a lower temperature of heating may be used, and less discoloration (indicating decomposition) of the solution is apparent. Cellulose 1, triphenylchlormethane 6, pyridine 14, all anhydrous, are preferably heated in a closed tube for better exclusion of mois-

1. Ber. 1902, **35**, 3912.
2. Ber. 1907, **40**, 2023.

ture. When a clear solution results, which requires 14-32 hrs. heating depending upon the temperature, the mass is poured into water at about 80°, washed, boiled with alcohol for removal of triphenylcarbinol, and finally dissolved in anhydrous pyridine and slowly dropped with stirring into much alcohol. The product after drying forms a fine, rose colored powder, yield 2.1 from 1 of cellulose, or 84% of theory. The ether swells in ethylene bromide, carbon bisulfide, acetylene tetrachloride, ethyl benzoate and acetic anhydride. M. pt. around 260° with decomposition. Its solution in pyridine at first shows no rotation, but after standing 4 months at room temperature, was laevorotatory.

A triphenylmethyl starch may also be prepared in the same manner as above, using rice starch preserved for some time over phosphorous pentoxide. Yield, 2 of ether from 1 of starch, or 80% of theory. The ash was 0.24%. Like cellulose, a monotriphenylmethyl starch was the maximum of substitution that could be prepared. Chloracetyltriphenylmethyl starch has also been produced.

According to the Society of Chemical Industry[1], when 8 parts cellulose in 160 parts of a mixture of benzylpyridinium chloride and pyridine are introduced at 90° into 20 parts dry triphenylchlormethane and the mixture stirred at 90-100°, triphenylmethylcellulose is formed. After the reaction has proceeded for 1.5 hrs., the cellulose ether is poured into methyl alcohol, whereupon the triphenylmethylcellulose separates as a soft, fibrous mass which soon becomes hard and brittle. It is coarsely pulverized, extracted with methyl alcohol and dried. Thus obtained, it is a pure white, brittle mass which dissolves in pyridine, but is sparingly soluble in chloroform.

Carbohydrate Allyl Ethers. Allylcellulose. The first allyl derivatives of the carbohydrates prepared were the allyl glucosides reported upon by E. Fischer and H. Strauss[2] in 1912, who prepared allyltetracetyl-, allyl-, and monobrom-

1. E. P. 359249.
2. Ber. 1912, **45**, 2474; abst. C. A. 1913, **7**, 87.

allyl-*d*-glucoside, and E. Bourquelot and M. Bridel[1] who, the same year, described *b*-allylglucoside, and in 1913 that of *a*-allylglucoside[2]. The subject remained dormant for a decade, and until C. Tomecko and R. Adams described various allylcarbohydrate ethers[3], including an allylated cellulose. The compounds which they prepared were:

Tetra-allyl-*a*-methyl glucoside, thick, colorless oil, insoluble in water, soluble in alcohol and ether.

Penta-allyl sucrose, colorless, thick oil, distilling with decomposition. Insoluble in water, soluble in alcohol and ether.

Monoallyldextrin. Gummy mass, soluble in chloroform, insoluble in ether. Shrinking (not melting) at 155-165°, decomposing at 240-250°.

Monallylinulin. Nearly white product, soluble in alcohol, insoluble in ether.

Monoallyl potato starch. Soluble in alcohol and glacial acetic acid, insoluble in ether. Shrank at 160-165°, decomposing without melting at 260-270°.

Monoallyl corn starch. White, amorphous; became brown at 250-265°, but did not shrink or melt.

Allylated cellulose. Pure filter paper was hydrated by dissolving in cuprammonium hydroxide and precipitating. 10 gms. of this, 85 gms. allyl bromide and 65 gms. KOH, were heated on a water-bath for 1 hr. after all the bromide had been added. The reaction mixture was then steam distilled to remove allyl alcohol and allyl bromide, the gummy reaction product washed with water, then with several portions copperammonium hydroxide to remove unchanged cellulose, dried at 100°. The ester was admittedly impure.

Frey[4] allylated hexose and sucrose and studied the latter compound closely, but did not attempt the allylation of cellulose.

1. Compt. rend. 1912, **155**, 439; abst. C. A. 1913, **7**, 78.
2. E. Bourquelot, H. Herissey and M. Bridel, Compt. rend. 1913, **156**, 1494.
3. J. A. C. S. 1923, **45**, 2698.
4. Diss., Eidgenoesschem. Techn. Hochschule, Zurich, No. 452.

I. Sakurada[1] subjected shredded cotton paper, suspended in 40-50% NaOH solution to the action of allyl bromide, and in a single treatment obtained both a di- and tri-ether based on C_6 cellulose. The determination of the halogen absorption gave results agreeing with the elementary analysis, indicating that the double bond had remained intact. A diallylcellulose tetrabromide was also isolated. Both di- and tri-allylcellulose are soluble in ethyl alcohol, benzene and carbon tetrachloride, but the solubility is not high. The ethers are resistant to heat, remaining snow white when heated to 210°. Best results were obtained by soaking cotton paper in 40-50% NaOH, pressing to 4-5 times the weight of the cellulose, allowing to stand 24 hrs., allyl bromide added, and the mass heated on the water bath under reflux condenser. If the allyl bromide is first diluted with benzene, the reaction proceeds more smoothly. It is significant that the triallyl ether was produced in a single treatment, whereas a number of treatments are required for maximum methylation or ethylation of cellulose.

The reaction product is purified by nearly neutralizing with acetic acid, the allyl bromide and allyl alcohol distilled off with steam, and the salts removed by extraction with water in a Soxhlet. After drying, the product is repeatedly exhausted with alcohol, in which a portion dissolves. The insoluble portion is then washed with water and dried. Allylhydrocellulose was similarly prepared. Yield 1.69 on the original cotton used, theory requiring 1.25, 1.49 and 1.74 for the mono-, di- and tri-allyl cellulose respectively. In the allylation of hydrocellulose the loss is considerable. The constitution of mono-, di- and tri-allylcellulose is $C_6H_9O_5.C_3H_5$, $C_6H_8O_5(C_3H_5)_2$ and $C_6H_7O_5(C_3H_5)_3$.

The I. G. Farbenind.[2] have described allylcelluloses containing a proportion of nitrogen, and obtained by introducing allylcellulose into liquid ammonia. After standing

1. Zts. ang. Chem. 1929, **42**, 549. J. S. C. I. (Japan), 1928, **31**, 638; Supplemental Binding, 1928, **31**, 157-B. Cellulosechem. 1929, **10**, 145. Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 114.
2. D. R. P. 542004; abst. C. A. 1932, **26**, 2316.

48 hrs. at room temperature, or 10 hrs. at 100° and 35 atms. pressure, the ammonia was driven off and the solid residue leached out with water. A nitrogen content of 2.75% and 2.02% respectively was shown. Similarly, when cellulose dicrotonate was treated at 100° in a closed pressure vessel with ammonia gas, a reaction mass of about equal parts of alanine and a water-insoluble product with 2.1% N was obtained, which contains cellulose aminopropionate groups.

A cellulose derivative has been described obtained by treating alkalicellulose with a mixture of carbon bisulfide and allyl bromide, and subjecting the product to the action of piperazine. The derivative has a strong affinity for acid dyestuffs and is said to be useful for the production of textile fibers.

The method is clarified by the following examples:

1. 5 gms. allylcellulose are placed in liquid ammonia. After standing 48 hrs. at room temperature, the ammonia is driven off, and the solid residue leached out with water. There is obtained 4.7 gms. of a compound showing the grouping—$O.CH_2.CH_2.CH_2.NH_2$, and shows a 2.75% N content.

2. 10 gms. cellulose crotonate are treated with ammonia gas for 10 hrs. at 100° in a closed pressure vessel. There is obtained a reaction mass which consists of about equal parts alanine and a water-insoluble product with 2.1% N, which comprises cellulose aminopropionate.

3. 5 gms. oxyethylcellulose undecylenate are treated with 100 cc. liquid ammonia in an autoclave for 48 hrs. at 25-30° and 20 atms. pressure. The reaction product is purified with methyl alcohol. There is obtained 1.7 gms. of the aminated cellulose derivative with 1.1% N.

4. 5 gms. oxypropylcellulose crotonate are treated with 100 cc. liquid ammonia in an autoclave for 48 hrs. at 25-30° and 20 atms. pressure. The reaction product is likewise purifiable with methyl alcohol. Yield, 3.2 gms. of the aminated cellulose derivative, containing 2.1% N.

When alkalicellulose is treated with a mixture of carbon bisulfide and alkyl halide or aralkyl halide, there is produced a change in the cellulose accompanied by a considerable increase in weight of the fiber, the products formed being insoluble in water. If, for instance, a solution of 100 parts allyl bromide and 600 parts carbon bisulfide is caused to act on alkalicellulose for 1-4 hrs. in the cold, and the bright, yellow material of a garlicky odor rinsed in cold or warm water[1], and then warmed for 1-2 hrs. in a 10% aqueous solution of ethylethylenediamine (piperazine or piperidine), the yellow color passes to a white, and after rinsing in hot water, is nearly white. The product obtained may be dyed with acid wool colors (tartrazine, benzyl violet 10 B), or those insoluble dyestuffs which are suitable for acetate silk dyeing.

The dyeing properties of cellulosic materials may be varied by converting them into allylcelluloses, either superficially or profoundly[2], these ethers being insoluble in the usual organic solvents, having no affinity for direct dyestuffs, and being obtained while still conserving the original structure and strength of the fiber, by treating the cellulose with a caustic alkali and then with an allyl halide in such a manner that dissolution of the cellulose ether produced cannot occur. The process is exemplified by the following two examples:

(1) Cotton yarn is impregnated for 1 hr. with external cooling in ice, with 15% NaOH solution, then pressed so that it has not more than double the weight of the original yarn (a very difficult thing to do). In order to avoid the contraction due to mercerization, the yarn is stretched on a frame during the alkalizing treatment. The skein is

1. Soc. Anon. pour L'Ind. Basle, E. P. 341237; abst. C. A. 1931, **25**, 5030. Swiss P. 144227; abst. C. A. 1931, **25**, 4124. F. P. 686575; abst. C. A. 1931, **25**, 591. Swiss P. 141558.

2. *Ibid.* E. P. 342689; abst. C. A. 1931, **25**, 5578. J. S. C. I. 1931, **50**, 485-B; Chem. Zentr. 1931, II, 3046. F. P. 684183; abst. C. A. 1930, **24**, 5496. U. S. P. 1879742.

then rapidly wetted with allyl bromide, and then suspended in a tube, still in the stretched condition, through which is passed a current of allyl bromide, heat being applied by means of steam in a tube surrounding the first tube. After 2-3 hrs. the alkalicellulose has been converted, which may be recognized by the fact that the skein no longer renders alkaline, hot water with which it may be washed. During this treatment there is a slight bleaching of the goods, accompanied by a tint tending towards cream. The tenacity is not diminished, and the increase in weight amounts to 18-24%. Monoallylcellulose gives a theoretical increase of 25%.

Instead of allyl bromide, there may be used equal parts of allyl chloride and allyl bromide. The increase in weight then amounts to 26.5%, and the product formed is immune to direct dyeing dyestuffs.

(2) In a solution of 5-7% strength allyl bromide in carbon tetrachloride (70 parts of the former to 1000 parts of the latter), is immersed yarn that has been wetted in hot water and pressed, and while vigorously stirring, 60 parts of 20% NaOH are dropped in while the solution is being heated to boiling in a reflux apparatus on the water-bath. The solution, at first turbid, soon becomes clear, while on the surface collects some unconsumed NaOH and water. After 24 hrs. the yarn is washed and dried, the increase in weight being 17-18%, and the length is not appreciably diminished.

Cellulose derivatives containing both sulfur and nitrogen have been described[1], in which cellulose is impregnated in the cold with 20% NaOH solution, and the alkalicellulose thus formed treated in a solution of alkyl halide in carbon bisulfide as in the following example: a solution of allyl bromide 100, in CS_2 600, is caused to act on the alkalicellulose for 1-4 hrs. in the cold, a bright yellow material

1. R. Haller, A. Heckendorn and Soc. Chem. Industry, Basle, U. S. P. 1838038. E. P. 341237.

smelling like garlic being formed, which is then rinsed in cold or warm water.

The material thus prepared is now, without previous drying, warmed for 1-2 hrs. on the water-bath in an aqueous solution of 10% diethyl-ethylenediamine (or piperazine, mono- or di-ethylamine or -methylamine, aniline, dimethyl-*p*-phenylenediamine, ethylenediamine) and until the yellow color passes to gray-white. After having been rinsed in hot water for 0.5 hr., the material is almost white. Acid wool dyestuffs as tartrazine or benzyl violet 10 B dye the material deeply, as do most of the dyestuffs for acetate silk. The allyl bromide may be replaced by benzyl bromide, or by a mixture of allyl and benzyl bromides.

It is claimed[1] the allylation of polysaccharides takes place more readily than their methylation, but it does not lead to completely allylated products, notwithstanding the fact that the allyl group is over twice as great as the corresponding methyl.

Cellulose Thiourethanes. Cellulose Urethane Ethers. These compounds were first described by L. Lilienfeld[2] in 1924, and are obtained by neutralizing viscose with acetic acid (see preceding topic) and then treating with sodium monochloracetate, the mixture being again neutralized and finally treated with 50-120 parts aniline per 100 parts original cellulose. The reaction product gradually separates during 3-4 days, may be washed with alcohol and ether, cautiously dried under vacuum at room temperature, when a white powder of cellulose phenylthiourethane is obtained,

1. H. Staudinger, K. Frey, R. Signer, W. Starck and C. Widmer, Ber. 1930, **63**B, 2308.

2. U. S. P. 1674401. E. P. 231801; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 955-B; Chem. Zentr. 1925, II, 2190. Ann. Rep. S. C. I. 1926, **11**, 618. F. P. 700535; abst. C. A. 1931, **25**, 3833. D. R. P. 438918; abst. Chem. Zentr. 1927, I, 1770. D. R. P. 527254, Addn. to D. R. P. 467003. Aust. P. 102306, 118235 and Addns. 121030, 121031, 121032. Norw. P. 42811. Swed. P. 61131. Holl. P. 19083. See Holl. P. 17632. He has described products (F. P. 719340) obtained by combining the cellulose thiourethanes with compounds formed by the action on alkalicellulose of mustard oils (isothiocyanic acid esters, alkyl thiocarbimides), and methyl, ethyl and allyl mustard oil. See E. P. 274521, 274690, 281351.

and may be represented as formed by the interaction of aniline upon sodium cellulosexanthacetate, sodium thioglycollate being split off and remaining in the mother liquor.

The process, in its general scope, is elucidated in the following examples:

1. *Cellulose Phenylthiourethane, Cellulose Xanthanilid, Cellulose Phenylthiocarbamate.* 100 parts crude viscose as prepared for rayon manufacture are neutralized with sufficient acetic acid to form a neutral solution and liberate the CS_2 previously in combination with the cellulose. The viscose solution, which has become light in color, is treated with a solution of 6-10 parts sodium monochloracetate in 48-80 parts of water, and this is neutralized with powdered sodium bicarbonate. The mixture is then stirred, then allowed to stand at room temperature for 6 or more hours, and then 6-12 parts aniline stirred in. After several hours the reaction product begins to separate and finally settles to the bottom. As soon as precipitation is complete, the magma is separated, acidified with sulfuric acid, extracting the thioglycollic acid with ether, washed with alcohol, then with water and finally cautiously dried. Instead of aniline, an equivalent amount of *o*-toluidide may be used, producing a cellulose xanthatoluidide.

2. *Cellulose Methylthiourethane.* The aniline is replaced in the above example by methylamine or ethylamine. The reaction progresses quicker, and precipitation occurs in small jelly-like lumps. The cellulose methyl- or ethylthiourethane, after washing and drying, dissolves in dilute caustic soda solution, and in a 90% aqueous pyridine solution. From the latter, clear, flexible films may be made.

3. *Cellulose Diethylthiourethane.* Instead of employing aniline as in (1), there is added to the cellulose xanthacetic acid an equivalent amount of diethylamine, reaction taking place very quickly. The product separates in a finely divided condition, barely soluble in caustic soda solution of 1-10% strength, but readily soluble in aqueous pyridine of 90% strength, and yields films resistant towards water.

4. *Cellulose Phenylethylthiourethane.* Instead of aniline in Ex. 1, an equivalent amount of phenylethylamine is used, the product separating in flakes shortly after the addition, and after washing and drying, is insoluble in caustic soda solution, but is likewise soluble in aqueous pyridine.

Instead of using monochloracetic acid, an equivalent amount of a halogen derivative of a homologue of acetic acid may be employed, as *α*-brompropionic acid, *α*-brombutyric acid or bromsuccinic acid, the mother-liquor then containing thiolactic acid, thio-oxy-*α*-butyric acid and thiomalic acid, instead of thioglycollic acid. These substituted thiourethanes, on account of their viscosity in dilute alkaline solutions, are indicated for sizes, cements, adhesives in general and finishing and coating compositions[1].

Cellulose Xanthanilid Alkyl-ethers. Cellulose Phenylimidothiolcarboxylate Ether. One mode of carrying out the manufacture of these compounds comprises converting an N-substituted cellulose thiourethane into a salt as the silver salt, by treating an ammoniacal solution of a substituted or non-substituted thiourethane which is soluble in ammonia, with ammoniacal silver nitrate solution, and treating this salt with an alkyl-, aralkyl- or aryl-ester of an inorganic acid, and in presence or absence of free alkali. Thus, 10 parts of phenyl- or tolyl-thiourethane are dissolved in 490 parts 10% NaOH solution, which is then mixed with 60-100 parts ethyl sulfate and the whole agitated. After 0.5-1 hr. the reaction product is precipitated, immediately separated from the mother-liquor and washed with water until alkali-free. It is then stirred with 1-10% sulfuric acid, washed free from acid, and dried. The ethyl-

1. L. Lilienfeld, U. S. P. 1674402. E. P. 231806; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 985-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1925, II, 2331. F. P. 719340; abst. C. A. 1932, **26**, 3376. Can. P. 259330, 259331; abst. C. A. 1926, **20**, 3567. Aust. P. 104709 and addn. 108107. See Aust. P. 102305. Dan. P. 36928. Norw. P. 44419. India P. 11142, 1925.

cellulose xanthanilide or ethyl cellulose xanthtoluidid[1] is a fine, flocculent, nearly white powder. Substituting ethyl sulfate by methyl sulfate or benzyl chloride, the corresponding methyl (or benzyl) cellulose xanthanilid or -xanthtoluidid results.

These bodies have excellent solubilities. They dissolve in 96% alcohol, in alcohol-ether (2:1), acetone (particularly in the presence of small amounts of water), ligroin-alcohol (1:1 or 1:2), in hexane-alcohol, and in chloroform, alcohol-chloroform, carbon tetrachloride-alcohol, methyl acetate, methyl alcohol, methyl alcohol-methyl acetate, methyl alcohol-chloroform, alcohol-benzene, glacial acetic acid, diethylaniline-alcohol, quinoline, *α*-dichlorhydrin, tetrachlorethane-alcohol, nitromethane-alcohol, acetylene dichloride-alcohol, pyridine, amyl acetate-alcohol, ethylenechlorhydrin-benzyl alcohol, ethyl benzoate-alcohol, ethylene chloride-alcohol, ethyl citrate-alcohol, ethyl naphthol-alcohol, ethylene bromide-alcohol, amyl alcohol-alcohol, and with chlornaphthalene, dibenzyl ether, eugenol, acetylene acetone, ethyl lactate, *α*-picoline, epichlorhydrin, *o*-chlorphenol. Solutions in volatile solvent combinations may be worked up with plasticizers, extensifiers, softeners and flexilizers to produce thermoplastic cellulose compounds of the celluloid class.

Instead of using a dilute acid for precipitating the cellulose thiourethane compounds[2], concentrated mineral acids as 40-70% phosphoric, 25-65% sulfuric, 20-35% hydrochlo-

1. L. Lilienfeld, U.S.P. 1674403; abst. J.S.C.I. 1928, **47**, 853-B. E. P. 231808; abst. J. S. C. I. 1925, **44**, 914-B. E. P. 241149; abst. J. S. C. I. 1926, **45**, 47-B; Chem. Zentr. 1926, I, 2267. E. P. 248246; abst. J. S. C. I. 1926, **45**, 400-B; Chem. Zentr. 1926, II, 2513. D. R. P. 455589; abst. Chem. Zentr. 1928, I, 1732. D. R. P. 467003; abst. C. A. 1929, **23**, 512, 1268; Plastics, 1929, **5**, 390. D. R. P. 526197, Addn. to D. R. P. 438916; abst. C. A. 1931, **25**, 4401. D. R. P. 527254, Addn. to D. R. P. 467003; abst. C. A. 1931, **25**, 5289. Aust. P. 108143, 108400. Swiss P. 121030, 121820, 124917, 124918, 124919. Belg. P. 325272, 325273, 329338. India P. 11142, 1925. Holl. P. 19099. Swed. P. 64340.

2. *Ibid.* U. S. P. 1674404; abst. J. S. C. I. 1928, **47**, 853-B. E. P. 248994; abst. C. A. 1927, **21**, 822; J. S. C. I. 1926, **45**, 532-B; Chem Zentr. 1926, II, 2514. Swiss P. 121031.

ric, or acetic acid 70%. Instead of combining the cellulose xanthate or xanthoacetate with aniline and etherifying, methyl-, ethyl- or benzyl-cellulose thiourethanes may be used as such, either in the crude or purified state for precipitating, remembering that when dissolving benzylcellulose thiourethanes in alkali, a small proportion of alcohol added to the solution facilitates the dissolving process.

Instead of applying the process to cellulose in the form of pulp or linters, textile fibers in the form of yarn or fabrics may be superficially or incompletely treated, first by mercerization, then with the successive steps so that the textile will have deposited thereon and therein, an alkyl- or aralkyl-cellulose thiourethane or alkyl- or aralkyl-cellulose xanthanilid[1]. By using 1.3.4-xylidin instead of aniline, cellulose xylylthiourethane results, which may be etherified into the aryl- or aralkyl-ethers, an example being ethylcellulose xylylthiourethane or ethylcellulose xanthaxylylidid.

To render the treated textile highly flexible[2], it may be given an after-treatment with the vapors of a solvent for the thiourethane, or of an agent which imparts plasticity, as the vapors of pyridine.

W. Harrison[3] has described the formation of difficultly characterizable compounds of the cellulose ether class, and obtained by treating with an oxidizing agent cellulose or starch compound containing the CSS group, with an organic compound containing one or more amino or imido groups, which may be regarded as ammonia derivatives in which one H atom is free. Included in this classification are alkylamines, arylamines, aralkylamines and aryl-alkylamines as acetamide, benzamide, phthalimide, aminoacetic acid, amidines, urea, cyanamide, dicyanodiamide, dicyanimide, guanidine, urethanes and thiourea.

1. L. Lilienfeld, E. P. 357190, Division of E. P. 357120; abst. Silk J. 1932, **8**, #95, 52. Swiss P. 121032.

2. *Ibid.* E. P. 253854, Addn. to E. P. 231806; abst. J. S. C. I. 1926, **45**, 782-B. Swiss P. 122076.

3. U. S. P. 1684732; abst. C. A. 1928, **22**, 4536. E. P. 286331, 286332; abst. C. A. 1929, **23**, 155; Chem. Zentr. 1928, II, 305. D. R. P. 497240; abst. C. A. 1930, **24**, 3646.

The following general method of manufacture is typical: 100 parts viscose containing 10 parts cellulose are diluted with 200-1000 parts water, 30 parts aniline well stirred in, and then 200 parts 10% solution of potassium ferricyanide vigorously stirred in at room temperature. The mass soon sets to a jelly, which is acidified with sulfuric acid, separated, washed and dried. The product on drying forms a hard mass which may be reduced to powder form, which is soluble in caustic soda, and swollen by, but does not dissolve in, aqueous pyridine.

H. Fink and R. Stahn[1] employ methyl- and ethyl-cellulose N-phenylurethane in conjunction with glyceryl-*a*-chlorhydrin or diethyl tartrate as ultrafiltering films, on account of their resistance to alkalis.

T. Nakashima[2] has investigated the cellulose xanthamides (cellulose thiourethanes), and finds that the reaction of ammonia or primary or secondary amines with solutions of sodium cellulosexanthoacetate slowly yields gelatinous products, the composition of which approximates the general formula $C_{12}H_{19}O_9.O.CS.RR'$. Cellulose thiourethane was found stable to dilute mineral acids, and was unchanged by heating at 105°.

T. Lieser[3] has studied the mechanics of methylation and benzylation of sodium cellulose xanthate, in attempts to replace the sodium by methyl or benzyl. Methyl sulfate is unsuitable for etherification, but if methyl iodide is used, and allowed to react upon cellulose xanthate in alcohol, instantaneous reaction takes place, but only one-fourth of the methyl content appears to enter into chemical reaction, there appearing a partial methylation, a partial disulfide formation and a partial hydrolysis. The latter also takes place in the reaction of benzyl chloride on xanthate, so that the benzylation does not lead to a homogeneous product.

1. D. R. P. 542063; abst. C. A. 1932, **26**, 2317.
2. Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 109; abst. J. S. C. I. 1929, **48**, 431-A.
3. Ann. 1928, **464**, 43; abst. J. S. C. I. 1928, **47**, 742-B; C. A. 1928, **22**, 4792.

Most favorable results were obtained by proceeding as follows: 0.766 gm. cellulose was converted into xanthate in the usual manner and after purification with methyl alcohol, the latter was displaced with ethyl alcohol. The xanthate was shaken with a mixture of 1.76 cc. methyl iodide in 20 cc. 80% alcohol for 7 min. After 25 min. it was repeatedly washed with alcohol, then with ether. Yield 0.988 gm.

According to the Society of Chemical Industry, Basle[1], cellulose ethers are prepared by treating acyl derivatives of cellulose containing a mobile halogen atom in the acyl group, with tertiary amines. Thus, chloracetylated acetylcellulose or chloracetylated cotton (cellulose hydroxyacetate) is heated with a solution of pyridine or trimethylamine in pyridine. Other tertiary amines such as triamylamine, quinoline, *N*-alkylated piperidines, or alkaloids such as nicotine (*a*-pyridyl-*b*-tetrahydro-N-methylpyrrole) or brucine may also be used.

Or[2], cellulose may be treated in the presence of a tertiary base with the partial reaction products of an alcohol or a phenol and a halide of an oxygenated acid of phosphorus, as phosphorous trichloride, pentachloride and oxychloride. New cellulose ethers are said to result which are insensitive to direct dyes but have a marked affinity for basic dyes. Thus, cotton yarn may be treated on a boiling water bath with a pyridine solution of triphenylmethoxyphosphorous dichloride. By impregnating 15 parts cellulose with 25% NaOH solution, pressing to 5 times the original weight and then treating with 15 parts chlorethylpiperidine in acetone for 5 hrs. at 40-60°, there is obtained after washing, 17 parts of a new cellulose ether of special applicability in the textile industry[3].

1. F. P. 717524. D. R. P. 550259; abst. C. A. 1932, **26**, 2862, 4172.
2. Soc. of Chemical Industry, Basle, D. R. P. 550258; abst. C. A. 1932, **26**, 4172.
3. *Ibid.* Swiss P. 145053, Addn. 141556.

CHAPTER XI

CARBOHYDRATE ETHER-ESTERS AND ESTERS

Partially bridging the gap between the etherified celluloses on the one hand and the esterified celluloses on the other—especially those acylcelluloses containing organic acid radicals therein—are the etherified cellulose esters or esterified cellulose ethers, an intermediate class of bodies of high stability, unaffected by alkalis, of excellent solubility in a wide range of comparatively inexpensive solvents, and which appear, in many instances at least, to partake to a high degree of the desirable characteristics of both cellulose ether and ester, with a diminution or absence of the undesirable properties of both classes of substituted carbohydrates.

Up to the present time this is a field which has been but imperfectly and superficially investigated, but whose potentialities appear almost limitless. When it is remembered the large number of acids which have been chemically combined with cellulose to form esterified derivatives, and the number of different cellulose ethers known, both alkyl, aryl and aralkyl, the possible permutations of ether radical against acid substituent must be very great, and correspondingly, the ability to synthesize members of varying physical properties and chemical deportment.

This number is augmented by the fact that of the three replaceable hydrogen atoms in the three hydroxyls in cellulose as assumed on a C_6 basis, a total of two of the three may be replaced, one by ether and the other by an acid, forming the so-called hydroxyether cellulose esters, as hydroxypropylcellulose acetate; or three hydroxyls may be replaced, one by ether and the two remaining by an inorganic acid (ethylcellulose dinitrate), organic acid (methylcellulose diacetate); or the two acid radicals may be dissimilar (methylcellulose acetophosphate). Conversely, where two ethers are substituted, they may be the same

(diethylcellulose formate) or different (methylethylcellulose propionate). Representatives of all of the above classes are known. This attempt to divide these compounds into mono-, di- and tri-derivatives is, of course, but a wide approximation. It is known, for instance, that a partially ethylated cellulose may be benzylated to the extent of less than 1% benzyl in combination, and this is translatable to a mono-benzyl ether of a cellulose of greater than a C_{24} molecule.

The suggestion is made that the word "esther," combining the *est* of *ester* and the *her* of *ether,* be adopted to designate these ether-ester bodies, being shorter and equally as euphonious.

In 1913, W. Denham and H. Woodhouse[1] acetylated methylated cellulose made from cotton with a mixture of acetic acid and acetic anhydride containing a trace of sulfuric acid, and obtained a methylcellulose acetate readily soluble in chloroform. Analysis showed the percentage of C, H and methoxyl to be less than in a completely acetylated methylated cellulose, indicating that partial elimination of the methoxyl group took place incident to acetation[2].

K. Hess[3] studied the acetates of diethylcellulose, and obtained a low melting product, the chemical composition and molecular weight of which corresponded to a diethylcellulose monoacetate, the solubility and melting point of the individual preparations differing quite widely.

E. Heuser and W. v. Neuenstein[4] have investigated di-

1. J. C. S. 1913, **103**, 1735; abst. C. A. 1914, **8**, 243; J. S. C. I. 1913, **32**, 974; Ann. Rep. S. C. I. 1913, **10**, 88; Bull. Soc. Chim. 1913, **14**, 1495; Chem. Zentr. 1913, II, 1857; Chem. Ztg. Rep. 1914, **38**, 241; Meyer Jahr. Chem. 1913, **23**, 536; Cellulosechem. 1920, **1**, #2, 14; #3, 22; Paper, 1920, **27**, #11, 19. See this work, p. 29, last paragraph.

2. See pages 191, 242, 287, 289.

3. K. Hess and W. Wittelsbach, Ber. 1921, **54**B, 3232; abst. C. A. 1922, **16**, 2027; J. C. S. 1922, **122**, i, 116; J. S. C. I. 1922, **41**, 91-A; Ann. Rep. S. C. I. 1922, **7**, 136; Bull. Soc. Chim. 1922, **32**, 461; Caout. et Gutta. 1922, **19**, 11334; Zts. ang. Chem. 1921, **34**, 449.

4. Cellulosechem. 1922, **7**, 89, 101; abst. C. A. 1923, **17**, 875; J. C. S. 1923, **124**, i, 17; J. S. C. I. 1922, **41**, 977-A; 1923, **42**, 91-A; J. Textile Inst. 1923, **14**, 40-A.

methylhydrocellulose acetate, using the method of K. Hess employing a smaller amount of sulfuric acid catalyst as less liable of yielding a partially degraded cellulose ether-ester. They obtained mainly a monoacetate of dimethylhydrocellulose, the acetylation method giving a substance 30% of which was extractable by acetone, giving 26% methoxyl and 17% acetyl, and melting at 110°. The acetone-insoluble residue upon extraction with ether gave a 2-6% yield (methoxyl 23%, acetyl 17%, m. pt. 140°), and from chloroform a 9% yield (methoxyl 27%, acetyl 16%, m. pt. 99°). Dimethylcellulose monoacetate requires 26.72% methoxyl, 18.57% acetyl; dimethylcellulose diacetate, 22.63% methoxyl, 31.39% acetyl; monomethylcellulose monoacetate, 14.2% methoxyl, 19.72% acetyl; while monomethylcellulose diacetate requires theoretically 11.92% methoxyl and 33.08% acetyl. All the products prepared showed no reducing power, and had low melting points.

According to E. Heuser and N. Hiemer[1], dimethylcellulose monoacetate 2.5 gms., when treated with 50 gms. NaOH in 50 cc. water and 60 cc. methyl sulfate at 60° in the presence of small quantities of ethyl alcohol, followed by treatment with 45 gms. NaOH in 45 gms. water and 30 gms. methyl sulfate, gives trimethylcellulose (44.3% methoxyl) in a single operation. On further methylation in the presence of solid NaOH 5 gms., a methylcellulose was obtained of 45.4% methoxyl, as against 45.6% theory. Cellulose triacetate prepared from cotton in a 2-phase methylation yielded a product containing 38.3 methoxyl, and upon further methylation gave a trimethylcellulose (45% methoxyl), melting at 220-225°, fairly soluble in cold water, completely soluble in acetic acid or chloroform.

Carbohydrate Ether-Esters. The manufacture of the carbohydrate ether-esters is either, (I) by the esterification of a partially etherified cellulose, and this is by far the most general method; (II) by the etherification of an incompletely acylated cellulose; or, (III) by physical ad-

1. Cellulosechem. 1925, **6**, 101; abst. C. A. 1926, **20**, 818.

mixture of pre-formed cellulose ethers and esterified cellulose. The latter method is relatively unimportant.

I). *Esterification of Etherified Cellulose.* These methods may be subdivided into the disclosures of the (a) I. G. Farbenindustrie co-workers, (b) scientists affiliated with Courtaulds, Ltd., and (c) miscellaneous processes.

(a). *I. G. Farbenindustrie Methods.* Dimethylcellulose formate and diethylcellulose formate are producible as indicated in the following examples: 200 gms. diethylcellulose are dissolved in 800 gms. 90% formic acid, and the solution stirred for 6-7 hrs. at room temperature. The diethylcellulose gradually passes into solution, and is then poured into cold water with constant stirring, the deposited product washed until neutral and dried. The ethylcellulose formate thus obtained contains 30-40% ethoxyl and 7-8% formic acid. It is said to be entirely stable and waterproof. To produce the corresponding methyl compound, 100 gms. of water-soluble methylcellulose are dissolved in 900 gms. 90% formic acid, and thoroughly stirred for 24-30 hrs. The solution is then precipitated by pouring into water, washed until neutral and dried. It is insoluble in water, but soluble in organic liquids[1].

Whereas the methylated celluloses of all stages of methylation are almost without exception soluble in water or else more or less strongly swell therein, and monoethylcellulose is completely soluble, celluloses ethylated up to the diethyl stage as well as the lower ethylated derivatives which contain but one ethyl group per 2 mol. C_6 cellulose show a distinct tendency to swell in water, and if these ethers be acetylated by the action of acetyl chloride or acetic anhydride in the presence of a small amount of catalyst, bodies are formed which show entirely different chemical properties. They are substantially unaffected by water, and display towards volatile organic solvents a different

1. E. P. 347651; abst. Silk J. 1931, **8**, #89, 54. G. Balle, H. Lange, K. Ost and I. G. Farbenindustrie, Akt. Ges., U. S. P. 1823847. Can. P. 305458. Belg. P. 371607.

behavior in that they become soluble in acetone and in methyl, ethyl, propyl, butyl and amyl acetates to varying degrees, in which solvents before esterification, the methyl- and ethyl-celluloses were insoluble. Instead of using acetyl chloride, benzoyl chloride or *p*-toluene sulfochloride may be employed, giving rise to bodies of the order of methyl (and ethyl) cellulose benzoate and *p*-toluenesulfonate[1].

For example, 100 parts by weight of dimethylcellulose (about 33% methoxyl) are treated with 2-3 of acetic anhydride, 3 of acetic acid and 0.3 of sulfuric acid at 30-50°, until a sample withdrawn is clearly soluble in acetone. The reaction mass is then precipitated in water with stirring whereupon the methylcellulose acetate separates in flakes, and is washed to neutrality and dried. By the etherification in presence of a non-solvent diluent as benzine, ether or benzene, and esterification in the presence also of a non-solvent, fibrous ether-esters are obtained.

Monoethylcellulose Monobenzoate is obtained by soaking 1 part monoethylcellulose (23% ethoxyl) in 6 parts 30% NaOH solution, and to this is added 3 parts benzoyl chloride in 3 parts benzene, and mixed by stirring. The initially vigorous reaction is aided by heat when it subsides. After completion the product is washed free from salt and alkali and the benzene evaporated off, or the product may be precipitated by the addition of ether, washed until neutral and dried. It contains 35.5% C_6H_5CO, is soluble in benzene, acetone, pyridine and chlorinated hydrocarbons, insoluble in ether and alcohol, and yields clear and elastic films. If 1 part ethylcellulose (30% ethoxyl) is saturated with 4 parts dimethylaniline, then 1 part benzoyl chloride gradually added and the mass allowed to stand, there is a gradual heating-up, which upon subsidence of temperature is heated to 60° for 1 hr., precipitated by dilute HCl, washed free from dimethylaniline and HCl, finally washed neutral and dried. A 2.5-substituted cellulose results with 39%

1. I. G. Farbenindustrie, Akt. Ges., G. Balle and K. Sponsel, D. R. P. 525835; abst. C. A. 1931, **25**, 4706; Nitrocellulose, 1931, **2**, #5, 104.

C_6H_5CO, soluble in benzene, acetone and the chlorinated hydrocarbons, dissolving to a viscous, clear solution.

Ethylcellulose Stearate results when 112 parts ethylcellulose (0.5 ethoxyl, and capable of strongly swelling in water) are treated with 80 parts pyridine, 302 parts of stearyl chloride and 600 of benzene. The mixture is heated 6-8 hrs. under refluxation, then treated with water and excess of pyridine and benzol driven off by steam distillation. The residue is washed with water, then dilute alkali, for the purpose of removing some stearic acid which did not enter into reaction, and dried. The product dissolves in benzine and benzene.

Propylcellulose Oleate. 102 parts monopropylcellulose are treated with 150 parts dimethylaniline and a solution of 300 parts oleyl chloride in 600 parts toluene, then refluxed 4-8 hrs., and the product purified as indicated in the preceding example. It likewise is soluble in benzine and benzene.

It has also been found[1] that when methyl- or ethyl-cellulose of 1-1.5 alkyl per C_6 cellulose, and which in general are soluble in cold water, pyridine and glacial acetic acid, are acidylated so that the acid groups introduced stand in the proportion 1 alkyl:4 acidyl, or 2 alkyl:3 acidyl or even 3 alkyl:2 acidyl, the products lose their water solubility and tendency to swell in water, and become soluble in *neutral* volatile solvents as acetone, ethyl acetate, alcohol-benzene, dichlorethylene and other haloid substituted methanes and ethanes. The viscosity in solution, and film elasticity and tensile strength materially increase, and they become substantially water-resistant. It is unnecessary for the alkyl content of the cellulose ether to be brought to a definite percentage composition prior to esterification, since mixtures within the range of 0.5-1.5 alkyls may also be readily acylated to products of solubility as above indicated.

1. I. G. Farbenindustrie and E. Teupel, D. R. P. 510424; abst. C. A. 1931, **25**, 1083; Chim. et Ind. 1931, **25**, 1214; Kunst. 1931, **21**, 46. F. P. 671110; abst. C. A. 1930, **24**, 1979.

The method of procedure is indicated in the following two examples:

1. 100 parts monoethylcellulose, prepared from alkalicellulose and ethyl halide in the presence of 4 parts water to 1 part alkali, soluble in cold water and strong alkalis, are introduced into a mixture of 300 glacial acetic acid, 200 acetic anhydride and 0.5 sulfuric acid (calculated on the cellulose ether), agitated 40 min., and cooled. A clear, fiber-free mass is obtained, which is precipitated by water and washed until neutral. Acetyl content 36%, equivalent to 0.5-ethylcellulose, 2.5-acetate or monoethylcellulose penta-acetate on a C_{12} basis.

2. 100 parts methylcellulose prepared from alkalicellulose and methyl sulfate corresponding to 1 methoxyl per C_{12} molecule, soluble in ice water, are kneaded with 250 parts glacial acetic acid, 200 acetic anhydride and 0.25 sulfuric acid for 0.5 hr. The methylcellulose rapidly dissolves to a clear solution, which is precipitated by water and washed. 2.6 groups have been substituted by acetyl. It is soluble in acetone, alcohol and dichlormethylene and is water-resistant.

Ethylcellulose Benzoate[1]. Ethylcellulose (alkali-insoluble and containing 5 ethoxyl per C_{12} unit) is introduced into 3 times its weight of molten benzamide at 130°. The cellulose ether dissolves within 3 min. After solidification, the mass is repeatedly extracted with water until the acid amide has been completely separated, ethylcellulose benzoate remaining. This ether-ester may also be made[2] by mixing 40 parts ethylcellulose with 200 parts benzoic acid and heating 3 hrs. with stirring at 130-150°. Excess benzoic acid is then removed by washing with dilute sodium

1. I. G. Farbenindustrie, E. P. 300942; abst. C. A. 1929, **23**, 4071; J. S. C. I. 1929, **48**, 126-B. F. P. 34859, Addn. to F. P. 629861; abst. C. A. 1930, **24**, 1216. I. G. Farbenindustrie, M. Hagedorn, O. Reichert and E. Guehring, D. R. P. 511208; abst. C. A. 1931, **25**, 1379. D. R. P. 533126, 535235; Addns. to D. R. P. 511208; abst. C. A. 1932, **26**, 598, 1119.

2. I. G. Farbenindustrie, E. P. 334897; abst. Br. Plastics, 1931, **2**, 317; J. S. C. I. 1930, **49**, 1146-B. F. P. 695323; abst. C. A. 1931, **25**, 2866.

carbonate solution, and the product dried. This ethylcellulose benzoate is a white powder soluble in benzene-alcohol, and said to produce excellent films and lacquers. In the above process, the benzoic acid may be replaced by salicylic acid (hydroxybenzoic acid), phenylacetic acid, undecylic acid, lauric acid, or palmitic acid, forming ethylcellulose salicylate, phenylacetate, undecylate, laurate, or palmitate.

Ethylcellulose Stearate. One part ethylcellulose (39.1% ethoxyl) is heated with 7 parts stearic acid 5-6 hrs. with stirring at 150°. By boiling with benzine the ethylcellulose stearate is freed from excess stearic acid, and thus obtained as a white, granular mass, soluble in alcohol-benzene, alcohol-toluene and alcohol-xylene, ethyl acetate or butyl acetate.

Butylcellulose Linoleate. 30 parts butylcellulose (49% butoxyl) are introduced into 150 parts linoleic acid and 0.5 of boric acid. The mixture is stirred and heated 8-10 hrs. at 150°, then treated with methyl alcohol to remove free linoleic acid. Butylcellulose linoleate at ordinary temperature is a tough mass, readily soluble in benzine, benzene, toluene, xylene and esters.

Ethylcellulose Caprate, Caprylate, Caproate, Myristate, Laurate, Palmitate, Oleate. Cocoanut oil contains myristin, laurin, caprin, caprylin, caproin, palmitin and triolein. When 200 parts of the total fatty acids from cocoanut oil are heated with stirring with 40 parts ethylcellulose (40% ethoxyl) 8 hrs. at 130-150°, the esterification being assisted by the addition of a small amount of boric acid, the above ether-esters are formed. After completion of the reaction the mass is treated with a low boiling benzine which dissolves the excess fatty acids while the ether-ester is precipitated. It is washed with hot benzine, then with water, and forms a white powder, soluble in aromatic hydrocarbons, in turpentine and alcohol, and yields flexible films. The product is plastic when hot, and may be used in this condition for extruding or squirting into any desired shape.

Hydroxyethylcellulose Acetate[1]. 100 parts cotton linters, 60 ethylene and 5 diethylaniline are stirred together 3-4 hrs. in a pressure vessel at 40-50°. Excess of ethylene oxide and diethylaniline is then removed by means of feebly acidified water or an organic solvent. The product contains 1 hydroxyethyl group for each 3 C_6 groups, and may be acetylated at 35-40° in a pressure vessel with acetic anhydride 250, liquid sulfur dioxide 200, and zinc chloride 20-30. After about 3 hrs. the mass is precipitated and worked up in the usual manner. The product is soluble in acetone.

In another method[2] 300 gms. acetyl chloride are dissolved in 2 liters petroleum ether, and into this solution is placed 100 gms. fibrous oxyethylcellulose, and the mixture stirred for several days at room temperature. Without apparent visible change in structure, the cellulose ether has become acetylated, and the ether-ester dissolves in aceton and in chlorinated hydrocarbons.

Oxypropylcellulose Butyrate. 100 gms. oxypropylcellulose are suspended in 490 gms. butyryl chloride and heated on the water bath for 3-5 hrs. with stirring. Excess of HCl and butyryl chloride is then distilled off, washed with water to remove small quantities of butyric acid and then dried. The ether-ester formed dissolves in the cold in chlorinated aliphatic hydrocarbons, acetone, ethyl acetate, and in a heated mixture of methyl alcohol and benzene.

Hydroxyethylcellulose Acetobutyrate[3]. Cotton linters 100 and ethylene oxide 30 are thoroughly kneaded in a vessel with stirrer at ordinary temperature until the ethylene is used up. The product contains 1 hydroxyethyl group per C_6 cellulose. It is then esterified with 200 parts acetic anhydride, 100 parts butyric acid and 300 glacial acetic acid and 8 parts concentrated sulfuric acid. In 2-3 hrs. the

1. I. G. Farbenindustrie and M. Hagedorn, D. R. P. 527617; abst. C. A. 1931, **25**, 5287. F. P. 698392; abst. C. A. 1931, **25**, 3167. E. P. 358510. See U. S. P. 1502379. D. R. P. 363192.
2. *Ibid.* F. P. 717623.
3. *Ibid.* F. P. 695283; abst. C. A. 1931, **25**, 2847.

reaction is complete and is precipitated by water, washed until neutral and dried. It is soluble in acetone.

Dibasic esters of hydroxyalkylcellulose, soluble in organic acids, are made by causing the hydroxyalkylcellulose (as hydroxymethylcellulose, hydroxyethylcellulose) to react with anhydrides of mono- and especially di-basic acids at a high temperature in the absence of catalysts and diluents. If dibasic acids as malonic, succinic, glutaric, fumaric, malic, tartaric, phthalic or naphthalene-1.8-dicarbonic acids are used with hydroxymethyl- and hydroxyethyl-cellulose, a series of 18 ether-esters is possible, hydroxymethylcellulose malonate being an example[1].

Ethylcellulose Naphthenate. 10 parts of wood pulp are treated with 2670 parts 50% NaOH solution at the ordinary temperature 7 and after 2 hrs. pressed to 283 parts. After the alkalicellulose has stood in a closed container 18 hrs. at room temperature, there is added benzene 200, powdered NaOH 47 and ethyl chloride 300, and the mixture heated in an autoclave 6 hrs. at 120°. The mass is then diluted with 200 parts benzene, excess of alkali neutralized by acetic acid until a strong acid reaction results. There is then introduced pyridine bases 70, and naphthenic acid chloride 133, and the whole heated with continuous stirring for 3 hrs. at 80°. The reaction mixture is then heated 0.5 hr. at 105°. The ethylcellulose naphthenate thus obtained contains 40-43% ethoxyl and 20-25% naphthenic acid residue, dissolves readily in benzene, toluene and xylene and in chlorinated aliphatic hydrocarbons, and a film prepared from it is less readily scratched than one made from the ethylcellulose before acylation[2].

In a patented process issued in 1927, this firm[3] describes a general process for cellulose ether-ester formation by the action of an organic acid anhydride upon a partially etherified cellulose as indicated by the following:

1. I. G. Farbenind. and M. Hagedorn, F. P. 705816; abst. C. A. 1932, **26**, 303.
2. M. Hagedorn and G. Hingst, U. S. P. 1867942.
3. I. G. Farbenindustrie, F. P. 629861. See also F. P. 332203, 581160.

1. *Ethylcellulose Myristate.* Ethylcellulose containing 2.5 ethoxyl groups is heated on an oil bath with double the theoretical quantity of myristic anhydride required. At a temperature of about 140° the ethylcellulose gradually passes into solution, and at this point heat is continued 30 min. longer. After cooling, the mass is purified by precipitation with benzine or petroleum ether.

2. *Ethylcellulose Benzoate.* A 2.5 ethoxyl ethylcellulose is treated with triple the theoretical quantity of benzamide at 130°, the cellulose ether going into solution in about 3 min. After coagulation of the mass, the acid amide is eliminated by repeated extraction with water.

Mono-oxyethylcellulose Acetate. Oxyethylcellulose Acetate. One part cotton as linters is heated at 100° with 2 parts aqueous ammonia of 25% strength and 60 parts ethylene. The product obtained corresponds to mono-oxyethylcellulose which may readily be acetylated with acetic anhydride and glacial acetic acid to the corresponding acetate, which is soluble in acetone. Instead of ammonia, equivalent quantities of oxyethylamine in aqueous solution may be employed, and ethylene oxide may be replaced by propylene oxide or butylene oxide, with the formation of oxypropyl- and oxybutyl-cellulose, which may likewise be acetylated to the corresponding acetates as above indicated[1]. Plastics as celluloid substitutes may be obtained from these ether-esters[2], as indicated:

1. 100 parts hydroxyethylcellulose acetate (containing 3 acetic residues per C_6 cellulose, and soluble in chloroform, acetone and hot benzene), 20 parts tricresyl phosphate and 5 parts each benzene and ethyl alcohol are homogenized in a kneader at 100°. The transparent mass thus obtained is directly usable in the plastics industry.

2. 100 parts hydroxyethylcellulose acetate, 20 parts *p*-toluenesulfonamide, 50 parts lithopone and 10 parts ethyl

1. I. G. Farbenindustrie, F. P. 708538. D. R. P. 542867; abst. Chem. Zentr. 1932, I, 2114.
2. *Ibid.* E. P. 366116.

alcohol are homogenized at 90-100° until incorporated. The mass is especially useful for comb manufacture.

In another patented method, organic acid radicals are introduced into oxyalkylcellulose by a simple treatment, preferably at a raised temperature, with the anhydride of the acid in the absence of either a catalyst or a diluent, the free hydroxyl groups of the cellulose, as well as the hydroxyl groups of the side-chains entering into the reaction. Examples of manipulation are as follows[1]:

Hydroxyethylcellulose Acetate. Hydroxyethylcellulose made by treating alkalicellulose with 4-5 times its weight of ethylene oxide in the presence of benzene is introduced into 10 times its weight of acetic anhydride. The mixture is heated 2.5 hrs. at 120° until a clear, viscous solution is produced from which, after cooling, hydroxyethylcellulose acetate is obtained free from acid by precipitating with water, and prolonged washing with warm water. The product dissolves in acetone without further hydrolysis.

Hydroxypropylcellulose Butyrate. Hydroxypropylcellulose made by boiling alkalicellulose with propylene oxide in a reflux condenser for 6 hrs., washing to remove excess of alkali and drying the product, is introduced into 10 times its weight of butyric anhydride, and heated for 2.5 hrs. at 120°. A clear, viscous solution results, which after purification, is soluble in acetone, and in those solvents in which cellulose butyrate dissolves.

Hydroxybutylcellulose Cocinate. Hydroxybutylcellulose made by boiling alkalicellulose in an excess of butylene oxide in a reflux condenser for 6 hrs., washing to remove excess alkali and drying, is mixed with 8-10 times its weight of cocinic anhydride (the anhydride of the fatty acids of cocoanut oil), and the mixture heated 4-6 hrs. at 130-140°. The temperature is then allowed to drop to 100°, the mixture freed from excess anhydride and from the free acid formed during the reaction, by boiling for a considerable time with aqueous sodium carbonate. The product is soluble

1. I. G. Farbenindustrie, E. P. 365250; abst. J. S. C. I. 1932, **51**, 501-B.

in aromatic hydrocarbons and chlorinated aliphatic hydrocarbons, in ether and in ethyl acetate.

Dihydroxypropylcellulose Acetate. 1 part of hydroxyethylcellulose is prepared by causing glycide to act upon an equal weight of alkalicellulose in presence of 4 times its weight of chloroform, while stirring, for 6 hrs. at 57-58°, washing the product with water and drying. The product is then acetylated as indicated above, the ether-ester being soluble in acetone.

Hydroxyethylcellulose Naphthenate. 1 part by weight of hydroxyethylcellulose[1] is heated with 8 parts naphthenic anhydride 3-4 hrs. at 130-140°. After cooling the ester is obtained in purified form by exhaustive extraction with methyl alcohol. It is soluble in benzene, toluene, xylene and in chlorinated aliphatic hydrocarbons.

Hydroxypropylhydroxybutylcellulose Benzoate. Alkalicellulose is heated with an excess of a mixture of equal parts of propylene oxide and butylene oxide in solution in benzene for 6 hrs. in a reflux apparatus, and the product washed and dried. 1 part of the hydroxypropylhydroxybutylcellulose thus produced is heated with 8-9 parts of benzoic anhydride to about 130°. After cooling, the benzoic acid formed and the excess of benzoic anhydride are removed by extraction with methyl alcohol. The ether-ester remaining is soluble in chlorinated hydrocarbons, and suitable for film formation.

In order to increase dye penetration in fabric coloring[2], use is made of the wetting property of the "alkali salt of carboxymethylcellulose."

1. Made according to D. R. P. 365192.
2. H. Franke, Dtsch. Faerber-Ztg. 1932, **86**, 85; abst. Chem. Zentr. 1932, I, 2240. C. Gränacher (E. P. 347117; abst. C. A. 1932, **26**, 2862) has described cellulose ethers and ether-esters obtained by treating mercerized cellulose or partially acetylated cellulose with etherifiants as homologues of nitrobenzylhalides or with a chlornitrobenzene derivative other than an *o*-dinitro compound, containing halogen in the *o*- or *p*-position to a nitro group, such as nitroxylyl chloride, *o*- and *p*-nitrochlorbenzene, 1-chlor-2.4-dinitrobenzene or their homologues or halogen derivatives, in the presence of an acid-binding agent other than caustic alkali, as lithium carbonate, the product being afterwards reduced.

(b). *Methods of Courtaulds, Ltd.* W. Glover and E. van Weyenbergh[1] have found that cellulose ethers which are insoluble in alkali, when treated with formic, acetic or propionic acids with the addition of a suitable catalyst if necessary, are converted into the corresponding esters; the method being applicable especially to the cellulose diethers. A diethylcellulose soluble in, or gelatinized by cold water and incompletely soluble in organic solvents, upon being esterified with one of the fatty acids above mentioned, gives an ether-ester resistant to water, even at 2°, and readily soluble in organic solvents to clear solutions.

As an example, ethylcellulose (26.3% ethoxyl), soluble in cold water and incompletely soluble in acetic acid, pyridine, benzene, alcohol, methyl acetate or dichlorethylene, is treated with glacial acetic acid at 70-90° until the cellulose ether goes completely into solution. The product is then precipitated, washed and dried. The ether-ester so obtained is insoluble in water, but readily soluble in acetic acid, pyridine, benzene, alcohol, methyl acetate or dichlorethylene to perfectly clear solutions. If 2-4% sulfuric acid be added to the acetylating mixture, a similar result is obtained without the temperature of the mixture being raised above 20°.

Where alkalicellulose is heated with such a restricted quantity of ethyl sulfate at temperatures not exceeding the normal, a homogeneously ethylated cellulose is obtained of about 4% ethyl (1 ethyl group per C_6 cellulose)[2], which may readily be acetylated. It is advocated to thoroughly dry the ethylcellulose before acylating, so that it contains not to exceed 2-4% moisture, acetylation being materially

1. U. S. P. 1613451; abst. C. A. 1927, **21**, 649; J. S. C. I. 1927, **46**, 139-B; Plastics, 1927, **3**, #4, 219. E. P. 241679; abst. C. A. 1926, **20**, 3567; J. S. C. I. 1926, **45**, 48-B; J. Soc. Dyers, 1926, **42**, 67; Chem. Zentr. 1926, I, 1744; Ann. Rep. S. C. I. 1926, **11**, 130. F. P. 29866, Addn. to F. P. 520101; abst. Chem. Zentr. 1926, I, 1744.

2. W. Glover and C. Diamond, U. S. P. 1763428; abst. C. A. 1930, **24**, 3900; J. S. C. I. 1930, **49**, 708-B. Can. P. 277024; abst. C. A. 1928, **22**, 2663. Courtaulds, Ltd., W. Glover and C. Diamond, E. P. 268552; abst. J. S. C. I. 1927, **46**, 473-B; C. A. 1928, **22**, 1473; Plastics, 1928, **4**, 508; Chem. Zentr. 1927, II, 655; Chem. Age. 1927, **16**, 467. D. R. P. 514892.

facilitated when working with a bone-dry cellulose ether. Those ethylcelluloses containing 4-7% ethyl swell considerably in 10% NaOH solution but do not dissolve. With a more highly ethylated cellulose (7-15.5% ethyl), the etherized cellulose is insoluble in alkali.

The method is illustrated in the following three examples:

1. 100 parts sulfite wood pulp are steeped in an excess of 21% NaOH, pressed to 300 parts, ground for 2 hrs. at 15-20°, and then 290 parts ethyl sulfate added, the milling being continued for 30 min. at 15-20°. The mass is then transferred to a closed vessel and aged at 15-20° for 3-5 days, preferably in an atmosphere of nitrogen. The mass is then washed free from alkali and dried to a moisture content of not more than 3%. This intermediate product is an ethylcellulose of about 15% ethyl. 100 parts of this are introduced into a mixture of acetic anhydride 200, acetic acid 500 and sulfuric acid 2, and the whole continually stirred at not above 10°. The temperature is subsequently allowed to rise to 15° where it is maintained until acetylation is completed (about 10-15 hrs.). The ether-ester may be hydrolyzed in the usual manner, or immediately precipitated.

2. 100 parts bleached sulfite wood pulp are steeped in an excess of 17.5% NaOH (the strength used to produce alkalicellulose for viscose rayon manufacture) for about 2 hrs., pressed to 3 times the original weight of the cellulose, and milled at 15-20° 2 hrs. Then 220 parts ethyl sulfate are added and the milling continued for 0.5-1 hr., after which the mass is kept in an inert atmosphere 3-5 days at 15-20°. The mass is then washed and dried to not more than a 3% moisture content. This ethylcellulose is of 13.5% ethyl content, and is acetylated as above, using 200 parts acetic anhydride per 100 parts of ether, the latter dissolving in the acetylating bath to a clear solution.

3. 100 parts bleached sulfite wood pulp are treated with an excess of 17.5% NaOH solution, pressed to 2.5-3

times the original cellulose weight, disintegrated 2 hrs. at 15-20°, and then 50-60 parts ethyl sulfate added, the whole mixed for 1 hr., and kept for 2-4 days at 15-20°, preferably in an inert atmosphere. The mass is then washed free from alkali and salt and dried to low moisture content. The cellulose ether formed contains 5% ethyl. In the dry state it is introduced into a mixture of acetic anhydride 225, acetic acid 500 and sulfuric acid 2.5 for each 100 parts ethylcellulose. Acetylation proceeds smoothly at 18-20° and is complete in 16-20 hrs., giving a viscous solution from which the acetate may be precipitated directly by water, or may be partially hydrated to the degree of acetone solubility desired, and then precipitated.

(c). *Other Cellulose Ether-Ester Methods.* Ethylcellulose acetate process of L. Lilienfeld[1]. 200 parts sulfite cellulose are impregnated with 1800 parts 9-18% NaOH solution at room temperature, allowed to stand 12-24 hrs., pressed to 500-700 parts, then comminuted. The finely divided mass after standing 2-3 days at room temperature is treated with 25-90 parts ethyl chloride in an autoclave under pressure, and with stirring, brought to 80-85° and maintained for 6-13 hrs. A test sample withdrawn at this stage is soluble in 5-10% NaOH solution to form a viscous solution which may be precipitated by acidification. The mass is now stirred with sufficient HCl or sulfuric acid to induce an acid reaction, freed from mother liquor by filtration, washed with water until neutral and dried. 100 parts of this dried mass are kneaded into a mixture of acetic anhydride 200, glacial acetic acid 200-300 and sulfuric acid 5-15, with constant cooling. Solution takes place in a few minutes, forming a transparent, easily kneaded paste. After standing for some time, the cellulose ether-ester is pre-

1. U. S. P. 1589607; abst. C. A. 1926, **20**, 3084; J. S. C. I. 1926, **45**, 661-B. E. P. 177809; abst. C. A. 1922, **16**, 3545; J. S. C. I. 1924, **43**, 11; Chem. Zentr. 1922, IV, 682; Faserstoffe, 1924, **6**, 10; Caout. et Gutta. 1922, **19**, 11497. D. R. P. 488446; abst. C. A. 1930, **24**, 2599. F. P. 549568; abst. Chim. et Ind. 1923, **10**, 1131. Can. P. 248232; abst. C. A. 1925, **19**, 3163. Aust. P. 83400. See also E. P. 177810; abst. C. A. 1922, **16**, 3206.

cipitated by water, washed until neutral and dried. This product may be formylated or nitrated, producing ethylcellulose acetoformate (formylacetate), or cellulose acetonitrate (nitroacetate)[1].

Diethylaminoethylcellulose Acetate. When halogenated alkylamines as chlorethyldiethylamine are allowed to react upon alkalicellulose, and the products afterwards treated with acylating, alkylating, aralkylating or arylating agents, or a combination of both etherification and esterification applied[2], complicated cellulose ether-esters result. The following examples are indicative of the scope of the process:

1. 16 parts cellulose are immersed in 160 parts 18% NaOH solution for 3 hrs., excess liquid centrifuges off, and the alkalicellulose placed in a solution of 7 parts chlorethyldiethylamine in acetone. After 3 hrs. with vigorous stirring meanwhile, the product is washed with water and finally with dilute acetic acid, washed and dried. A light colored product is obtained.

2. 15 parts loose cotton are converted into alkalicellulose, and after pressing, treated with 18 parts chlorethyldiethylaminochlorhydrate. The organic base is liberated by the excess alkali. Kneading is continued for 8 hrs., after which the material is washed and dried.

3. One part diethylaminoethylcellulose is heated with 2 parts glacial acetic acid and 4 parts acetic anhydride with addition of zinc chloride as catalyst, the cellulose ether rapidly passing into solution. The product is then precipitated with water and washed until neutral. In the dry state this is a light powder, nearly white in color, and

1. See I. G. Farbenindustrie, E. P. 305947; Addn. to E. P. 283181, 297766; abst. C. A. 1929, **23**, 5041; J. S. C. I. 1930, **49**, 814-B; Brit. Plastics, 1930, **2**, #17, 229; Chem. Zentr. 1929, II, 112. E. P. 305661; abst. C. A. 1929, **23**, 4818. See E. P. 284298, 292929.

2. Soc. Anon. Pour L' Ind. Chim. a Basle, F. P. 680956; abst. C. A. 1930, **24**, 4156. Swiss P. 141556; abst. C. A. 1931, **25**, 2288. Swiss P. 142175; abst. C. A. 1931, **25**, 2288. In this connection see F. P. 686575; abst. C. A. 1931, **25**, 591. Swiss P. 144227; abst. C. A. 1931, **25**, 4124. Swiss P. 144228, Addn. to 142175; abst. C. A. 1931, **25**, 4124.

soluble in organic solvents. The mere treatment of the cellulose ether with nearly absolute formic acid in the cold, the reaction being facilitated by an elevation of temperature, causes the ether to pass into solution, from which solution diethylaminoethylcellulose formate is precipitable by the simple addition of an excess of water.

Ethylcellulose Linoleate, Stearate, Oleate. By heating 5 parts ethylcellulose with 10 parts linseed oil to 140°, esterification ensues, and an ethylcellulose linoleate is formed, which may be precipitated by means of water with stirring, washed free from impurities and dried. Likewise[1] when 50 parts ethylcellulose are heated with 50 parts stearic acid to about 130°, or with an oleate to 150-170°, the respective ethylcellulose stearate or oleate results.

Aminoethylcellulose Acetate. M. Hartmann[2] has described a series of cellulose ethers obtained by causing halogen alkylamines as chlorethylethylaniline, chlorethylamine, chlorpropylamine, chlorethyldiethylamine, mono-oleyldiethylethylenediamine,chlorethylpiperidino-chlorhydrate and similar bodies to act upon alkalicellulose, forming such ethers as diethylaminoethylcellulose, propylaminocellulose, oleylethylpropylcellulose and ethylaminocellulose. These cellulose ethers may be acetylated or propionated to form the corresponding ether-ester, as by the following general example: 1 part diethylaminoethylcellulose is heated with 2 parts glacial acetic acid and 4 parts acetic anhydride until the fibrous material has passed into solution. The mixed ether-ester is then precipitated with water, washed until neutral and dried.

II. *Etherification of Esterified Cellulose.* Due to the fact that in the etherification of cellulose by the usual methods, an excess of concentrated alkali is used, it is contraindicated to prepare cellulose ether-esters by etheri-

1. I. G. Farbenindustrie, F. P. 660510.
2. U. S. P. 1777970; abst. C. A. 1931, **25**, 204. E. P. 318255; abst. J. S. C. I. 1931, **50**, 108-B. Swiss P. 145054, Addn. to 142175. F. P. 717524; abst. C. A. 1932, **26**, 2862.

fying a partially acylated cellulose, for the reason that the alkali saponifies off the acid radical from the cellulose ester.

III. *Physically Admixed Cellulose Ethers and Cellulose Esters.* According to L. Malone[1], the physical admixture of cellulose ethers and esters by means of a mutual solvent as pyridine, either alone or in conjunction with volatile solvents, results in solutions of lower viscosity and other desirable characteristics, especially for film formation and in the lacquer industry. When 33 parts each cellulose nitrate, acetone-soluble cellulose acetate and water-insoluble ethylcellulose are dissolved in 400-600 parts pyridine, a viscous dope results from which films may be prepared by spreading and partial evaporation of the pyridine. Equal weights of cellulose nitrate and cellulose acetate, or equal parts cellulose acetate and ethylcellulose may likewise be incorporated together by virtue of the mutual solvent pyridine. If it is desired to speed up the rate of evaporation or otherwise modify the properties of the solution, there may be added ethyl alcohol, methyl acetate, ethyl acetate, acetone, or other solvent which is a nonprecipitant of one of the cellulose derivatives.

For the preparation of artificial coatings and plastic masses, combinations of ethylcellulose with cellulose trilaurate[2] and with ethylcellulose stearate and ethylcellulose linolenate have been described.

According to the researches of H. Persiel, G. Balle and K. Sponsel[3], cellulose ethers soluble in water, as the lower alkylated celluloses, and cellulose esters, water-insoluble elastic masses, foils and fibers may be prepared, the ether-esters of cellulose being insoluble in water, although the cellulose ether used is freely soluble. The application of the invention is indicated in the following five examples:

1. 50 parts 5% nitrocellulose solution prepared from collodion wool, butyl acetate 30, butyl alcohol 40, benzol 25,

1. U. S. P. 1429153.
2. I. G. Farbenindustrie, F. P. 660510.
3. D. R. P. 540872; abst. Chem. Zentr. 1932, I, 1316.

are mixed with 50 parts 5% aqueous methylcellulose solution whereby a stable emulsion is obtained, drying to an elastic transparent mass, insoluble in water, benzene, benzine, alcohol, ethyl acetate or butyl acetate.

2. 7 parts of 6% celluloid solution prepared from celluloid scrap, ethyl acetylglycollate 12, butyl acetate 18, butyl alcohol 45, xylol 10, benzine 8, are emulsified with 8 parts 5% aqueous methylcellulose and brought onto cardboard. The coating protects the paper from wetting and dampness and can be readily soaped and washed.

3. 20 parts nitrocellulose solution are prepared consisting of nitrocellulose 14, moistened with butyl alcohol, with a 65% content of dry nitrocellulose, and added to a solution of ethyl acetylglycollate 100, benzyl alcohol 10, ethyl acetate 50, methyl acetate 42. Into this is stirred 50 parts of 5% aqueous oxyethylmethylcellulose solution. A thick, whitish emulsion results which is very stable. On drying in thin layers it leaves behind a transparent film, insoluble in water and organic solvents, and distinguished by great mechanical strength and resistance to cold.

4. 30 parts 8% cellulose acetate solution comprising acetylcellulose, benzyl alcohol 10, ethyl acetylglycollate 40, cyclohexane 10 and methyl acetate 32, are emulsized with 50 parts of 5% aqueous water-soluble ethylcellulose. On drying, this emulsion leaves behind a flexible, sticky film, non-inflammable, and not attacked by water or organic solvents.

5. 30 parts benzylcellulose solution composed of benzylcellulose, benzyl alcohol, ethyl acetylglycollate, butyl alcohol and benzene 10 each, solvent naphtha 50, are emulsified with 50 parts of 6% aqueous solution of oxyethylcellulose. Fabrics saturated with this emulsion are waterproof after drying. Through several applications of the emulsion there is obtained a complete filling of the textile interstices, and finally a hard, horny, skin-like structure which may be worked up into drum-heads.

Likewise[1], methylcellulose which is water-soluble above 16°, may be mixed with other cellulose ethers or esters to produce compositions wherein the water solubility is completely lost. The following three examples are illustrative:

1. 75 parts methylcellulose are treated with such an amount of alcohol that an exactly complete gelatinization takes place. This is then mixed with 25 parts acetylcellulose gelatinized by acetone (hence non-hydrolyzed), the solvent is then evaporated leaving a product suitable for plastic masses.

2. A 10% solution of methylcellulose in water is capable of dissolving water-insoluble ethylcellulose up to 2% of the weight of methylcellulose used. Plastic masses prepared from this, or poured film strips, show, after drying, considerably higher water resistance. There can also be used, for example, 50 parts methylcellulose with 50 of water, homogenized. Then 50 parts ethylcellulose previously swollen by means of alcohol are added, and worked up to a homogeneous mass. The solvent is removed by evaporation, leaving a flexible, plastic mass to which softeners may be added.

3. 25 parts methylcellulose are mixed to a homogeneous paste with 20 parts water, and this worked up with 50 parts nitrocellulose previously swollen with a mixture of ethyl acetate, acetone and butyl acetate.

Applications of the Cellulose Ether-Esters. By a manipulation and selection of acid radical against cellulose ether, together with the choice of alkyl or acyl entering group or groups, it is possible to profoundly modify the properties of the cellulose ether or cellulose ester *per se*, especially in increasing the range of solubility in inexpensive solvents and solvent combinations, and lessening the sensibility to water of the cellulose ether. An important commercial point at the present time is that the introduction of relatively cheaper ester groups in the mixed ether-ester

1. I. G. Farbenindustrie, D. R. P. 534852.

cheapens the final cost of the product, since esterification to the increment of a given weight is less costly than etherification, even if a heavy group as benzyl is introduced into the cellulose.

In the manufacture of safety or laminated glass[1], ethylcellulose palmitate has been proposed as the intermediate layer between the plurality of sheets of glass. For the waterproofing of such articles as pulp milk bottles and food containers, it is recommended to coat the article with an ethylcellulose acetate solution in acetone, to which a preservative and bactericide are added before application[2]. Certain oils unobjectionable from a sanitary viewpoint may be added to the ether-ester solution in order to impart a softening effect, such as white poppy seed oil, walnut oil, refined cocoanut oil or corn oil. If the food product is a fruit, it may be pre-dipped in alcohol before submergence in the coating solution.

A layer for use in the bleach-out process of photography has been advocated[3] comprising a mixed film of nitrocellulose and ethylcellulose butyrate, and a protective layer applied to the back of a photographic film has been patented[4], comprising a cellulose ether-ester. To produce a film which has a small shrinkage during development and which will slide easily in a projector, the ester advocated is cellulose acetostearate or ethylcellulose stearate. Protection against electric discharges in the projector is afforded by a coating of cellulose acetophosphate, ethylcellulose phosphate or cellulose acetonitrate. The ethylcellulose stearate is used dissolved in a mixture of 1 part alcohol, 2 parts acetone and 3 parts benzene. This layer greatly diminishes the resistance of the film to sliding in the cinematograph apparatus.

1. M. Hagedorn and A. Jung, U. S. P. 1861915.
2. H. Buel, U. S. P. 1680934; abst. C. A. 1928, **22**, 3712; J. S. C. I. 1928, **47**, 782-B; Chem. Zentr. 1928, II, 2083.
3. I. G. Farbenindustrie, E. P. 343212.
4. *Ibid.* E. P. 270347; abst. C. A. 1928, **22**, 1552; J. S. C. I. 1927, **46**, 893-B; Chem. Zentr. 1927, II, 1324. F. P. 635281.

Insulation suitable for wires and cables[1] is prepared by saturating unsized paper or textile material with a solution of ethylcellulose palmitate or stearate. For the formation of molded masses ethylcellulose laurate at 3 atms. pressure and 120° is said to yield transparent, water-insoluble and very elastic masses[2].

A general method of plastics production to simulate the celluloids obtained from nitrocellulose has been evolved[3] employing hydroxyethylcellulose acetate, substantially without the addition of volatile solvent, thus minimizing the curing time after plastic formation, which, in heavier and thicker pieces often requires several months. The cellulose compound is kneaded with such bodies which exert when warm a swelling action but no solvent effect, i.e., they intumesce without incipient solution. These plastics, of course, are much less inflammable than celluloid. As an example, 100 parts hydroxyethylcellulose acetate (containing 3 acetic acid residues per C_6 cellulose molecule and soluble in chloroform, acetone and benzene) are incorporated with 20 parts triphenyl phosphate with 5 parts each benzene and ethyl alcohol, then homogenized in a kneader at 100°. A transparent water-insoluble mass results. Or, the cellulose ether-ester may be incorporated with a mixture of 20 parts *p*-toluenesulfonamide, 50 parts lithopone and 10 parts ethyl alcohol. This is homogenized at 90-100° in a calender or kneading machine, the mass, also transparent, being indicated for the manufacture of imitation ivory, white and non-transparent commodities, as combs and other toilet requisites.

A process for the production of gummed paper has been described[4], being rolls of paper or cloth which have

1. I. G. Farbenindustrie, E. P. 297749; abst. C. A. 1929, **23**, 2772; Br. Plastics, 1930, **1**, 448; J. S. C. I. 1930, **49**, 21-B.
2. *Ibid.* E. P. 289063; abst. J. S. C. I. 1930, **49**, 185-B; Chem. Zentr. 1928, II, 511. F. P. 648154; abst. C. A. 1929, **23**, 2822. F. P. 35906, Addn. to F. P. 648154; abst. C. A. 1930, **24**, 4159.
3. *Ibid.* E. P. 366116; abst. J. S. C. I. 1932, **51**, 357-B.
4. *Ibid.* F. P. 661039; abst. C. A. 1930, **24**, 213. E. P. 302588; abst. J. S. C. I. 1930, **49**, 185-B; Chem. Zentr. 1929, I, 2504.

applied to the non-gummed side, a coating of cellulose ether-ester of the higher fatty acids as ethylcellulose laurate to prevent sticking when the article is rolled. Products suitable for the manufacture of plastic masses have been described, especially valuable on account of the basic character imparted to them by virtue of the presence of amido groups therein[1], obtained by amidating cellulose ether-esters. For instance, if 5 gms. oxyethylcellulose undecylate are treated with 100 cc. liquid ammonia in an autoclave for 48 hrs. at 25-30° and 20 atms. pressure, and the reaction product purified by methyl alcohol, there is obtained 1.7 gms. oxyethylaminocellulose undecylate (?) containing 1.1% N. Likewise, by treating oxypropylcellulose crotonate in a similar manner, 3.2 gms. oxypropylaminocellulose crotonate results.

Cellulose Ether Nitrates, Phosphates, Silicates. It will be remembered that with the exception of the lower methylcelluloses and the salts of cellulose-glycollic acid[2], the dialkylcelluloses are substantially water-insoluble, but are readily dissolvable by organic solvents, and capable of film formation. However, cellulose ether films are more or less sensitive to water, as is evident from their diminished tensile strength when in the wet condition, although this sensitiveness diminishes with increase of alkyl groups introduced into the cellulose, increase in size of alkyl group, and increase in size of the substituent group (i.e. benzyl is more resistant than ethyl).

In order to diminish this sentiveness to water and obtain the maximum in tensile strength both in the wet and dry condition, the Deutsche Celluloid-Fabrik[3] have found that the introduction of 2.5% N in a diethylcellulose (2-2.5 ethyl groups), greatly increases resistance to water, while

1. I. G. Farbenindustrie, D. R. P. 542004.
2. Deutsche Celluloid-Fabrik, D. R. P. 332203. E. P. 138116. See E. P. 231811.
3. A. Weihe, O. Leuchs, E. Dörr and Deutsche Celluloid-Fab., E. P. 347423; abst. J. S. C. I. 1931, **50**, 672-B; C. A. 1932, **26**, 2862. D. R. P. 528147; abst. C. A. 1931, **25**, 4705. F. P. 692603; abst. C. A. 1932, **26**, 1781. U. S. P. 1871868.

the viscosity is unchanged, and the solubility materially increased, in comparison to the same ethylcellulose before the introduction therein. These cellulose ester-ethers, which may be described as nitrodiethylcellulose or diethylcellulose nitrate, are no more inflammable for the introduction of the relatively small proportion of nitro group. A dimethylcellulose which is soluble in water, by the introduction therein of 4% nitrogen (in the form of $O\text{-}NO_2$), becomes entirely insoluble in water, but dissolves to a clear solution in methyl, ethyl and butyl acetates. The dimethylcellulose nitrate is scarcely combustible, and forms clear, tenuous films. By increasing the nitrogen content up to the almost complete esterification of the one available OH group (on a C_6 cellulose assumption in which 2 OH have already been etherified) products are finally obtained which are soluble in ether, hydrocarbons and oil of turpentine.

The usual nitration process with nitric acid or a mixture of nitric and sulfuric acids is inapplicable, but the reaction proceeds smoothly by using diacetyl-*o*-nitric acid, either previously made or formed in the reaction mixture, in the presence of a dehydrating agent. The cellulose ethers dissolve in diacetyl-*o*-nitric acid and form a clear, viscous solution. On addition of a dehydrating agent, as acetic acid, the cellulose ether is nitrated within a few minutes. When cooling is adopted during the nitration process, but little degradation of the product is observable, the nitrogen content of the cellulose ether being controlled by the quantity of acid anhydride. It is surprising if a small proportion of acetic acid is not also combined with the cellulose, thus producing what might be termed diethylcellulose acetonitrate, as an example.

The following two methods of procedure are illustrative:

1. 100 gms. diethylcellulose are dissolved in 400 gms. diacetyl-*o*-nitric acid, and a mixture of 25 gms. each glacial acetic acid and acetic anhydride then added at 10° while stirring. After 10 min. the reaction mixture is poured into

water, the precipitated ether washed free from acid by means of cold water, and dried at a low temperature. It forms white flakes, similar to hydrated cellulose acetate, and dissolves in benzene-alcohol, butanol-toluene, ethyl alcohol-glycol, and other simple and mixed solvents.

2. Dimethylcellulose 100 are dissolved in diacetyl-*o*-nitric acid 600, and acetic anhydride 50 added while stirring and cooling. After 10 min. the product is precipitated in cold water and washed to neutrality. This ester-ether is soluble in methyl, ethyl or butyl acetates, or in mixtures of these acetates with alcohol, benzene, or in methyl or ethyl glycols, either alone or in conjunction with alcohol or/and benzene.

It has been found that difficulties of esterification may be greatly minimized[1] if the cellulose, or partially esterified cellulose as in the form of the mono- or di-ester, is further treated in the swollen or dissolved condition in organic solvents with acid chlorides. It is thus possible to introduce radicals of silicic, phosphoric or antimonic acids in the cellulose molecule which has been partially esterified or etherified, to produce linked derivatives of known compounds of the hexose and disaccharide group. Also, chlorides of organic acids may be combined in the same manner.

According to the manipulation of conditions of the reaction, varying amounts of acid chloride may be combined with the cellulose compound which has previously been nitrated, acetylated, etherified or otherwise partially substituted, and under maintenance of the same internal conditions of reaction, substantially identical results are obtained. As water-sensitive acid chlorides may be used, and any combinations of cellulose esters or ethers may be operated upon, the number of compounds possible is practically unlimited. Upon this observation has been built up a method for forming a technically significant group of cellulose compounds, since all chlorides of inorganic or or-

1. M. Hagedorn, O. Reichert and E. Gühring, D. R. P. 511208. E. P. 300942. F. P. 629861, and Addn. 34859.

ganic acids which dissolve in organic solvents, in which cellulose compounds with OH groups are capable of reacting, are applicable.

The process is exemplified by the following five examples, in which the first two read directly upon the cellulose ethers, and the last three may be modified for cellulose ether substitution or replacement by varying the conditions of operation and substitution:

1. Five gms. silicon tetrachloride are diluted with 10 cc. chloroform and 7.5 cc. pyridine carefully added under cooling. The addition product $SiCl_4.4C_5H_5N$ formed, is well mixed with a solution of 20 gms. water-insoluble ethylcellulose in 200 cc. xylene, all compounds being previously well dried. After a short heating the reaction commences and the mass is transformed into a stiff jelly. The solvents are then removed by steam, and excess of silicon-pyridine compound decomposed. The dried mass is dissolved in benzene and freed from silicic acid by filtration. The ethylcellulose silicic acid is purified through repeated precipitation from and solution in benzene with petroleum ether. It contains 3.8% SiO_2, is soluble in benzene and forms transparent films.

2. 300 gms. water-insoluble ethylcellulose are dissolved in 3 liters dichlormethane and 74 gms. urea added. Then 53 gms. phosphorous oxychloride are allowed to flow in with stirring, and the mixture agitated 3-4 hrs., after which it is poured into boiling water and heated until all dichlormethane is driven off. The reaction product is then washed, stabilized and dried, the ethylcellulose phosphate thus obtained assaying 48% ethoxyl and 2.7% PO_4. The same solubility is shown as that of the ethylcellulose starting material, but the viscosity has been lowered.

3. 30 gms. nitrocellulose (10.2% N) are allowed to swell in 100 cc. pyridine, after which there is added 13 gms. benzoyl chloride in 50 cc. pyridine, under strong cooling. After about 2 hrs. the temperature is allowed to rise to about 25°, and the reaction product precipitated with

ice water, washed with warm water and extracted with ether after drying. A cellulose nitrobenzoate (4.5% benzoic acid) is obtained. In the conversion a higher raising temperature is to be avoided or decomposition of the nitrocellulose ensues with the splitting off of nitrogen oxides.

4. 1200 gms. cellulose acetate (54.5% combined acetic acid) are dissolved in 10 liters acetone, and under cooling and with vigorous stirring, treated with 250 cc. phosphorous trichloride in 5000 cc. acetone. After 5 min., 800 cc. pyridine diluted with 1200 cc. acetone are added, further stirred for an hour and then precipitated. The product may be purified by heating with water for several hours with frequent replacement of the lost water. After drying, it is soluble in aqueous acetone, alcohol-benzene-acetone, and swells strongly in water. Composition 54.5% combined acetic acid, 0.5% phosphorus. The polysaccharide, amylopectin, contains but 0.175% P_2O_5. By varying conditions of manipulation, the phosphorus content may be considerably raised, however at the cost of solubility.

5. 100 gms. cellulose dilaurate (see pp. 154, 201, 537, 538, 541, 560, 648, 790, 899) are swollen in 1 liter benzene, 10 gms. phosphorous oxychloride added, and the mixture heated for 3 hrs. with stirring at 80°. The reaction product is diluted with ethyl alcohol, extracted and the solvent removed. The cellulose laurophosphate thus obtained contains 72.58% combined lauric acid and 7.24% PO_4, and is soluble in aromatic and chlorinated aliphatic hydrocarbons.

The etherification of cellulose acetonitrate[1] is a suggestive field in connection with the above that apparently has, as yet, been untouched.

In order to increase the solubility of cellulose ether[2], the cellulose before etherification may be preliminarily treated with nitric acid, or, what appears more sensible due to the saponifying action of the strong alkali on the nitrated

1. See this work, pp. 349, 367, 410, 432, 455, 476, 490, 557, 585, 594, 598, 666, 684, 781, 783, 791, 871, 872, 877, 878, 888, 929, 948, 949, 979, 1013, 1014, 1019, for data on cellulose acetonitrates.
2. British Celanese, Ltd., E. P. 319691.

cellulose, methyl-, ethyl- or benzyl-cellulose may be treated with nitric acid after formation. The nitric acid varies in strength from 5-70%. With the latter strength and much lower proportions of nitric acid, mixed ether-esters are formed as the corresponding nitrates of the three above mentioned cellulose ethers[1].

The I. G. Farbenindustrie[2] prepare solid plastic masses by physically incorporating nitrocellulose with methylcellulose, usually in combination with butyl naphthalenesulfonate, butyl stearate, dibutyl phthalate or coloring matter (Lithol red R), the method of procedure being to pass 5-10 times through malaxating rollers 50 parts nitrocellulose with 50-100 parts water added thereto, in order to diminish the viscosity of the nitric ester. Then a 10% solution of methylcellulose is added, and malaxation continued until a homogeneous mass results. An excellent plastic to be added to the nitrocellulose is claimed to result when to 9 parts water-soluble methylcellulose is added 1 part sodium butylnaphthalenesulfonate, 10 parts butyl stearate and 2.5 parts dibutyl phthalate.

The Deutsche Celluloid Fabrik[3] have described a rather indefinitely chemically characterized series of double esters. In order to obviate the well known volatility of certain otherwise excellent gelatinizing agents, the gelatinizers are chemically attached to the cellulose molecule which has previously been but partially esterified. This is accomplished by causing a chloride of the acid ester of a polybasic acid, whose neutral esters have a gelatinizing power or can be used as softening agents, to act upon cellulose or a derivative thereof as alkalicellulose containing one or more hydroxyl groups which can be esterified or etherified. The mixed esters or ester-ethers are quite insensitive to water. If a cellulose nitrate is used as a cellulose ester, the nitrogen is reduced from 10.8-6% by combining with a

1. L. Lilienfeld, U. S. P. 1589607. E. P. 177809. D. R. P. 488466. F. P. 549568. Can. P. 248232. Aust. P. 83400.
2. I. G. Farbenindustrie, F. P. 685162.
3. E. P. 355172.

molecular proportion of monobutyl phthalate, and to 5.4% by union with a molecule of methyl cyclohexyladipate.

Since there is available a large number of suitable acid esters of polybasic acids which are obtainable and readily transferable into the chlorides, the process can be carried out in a varied manner. Esters can be utilized derived from monohydric or polyhydric alcohols and phthalic, adipic, methyladipic or phosphoric acids. The process is also applicable to partially esterified cellulose with inorganic or organic acid radicals, or to partially etherified cellulose.

The following example reading upon nitrocellulose illustrates the possibilities: 255 gms. cellulose dinitrate (11% N) and 222 gms. mono-*n*-butyl phthalate are dissolved in 700 gms. ethyl acetate. The homogeneous solution thus obtained is mixed with stirring with 250 gms. thionyl chloride. The mixture becomes spontaneously heated to 30-40° with evolution of HCl and SO_2, monobutylphthalyl chloride being formed, which reacts smoothly with cellulose dinitrate. When gas evolution ceases, the reaction is complete. The mixture is then poured into water, the mixed ester being precipitated in white flakes, and may be purified by washing with water, then with alcohol. It is readily soluble in methyl and ethyl acetates, acetone, diacetone alcohol and mesityl oxide, insoluble in benzene, ether, alcohol, turpentine oil and mixtures of these substances.

Ethylcellulose phosphates are producible by treating 150 gms. raw cellulose with 4 kilos 50% NaOH solution at ordinary temperature for 2 hrs., squeezing until the weight is 425 gms., and grinding[1]. The alkalicellulose is allowed to stand in a closed vessel at ordinary temperature for some hours, then heated for 6 hrs. in an autoclave at 120° with 300 gms. benzene, 70 gms. powdered NaOH and 450 gms. ethyl chloride, an ethylcellulose being formed insoluble in alkali. After cooling, 220 gms. benzene and 165 gms. 40%

1. I. G. Farbenindustrie, D. R. P. 535253; Addn. D. R. P. 511208. E. P. 300942. See E. P. 270347.

NaOH solution are added, and while stirring, 80 gms. phosphorous oxychloride diluted by 220 gms. benzene are added drop by drop. The mixture becomes warm. After stirring for 0.5 hr. the mixture is allowed to settle and the aqueous portion discarded. From the benzene solution all electrolytes are removed by washing with hot water. From the solution by evaporating, or by precipitating with benzine, an ethylcellulose phosphate is obtained in which 5.5% PO_4 is bound. It dissolves in ethyl alcohol, ether, benzene, chloroform and ethyl acetate, and is insoluble in benzine.

The I. G. Farbenind. have found that ethylcellulose phosphate or ethylcellulose stearate are excellent when applied to the back of a photographic film to check shrinkage, and enable the film to slide more easily in a projector or afford protection against electrical discharges.

Cellulose Carbonate. When a chloroformic acid ester in the form of its alkali compound is allowed to act upon cellulose, cellulose carbonates are formed[1]. Hydrocellulose as obtained from the precipitation of viscose according to the method of E. Knoevenagel and H. Busch[2] is especially applicable as initial cellulosic material, since it is soluble in 5% NaOH solution, and as shown by E. Heuser and F. Eisenring[3], readily forms an alkali compound. By esterifying according to the Schotten-Baumann reaction, a cellulose dicarbonate results (found 30.35-31.2% CO_2, whereas 31.6% is calculated for $C_6H_8O_3(O.CO.OCH_3)_2$. Yield 20% on the hydrocellulose used.

The ester as obtained above is a white, amorphous, mostly granular mass, showing (of course) no fibrous structure. Insoluble in ether, alcohol, acetone and benzene, completely soluble in pyridine to a clear solution from which it may be precipitated upon the addition of water. Soluble also in chloroform or glacial acetic acid, but with slight turbidity, from which tenuous films may be formed by

1. E. Heuser and F. Schneider, Ber. 1924, **57B**, 1389; abst. C. A. 1925, **19**, 251.
2. Cellulosechem. 1922, **3**, 42; abst. C. A. 1922, **16**, 2779.
3. Cellulosechem. 1923, **4**, 13, 25; abst. C. A. 1923, **17**, 3249.

evaporation of the solvent. The ester is readily hydrolyzed by water, more rapidly in presence of alkali. At 60-70°, a 10% NaOH solution completely hydrolyzes the ester in 15-30 min. The hydrolytic reaction may readily be followed because the ester is insoluble in the alkali solution, whereas the hydrocellulose formed dissolves, hydrolysis being completed when all the ester has passed into solution.

The suggested method for preparation of cellulose carbonate is to dissolve hydrocellulose in 8% NaOH solution ice cold, adding slowly 1.5 times the theoretical quantity of chloroformic acid, meanwhile continually agitating. Stirring is continued until the odor of chloroformic acid is no longer noticeable, the ether coming down as a white, flocculent precipitate. The reaction mixture is diluted with water, filtered, the filtrate washed with ice water to neutrality, filtered as rapidly as possible and vacuum dried.

Cellulose Acetocarbonate. When 75 gms. acetylcellulose (containing 56% acetic acid) and soluble in dry acetone[1] are very carefully dried and then treated with the vapors from 90 cc. phosgene (carbonyl chloride) at 20-25° under 700 mm. pressure, the phosgene being a 15% solution in toluene, reaction takes place and the phosgene is absorbed by the cellulose acetate forming a mixed acetate-carbonate, which is precipitated by water, washed and dried. It is distinguished from the original cellulose acetate by being more absorbent to water and by an enhanced affinity for dyestuffs.

Cellulose Sulfate. W. Gintl[2] observed in 1869 that when pyroxylin is moistened with concentrated sulfuric acid it is dissolved to a viscous syrup, and in 1891 it was found[3]

1. I. G. Farbenind., F. P. 717623.

2. Wien. Akad. Ber. **59**, II, 809; J. prakt. Chem. 1869, **107**, 478; Zts. Chem. 1869, **12**, 703; Jahr. Chem. 1869, **22**, 753; Poly. Centr. 1870, **36**, 159; Chem. News, 1869, **20**, 323; Chem. News Amer. Reprint, 1870, **6**, 115; Bull. Soc. Chim. 1870, **13**, 435; Wag. Jahr. 1870, **16**, 220; Allgem. Oesterr. Apotheker Verein. 1869, 421; Chem. Tech. Rep. 1869, **8**, II, 98; Amer. Pharm. Assoc. 1870, **18**, 270.

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

that nitric and sulfuric acids under certain concentrations form cellulose nitrosulfates. C. Hake and R. Lewis[1] studied the formation of sulfuric esters in the nitration of cellulose, and cellulose acetosulfates were prepared in 1905[2]. C. Piest[3] and A. Herve[4] also contributed to this subject.

A. Caille[5] immersed strips of cotton in 20, 30, 40, 50 and 60% solutions of sulfuric acid in acetic acid for 30 min., and obtained cellulose sulfates (sulfocelluloses) containing 4.37, 4.49, 5.70, 8.83 and 7.48 gms. sulfuric acid per kilo of cotton treated. In another method[6], dried cotton is converted by chlorsulfonic acid in excess of pyridine at 100° into a homogeneous gelatinous product of cellulose sulfate, giving with water a transparent, colloidal solution. M. Samec[7] treated starch with sulfuryl chloride which when dialyzed, yielded a thin and a thick fraction containing 2.44% and 0.63% SO_3 respectively.

W. Traube[8] treats cellulose or starch with SO_2 dissolved in sulfuric acid or carbon bisulfide, and obtains a cellulose sulfate of value as a protective colloid or as an intermediate for the formation of cellulose esters or ethers. If cellulose is placed in an atmosphere containing a small

80, i, 672; Bull. Soc. Chim. 1902, **28**, 130; Chem. Zentr. 1901, II, 882; Jahr. Chem. 1901, **54**, 892; Wag. Jahr. 1901, **47**, I, 501; Meyer Jahr. Chem. 1901, **11**, 316.

1. J. S. C. I. 1905, **24**, 374, 914; abst. Chem. Zentr. 1905, I, 1170, 1702; J. C. S. 1905, **88**, i, 512; Jahr. Chem. 1905-8, II, 975; Meyer Jahr. Chem. 1905, **15**, 357.

2. C. Cross. E. Bevan and J. Briggs, Ber. 1905, **38**, 1859, 3531; abst. J. S. C. I. 1905, **24**, 685, 1251; J. C. S. 1905, **88**, i, 512, 862; Chem. News, 1905, **92**, 70; Bull. Soc. Chim. 1906, **36**, 638, 639; Rep. chim. 1905, **5**, 414; Chem. Zentr. 1905, II, 36, 1625; Chem. Ztg. Rep. 1905, **29**, 178; Jahr. Chem. 1905-1908, II, 986; Meyer Jahr. Chem. 1905, **15**, 357; Wag. Jahr. 1905, **51**, II, 399.

3. Zts. ang. Chem. 1913, **26**, 661; abst. C. A. 1914, **8**, 573; Chem. Zentr. 1913, II, 2184; Meyer Jahr. Chem. 1913, **23**, 363; Wag. Jahr. 1913, **59**, I, 457; Zts. Schiess. Spreng. 1914, **9**, 12.

4. Mon. Sci. 1918, **85**, 193, 241; abst. J. S. C. I. 1918, **37**, 718-A; C. A. 1919, **13**, 186, 516; Chem. Zentr. 1919, II, 297, 622.

5. Chim. et Ind. 1926, **15**, 189; abst. C. A. 1926, **20**, 1719.

6. E. Gebauer-Fuelnegg, W. Stevens and O. Dingler, Ber. 1928, **61B**, 2000; abst. C. A. 1930, **24**, 1502; J. S. C. I. 1928, **47**, 1226-A; J. A. C. S. 1930, **52**, 2849; Chem. Zentr. 1929, I, 47.

7. Monats. 1929, **53**, 852; abst. C. A. 1930, **24**, 345.

8. F. P. 657204; abst. C. A. 1929, **23**, 4342.

quantity of SO_3 vapors, an acid cellulose trisulfate results[1], which may be isolated in the form of well characterized salts, stable in the air. The ester contains 3 sulfuric acid residues to each C_6 cellulose group[2], and may be isolated as the rather difficultly soluble potassium salt. W. Traube has been granted patent protection for the method of treating carbohydrates with SO_3 in solution in sulfuric acid[3] or in carbon bisulfide[4].

Cellulose sulfate may be prepared[5] by treating cellulose with sulfuric acid in the presence of an aliphatic acid anhydride (acetic acid anhydride) under such conditions that no appreciable amount of organic cellulose ester is formed. G. Miles[6] treats cellulose with concentrated sulfuric acid and ether, and employs the cellulose sulfate thus formed as initial material for etherification or esterification purposes.

Cellulose sulfate has been proposed for storage battery plate manufacture[7] and as a plastic body in conjunction with naphthol esters or cresol esters[8]. A celluloid substitute made with cellulose acetosulfate (sulfoacetate) has also been described[9].

B. Wylam and J. Stevenson[10] use cellulose sulfate in dyeing with vat colors when the padding method, in which

1. W. Traube, B. Blaser and C. Grunert, Ber. 1928, **61**B, 754; abst. C. A. 1928, **22**, 4793.
2. W. Traube, B. Blaser and E. Lindemann, Ber. 1932, **65**B, 603; abst. C. A. 1932, **26**, 3236; J. S. C. I. 1932, **51**, 604-A.
3. E. P. 294572; abst. C. A. 1929, **23**, 2034; J. S. C. I. 1928, **47**, 621-A. F. P. 657204; abst. C. A. 1929, **23**, 4342. D. R. P. 490987; abst. C. A. 1930, **24**, 4931.
4. E. P. 322003, Addn. to E. P. 294572; abst. C. A. 1930, **24**, 2882; Chem. Zentr. 1930, I, 3355.
5. E. Orioli and Ruth-Aldo Co., E. P. 303493; abst. Silk J. 1929, **5**, #59, 76. Can. P. 286538, 286539; abst. C. A. 1929, **23**, 1504. Can. P. 291434.
6. Can. P. 319358; abst. C. A. 1932, **26**, 2051.
7. W. Wood and H. Smith, U. S. P. 1432937.
8. W. Merckens and H. Manissadjian,E. P. 8646, 8647, 1910; F. P. 414679. Aust. P. 47679.
9. H. Dreyfus, U. S. P. 1181858. For the manufacture of solvents for cellulose sulfate see A. Helbronner and G. Criquebeuf, U. S. P. 1260977.
10. U. S. P. 1868300.

the color is vatted after impregnation, is used. The cellulose sulfate is added to reserve and to discharge printing pastes, enhanced coloring effects being obtained, especially with such colorants as Caledon jade green or Soledon jade green (sulfuric ester of Caledon jade green).

Cellulose Sulfinate. There has been described by Knoll & Co.[1] cellulose derivatives of sulfinic acid, obtained by bringing normal or modified cellulose in contact with sulfinic acid and organic anhydrides. In the presence of the desired amount of solvents the cellulose passes into solution in the form of either sulfur-free or sulfur-containing derivatives.

Cellulose Sulfonate. Compounds readily soluble in water are formed by causing cellulose to react in the presence of an alkaline agent with an aralkylhalide sulfonic acid. The compounds are regarded either as cellulose-benzene-ether-sulfonic acids for example, or cellulose benzene-sulfonates. In order to prepare them in their pure state they are advantageously transformed into their calcium or barium salts which dissolve in water with difficulty, and from which the free acid may be isolated[2]. The following examples are illustrative, parts being by weight:

1. Mercerized cellulose 18 is kneaded for 2 hrs. with 20% alcoholic NaOH 100, then sodium-benzyl-chloride-*o*-sulfonate 22.8 in alcohol 100 added, and the mixture again kneaded 8 hrs. at 50-60°, the alcohol being then removed by evaporation. The residue forms a whitish mass, readily soluble in water, sparingly soluble in alcohol, almost insoluble in acetone and benzene.

2. 36 parts alkalicellulose and 200 parts 20% NaOH solution are boiled together 2 hrs., and the mass then kneaded with 92 parts sodium benzyl-chloride-*p*-sulfonate

1. D. R. P. 180666, 180667; abst. Chem. Zentr. 1907, I, 773.
2. G. Kraenzlein, A. Voss and F. Brunntraeger (I. G. Farbenindustrie), U. S. P. 1682382; abst. C. A. 1928, **22**, 2988. I. G. Farbenindustrie, E. P. 277317; abst. C. A. 1928, **22**, 2465. F. P. 640687; abst. C. A. 1929, **23**, 980.

at 50-60° until the product is entirely soluble in water. Properties as in Ex. 1.

3. 18 parts air-dry alkalicellulose are soaked with 100 parts 20% alcoholic NaOH. To this mass are then added, while stirring, 48.2 parts sodium xylylchloride-sulfonate in 100 parts alcohol, and the mass kneaded until it becomes soluble in water.

In the method of T. Nakashima and I. Sakurada[1], 10 gms. air-dry tissue paper are immersed in 100 cc. 22% NaOH solution, after 24 hrs. standing, then pressing to a weight of 350% on the cellulose, and to this is added 60 gms. *p*-toluenesulfochloride. 250 cc. benzene are then added, and after standing 24 hrs. the yield is 14 gms. Repeat the process and the yield goes to 17.5 gms. cellulose mono-*p*-toluenesulfonate, theory calling for 18 gms.

In the treatment of cellulose with alkali and *p*-toluenesulfochloride[2], temperatures of 8-30° have the same effect, while a higher temperature results in a lower degree of esterification. Increased proportions of chloride exert but little effect while excess of alkali increases esterification. If the concentration of NaOH and the proportion of *p*-toluenesulfochloride are constant, then as the NaOH is increased the degree of esterification reaches a maximum, after which further additions decrease esterification. The degree of esterification is practically constant, 1 mol. chloride reacting with 2 mols. C_6 cellulose[3].

Another method of preparing these esters comprises acting upon alkalicellulose with aryl or aralkyl sulfochlo-

1. Bull. Inst. Phys. Chem. Research, Tokyo, 1929, **8**, 272; Abstracts, 1929, **2**, 33; abst. C. A. 1929, **23**, 3572; J. S. C. I. 1930, **49**, 72-A.

2. I. Sakurada and T. Nakashima, Sci. Papers. Inst. Phys. Chem. Research (Tokyo), 1927, **6**, 214; abst. C. A. 1928, **22**, 683; Cellulosechemie, 1928, **9**, 86.

3. G. Kita, I. Sakurada and T. Nakashima, Cellulose Ind. Tokyo, 1926, **2**, 405; abst. C. A. 1928, **22**, 1038. Kunst. 1927, **17**, 269; abst. C. A. 1928, **22**, 684.

rides at ordinary temperature[1], with or without the addition of benzene, the products formed being soluble in epichlorhydrin, chloroform and ethyl acetate, and leaving upon evaporation transparent films. The "immune yarn" of the Chemische Fabrik vorm. Sandoz is prepared by treating swollen cotton with aromatic sulfochlorides in indifferent solvents[2], the fiber bundles being converted into a cellulose sulfonate, as cellulose *p*-toluenesulfonate. When this is heated with anhydrous hydrazine at 100° for 15-16 hrs., fission occurs, affording *p*-toluenesulfonic acid, a soluble product (4.55% N), and an insoluble product (2.28% N),—a monohydrazine of cellulose requiring 16.1% N. Both products absorb bromine. This indicates the partial formation of a hydrazine cellulose at the former point of esterification, which is considered to be the secondary OH group in position 2 or 3 in the $C_6H_{10}O_5$ unit.

The three processes of the Society of Chemical Industry, Basle are:

(1) Alkalicellulose is treated with a heterocyclic compound containing one or more N:C-Halogen groups, and then further treated with a compound containing an NH, OH or SH group[3] or, a salt of the same, the cellulose being etherified to a stage wherein it is immune to the usual cotton and substantive dyestuffs and has a pronounced affinity for acid colors.

(2) The cellulose usually in skein form is immersed at ordinary temperature in a saturated solution of potassium cyanide, or 50% calcium chloride or 50% magnesium chloride, excess pressed out, then treated for 6 hrs. at 80-90° with acetic anhydride[4].

1. Akt. Ges. fur Anilin-Fabrikation, D. R. P. 200334, 1907; abst. J. S. C. I. 1908, **27**, 1130; C. A. 1908, **2**, 2456; Mon. Sci. 1911, (5), **74**, 63; Chem. Zts. 1908, **7**, 909; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, II, 655; Jahr. Chem. 1905-08, 987; J. C. S. 1908, **94**, i, 955; Chem. Ind. 1908, **31**, 499; Wag. Jahr. 1908, II, 363.

2. G. Tagliani, Textilber. 1925, 425; abst. J. Soc. Dyers, 1926, **42**, 69.

3. E. P. 347926, Addn. to E. P. 342167; abst. Silk J. and Rayon World, 1931, **8**, #89, 54; Chem. Zentr. 1931, II, 3287.

4. E. P. 350137.

(3) The cellulose is treated with an aliphatic diamine and an oxidized cellulose xanthate derivative[1].

The Chemische Fabrik vorm. Sandoz[2] esterifies cellulose with a carboxylic acid chloride as benzoyl chloride forming a cellulose benzoate, or a sulfur chloride as *p*-toluenesulfochloride, benzenesulfochloride, *o*-toluenesulfochloride, xylenesulfochloride or naphthalenesulfochloride; or[3], as shown in the following examples:

1. One kilo bleached cellulose is boiled 15 min. in 30 liters 12% NaOH solution, centrifugalized until the weight has been reduced to 50%, and esterified with a toluene solution of 22% *p*-toluenesulfochloride at 18° for 1.25 hrs.

2. Alkalizing is carried out with 14% KOH solution and 0.5% cresol; esterification as in 1.

3. One kilo bleached mercerized cotton is alkalized as in Ex. 1 for 30 min., whizzed while hot until the weight is reduced to 60%, then treated 30 min. with 40 liters 1% solution of phosphorous oxychloride in xylene.

4. The cellulose may be esterified by 20 liters 2.5% benzoyl chloride in toluene for 30 min.

Cellulose fibers including viscose or other regenerated cellulose fibers are rendered capable of being dyed with acid dyes by treatment simultaneously with a sulfohaloid and a tertiary organic base[4], the chloride or bromide of any aliphatic or aromatic sulfonic acid as benzene-, toluene-, benzyl- or ethyl-sulfochloride being specified. Any tertiary aromatic amine or heterocyclic base may be used, the process being carried out by treating cellulose with the reaction products of the sulfo-haloids with the tertiary base. Indifferent solvents may be present, as nitrobenzene, dimethylamine, triethylamine, pyridine or quinoline.

In sulfonating cellulose in yarn form[5], a package of thread as cotton or regenerated cellulose (as from the vis-

1. E. P. 353930; abst. Text. Manufacturer, 1932, **58**, 37. See E. P. 353978.
2. E. P. 325961. 3. E. P. 345052.
4. Chemische Fabrik vorm. Sandoz, E. P. 284358.
5. R. Boehringer and H. Wolf, U. S. P. 1829735; abst. C. A. 1932, **26**, 857.

cose, cuprammonium or nitrocellulose rayon processes) having a hollow center, is alkalized with 12% NaOH solution, excess alkali removed, and then esterified with *p*-toluenesulfonyl chloride under pressure to force the esterizing liquid through the package. According to the recommendation of G. Kalischer and O. Bayer[1] cellulose as cotton yarn is alkalized in the usual manner, then treated with an amino-substituted arylsulfonic acid chloride as dimethylaniline-*p*-sulfonyl chloride, quinoline-8-sulfochloride or aminotoluene sulfochloride.

In 1928 E. Gebauer-Fuelnegg, W. Stevens and O. Dingler[2] prepared cellulose trisulfonate, and two years later extended the work to determine whether a cellulose trisulfonate obtained by the action of chlorsulfonic acid in an excess of pyridine was a degradation product of cellulose[3]. It was demonstrated that this ester is a true derivative of cellulose, by conversion into trimethylcellulose, the rotation of which in benzene was 18.46°, as against the rotation of trimethylcellulose obtained by the hydrolysis of triacetylcellulose, which gave in benzene, 18.58°.

O. Strecker[4] prepares cellulose hydroxybenzenesulfonates by treatment of disintegrated vegetable fiber with hydroxybenzenesulfonic acid.

Any cellulose sulfonate formed in the normal acetation of cellulose[5] may be removed by the addition of a small amount of calcium nitrate to a hot solution of the crude cellulose acetate.

Cellulose Phosphate. G. Miles and C. Dreyfus[6] have

1. U. S. P. 1835403; abst. C. A. 1932, **26**, 1135. See U. S. P. 1523742; D. R. P. 346883.
2. Ber. 1928, **61**B, 2000; abst. C. A. 1930, **24**, 1501; J. S. C. I. 1928, **47**, 1226-A.
3. J. A. C. S. 1930, **52**, 2849.
4. D. R. P. 505041, Addn. D. R. P. 486533; abst. C. A. 1931, **25**, 591.
5. W. Lindsay, U. S. P. 1338661. In this connection see U. S. P. 1236578, 1265216.
6. 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**, 338. E. P. 263810; abst. C. A. 1928, **22**, 164; Chem. Zentr. 1927, I, 2253.

found that clear and transparent solutions are obtained by treating cotton linters with 75-100% phosphoric acid at —1-10°. Aliphatic alcohols or acids may be added to the phosphoric acid, and the solutions thus formed used for the manufacture of artificial silk and films, or for producing cellulose ethers. Cellulose sulfoacetate, phosphoacetate, nitroacetate and formylactate[1] may be saponified in solution in anhydrous or aqueous phenols as phenol or resorcinol, or alkaline phenates, cresolates or resorcinates, cellulose acetate treated in this manner being modified with respect to their solubilities. The use of cellulose formylphosphate for the production of cellulose ethers[2], the production of cellulose phosphoformate[3] and its application to film formation[4] have been described.

The cellulose formylphosphates of the Vereinigte Glanzstoff Fabriken[5] are precipitable from their solutions by amyl acetate or toluene-alcohol, and with the addition of camphor or triphenyl phosphate, produce valuable plastic bodies.

Cellulose phosphates are prepared by the I. G. Farbenindustrie[6] by treating cellulose with moderately concentrated phosphoric acid in the presence of phosphorous oxychloride, with or without the addition of a diluent. The

1. Soc. des Usines Chim. 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**, 198; Silk J. and Rayon World, 1930, **6**, #69, 64. D. R. P. 539471; abst. C. A. 1932, **26**, 1782.

2. L. Lilienfeld, U. S. P. 1188376. E. P. 149320, 163016, 163017, 163018, 171661. F. P. 468162. D. R. P. 360651. Aust. P. 55527, 56250, 65288, 78217. Belg. P. 254591. Dan. P. 30677. Hung. P. 51653. Ital. P. 132825. Norw. P. 27507. Span. P. 55104. Swed. P. 38905. Swiss P. 66512.

3. E. Bronnert, U. S. P. 1153596; 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.

4. W. Merckens and H. Manissadjian, E. P. 8646, 8647, 1910; abst. J. S. C. I. 1911, **30**, 533, 616; Chem. Tech. Rep. 1911, **35**, 307. F. P. 413657, 413658; abst. J. S. C. I. 1910, **29**, 1101. F. P. 414679, 414680; abst. J. S. C. I. 1910, **29**, 1199, 1228. Swiss P. 51644, 51910; abst. Kunst. 1912, **2**, 77, 99. Belg. P. 223996. Aust. P. 47244, 47679, 53109; abst. Kunst. 1912, **2**, 255.

5. E. P. 29246, 1910. F. P. 423774. D. R. P. 249535. Aust. P. 54512.

6. D. R. P. 547812; abst. C. A. 1932, **26**, 3667.

product after 5 days treatment has a 72% phosphoric acid content. In another method[1], alkalicellulose is reacted upon with an oxygen-containing chloride of a polyvalent inorganic acid in the presence of an inert diluent. Thus, 100 parts bleached cotton linters are swollen in 40% NaOH solution, while cooling with a mixture of ice and salt. After 4 hrs. the cotton is pressed to 300 parts, and the mass introduced in small portions into an ice-cold solution of phosphorous oxychloride in 900 parts benzene. The heat evolved first raises the temperature of the benzene to the boiling point, after which a tough magma settles to the bottom of the vessel. After 12 hr. the supernatant liquid is drawn off, and the deposit washed with alcohol and ether, vacuum dried, and treated with water. The colloidal aqueous dispersion is freed from all electrolytes by dialysis, and from this purified dispersion, cellulose phosphate is precipitated by addition of methyl alcohol. It is a nearly white body, colloidally dispersed by water and containing 16% PO_4. Yield, 80% on the cellulose used.

Cellulose Acetochromate. When 75 gms. dry cellulose acetate (56% acetic acid) are brought in contact at 20-25° and 12 mm. pressure with the vapors of 3 ccm. chromium oxychloride[2], union takes place and a cellulose acetochromate results, soluble in acetone, from which transparent pellicles may be deposited.

Cellulose Acetosilicate. 10 gms. acetylcellulose (56% acetic acid) are treated with 10 cc. silicon tetrachloride for 1 hr. at laboratory temperature, and the product then extracted with methanol, a cellulose acetosilicate (silicoacetate) being obtained, insoluble in acetone, and containing 6.4% silicon dioxide.

Cellulose Thiocyanate. *Cellulose Sulfocyanide.* A. Dubosc[3] discovered that alkalicellulose is soluble in the thiocyanates of ammonium, sodium, potassium, aluminum, cal-

1. M. Hagedorn and E. Guehring, U. S. P. 1848524.
2. I. G. Farbenindustrie, F. P. 717623.
3. Bull. soc. ind. Rouen, 1905, **33**, 318. See H. Dreyfus, Belg. P. 327477.

cium and iron, and seven years later investigated the subject further[1]. If a mixture of NaOH 50, sodium carbonate 30, cellulose 100 and water 1000 is treated with a thiocyanate decomposable by heat or with thiocyanic acid at 2.5 atms. pressure for 3-4 hrs., solution takes place with cellulose thiocyanate formation.

Cellulose Formate. Chapter II on the historical development of the cellulose esters, as indicated by reference to the index in this volume exceeding one hundred on various phases of formylcellulose production, properties and uses, appears adequate for the purposes of this review. The manufacture of the cellulose formates is indicated on pages 361, 362, 386, 389, 640, 641, 642, 695, 700, 904, 928, 1017.

Cellulose Acetate. About every pertinent phase of cellulose acetate activity, both theoretical and practical, is intended to be chronologically developed in the 793 pages comprising Chapter II, as indicated by the several hundred references in the index herein. Insofar as aware, it is the only comprehensive attempt extant indicating the ramifications of the entire acetylcellulose art from its inception to the present time, and corroborated by references in the notes at the bottom of the page, to the original repositories of information exceeding eleven thousand. The methods of manufacture are indicated on pages 204, 495, 498, 515, 516, 522, 537, 543, 551, 552, 555, 585, 586, 589, 590, 597, 598, 614, 621, 629, 630, 635, 638, 642, 646, 650, 652, 666, 667, 669, 670, 688, 693, 694, 700, 705, 712, 724, 725, 728, 731, 755, 757, 759, 764, 766, 771, 773, 795, 804, 805, 806, 810, 811, 812, 817, 821, 822, 825, 826, 831, 838, 841, 850, 851, 859, 860, 865, 877, 882, 886, 887, 889, 890, 901, 918, 921, 928, 941, 942, 948, 949, 958, 1003, 1009, 1011, 1018, 1020, 1024.

Cellulose acetate has been employed primarily in airplane dope[2]; for coating airplane fabric[3]; as a celluloid sub-

1. A. Dubosc, Caout. et Gutta. 1913, **10**, 6895; abst. C. A. 1913, **7**, 2112.

2. U. S. P. 1156894, 1173931, 1303563, 1312708, 1315216, 1320290, 1325363, 1339728, 1347801, 1358250, 1363763, 1365049, 1388824, 1388825, 1388827, 1388828, 1393355, 1400430, 1426521, 1429295, 1440178, 1488608, 1521055, 1521056.

3. U. S. P. 1325363, 1389084, 1394890, 1427941, 1429295.

stitute[1]; waterproofing fabric[2]; manufacture of film[3], especially motion picture film[4] and in photography[5]; for fireproofing aircraft[6]; in electric insulation[7]; as a lacquer[8] and for artificial leather[9]; in plastics formation[10]; artificial silk[11]; in solutions with acetone[12], alcohol[13], benzene[14], chloro-

1. U. S. P. 1153596, 1156969, 1158960, 1181858, 1181859, 1181860, 1188797, 1188798, 1188799, 1188800, 1191801, 1195040, 1199798, 1200886, 1216581, 1217027, 1217722, 1241738, 1242783, 1245476, 1319229, 1331127, 1353384, 1353385, 1363763, 1386576, 1388472, 1394752, 1420028, 1437952, 1440006, 1454959, 1454960, 1454961, 1466819, 1488294, 1501206, 1508928, 1510779, 1512751.
2. U. S. P. 1156969, 1388824, 1388825, 1388827, 1388828.
3. U. S. P. 1181859, 1193178, 1199395, 1217027, 1217722, 1242783, 1342601, 1342602, 1347801, 1351652, 1353384, 1353385, 1354401, 1354726, 1363763, 1388472, 1398939, 1398949, 1400196, 1429153, 1437828, 1437829, 1440006, 1445382, 1454959, 1454960, 1454961, 1457131, 1467493, 1480016, 1484004, 1488608, 1501206, 1505044, 1508928, 1514283, 1518396.
4. U. S. P. 1133385, 1158963, 1183698, 1196799, 1205822, 1226655, 1232702, 1245822, 1250713, 1361783, 1469815, 1488294, 1496359, 1518409.
5. U. S. P. 1184772, 1188797, 1188798, 1188799, 1188800, 1199799, 1199800, 1203756, 1226339, 1226340, 1226341, 1226342, 1226343, 1229485, 1229486, 1229487, 1232702, 1261747, 1342601, 1342603, 1388472, 1431894, 1432366, 1432367, 1432368, 1437810, 1437828, 1437829, 1486245, 1488294, 1494479, 1507174, 1512751, 1519659.
6. U. S. P. 1388824, 1388825, 1388826, 1388827, 1388828, 1388829.
7. U. S. P. 1156969, 1185074, 1217722, 1241738, 1394752, 1485254.
8. U. S. P. 1156969, 1181859, 1185514, 1188798, 1188799, 1188800, 1195673, 1203756, 1226340, 1226343, 1229485, 1229486, 1229487, 1241738, 1347801, 1355976, 1440178, 1488608, 1505043.
9. U. S. P. 1140174, 1156969, 1173931, 1181859, 1217123, 1217722, 1263171, 1505043.
10. U. S. P. 1156969, 1158960, 1173337, 1175791, 1185074, 1188797, 1188798, 1188799, 1188800, 1191801, 1193178, 1199800, 1203756, 1216581, 1226340, 1226343, 1229485, 1229486, 1229487, 1241738, 1295533, 1317721, 1367886, 1370879, 1386576, 1388472, 1389084, 1403095, 1440006, 1466819, 1488608, 1488609, 1505044.
11. U. S. P. 1156969, 1181859, 1217028, 1217722, 1347801, 1353384, 1353385, 1440006, 1445382, 1465994, 1471699, 1484004, 1501206, 1505043, 1505044, 1508928, 1517627.
12. U. S. P. 1128468, 1132384, 1133385, 1136248, 1142619, 1143877, 1143878, 1143979, 1156894, 1160979, 1165179, 1175791, 1181758, 1181857, 1181860, 1184257, 1185514, 1188797, 1188798, 1188799, 1188800, 1195040, 1195673, 1199798, 1199800, 1201260, 1203756, 1216581, 1217722, 1226342, 1236578, 1242783, 1244107, 1244108, 1244347, 1244348, 1244349, 1245476, 1260977, 1275884, 1286172, 1303563, 1309980, 1310841, 1316311, 1319229, 1320290, 1338661, 1342601, 1342602, 1342603, 1343135, 1345354, 1351652, 1354401, 1357447, 1354726, 1363763, 1370879, 1386576, 1388472,

form[1], epichlorhydrin[2], ethyl acetate[3], ethyl alcohol[4], fusel oil[5], methyl acetate[6], methyl alcohol[7], nitrobenzene[8],

1389084, 1392849, 1393355, 1394890, 1395401, 1397103, 1397986, 1398939, 1406224, 1408095, 1408423, 1410790, 1417587, 1418347, 1420028, 1421341, 1426521, 1429153, 1429295, 1432367, 1434634, 1437828, 1437829, 1437952, 1440006, 1440178, 1449157, 1453764, 1454959, 1454960, 1454961, 1463864, 1465937, 1465994, 1467493, 1469815, 1476392, 1478137, 1484004, 1488294, 1494816, 1494830, 1501206, 1508928, 1516225, Re 14338.

13. U. S. P. 1153596, 1156894, 1158960, 1181758, 1181857, Re-14338, 1181858, 1181859, 1181860, 1195673, 1196799, 1199798, 1201260, 1217722, 1236578, 1242783, 1245476, 1258913, 1265217, 1286172, 1303563, 1338661, 1357447, 1363763, 1386576, 1388472, 1389084, 1397986, 1408095, 1420028, 1421288, 1421289, 1421290, 1421341, 1425580, 1434634, 1437828, 1437829, 1454959, 1454960, 1454961, 1463864, 1465994, 1480016, 1501206, 1503835, 1508928.

14. U. S. P. 1152625, 1156894, 1160979, 1188797, 1195673, 1196799, 1199395, 1217722, 1226339, 1226341, 1265216, 1286172, 1303563, 1310841, 1316311, 1357447, 1363763, 1394890, 1397986, 1406986, 1406224, 1425580, 1480016, 1488294, 1488608, 1501206, 1508928.

1. U. S. P. 1132384, 1158960, 1165179, 1175791, 1180704, 1181857, 1181858, 1181859, 1181860, 1188798, 1195673, 1199798, 1199799, 1199800, 1201260, 1217722, 1236578, 1236579, 1242783, 1244107, 1244108, 1244347, 1244348, 1244349, 1245476, 1258913, 1265216, 1275884, 1286172, 1319229, 1338661, 1355976, 1384188, 1386576, 1388472, 1420028, 1421341, 1429295, 1444786, 1494816, 1494830, 1516225, Re-14338.

2. U. S. P. 1226340, 1226343, 1236578, 1244107, 1244108, 1244347, 1244348, 1244349, 1265216, 1338661, 1357447.

3. U. S. P. 1127871, 1132384, 1143979, 1175791, 1199798, 1201260, 1203756, 1217722, 1244107, 1244108, 1244347, 1244348, 1244349, 1245476, 1254216, 1303563, 1310841, 1319229, 1330543, 1343135, 1351652, 1354401, 1355976, 1357447, 1386576, 1389084, 1393355, 1394890, 1400196, 1406224, 1408095, 1408423, 1410790, 1420028, 1421341, 1429153, 1434634, 1437952, 1449157, 1488294, 1501206, 1508928.

4. U. S. P. 1127871, 1128468, 1143979, 1160979, 1173931, 1188798, 1199799, 1199800, 1203756, 1205822, 1216581, 1226340, 1226343, 1244107, 1244108, 1244347, 1244348, 1244349, 1265216, 1265217, 1355976, 1384188, 1388472, 1393355, 1394890, 1395401, 1406224, 1408423, 1410790, 1418347, 1429153, 1437952, 1440006, 1449157, 1488294, 1488608.

5. U. S. P. 1165179, 1173931, 1181758, 1185514, 1199799, 1199800, 1265217, 1309980, 1342603, 1370879, 1388472, 1389084, 1437952.

6. U. S. P. 1181860, 1188799, 1226342, 1260977, 1275884, 1303563, 1310841, 1363763, 1370879, 1393355, 1394890, 1395401, 1410790, 1426521, 1429153, 1437952, 1440178, 1449157, 1501206, 1508929.

7. U. S. P. 1127871, 1128468, 1136248, 1143979, 1156894, 1160979, 1165179, 1173931, 1181860, 1185514, 1188797, 1188798, 1188799, 1188800, 1196799, 1199395, 1199799, 1199800, 1203756, 1205822, 1226339, 1226340, 1226341, 1226342, 1226343, 1244107, 1244108, 1244347, 1244348, 1244349, 1260977, 1265216, 1265217,

tetrachlorethane[1], especially *sym*- tetrachlorethane[2], trichlorethylene[3], trichlormethylacetanilid[4], trichlorpropane[5], tetrachlorethylacetanilid[6], and triphenyl phosphate[7]; in varnish manufacture[8] and waterproofing compositions[9].

Cellulose Alkoxyalkacyl Derivatives. These esters, substitution products of cellulose acetate or homologues, are prepared by substitution of one or more OH groups of the cellulose molecule by one or more alkoxy-aliphatic acidyl groups, i.e., the acid groups of alkyl ethers of hydroxy aliphatic acids (glycollic, lactic, hydracrylic). The substitution of the hydroxy group is best effected with the anhydrides of the alkyl ethers of hydroxyaliphatic acids (the glycollic acid group).

These anhydrides may be prepared from the sodium, potassium or other metallic salt of the acid by treatment

1309980, 1384188, 1388472, 1395401, 1406224, 1408095, 1408423, 1410790, 1420028, 1429153, 1440006, 1488608.

8. U. S. P. 1180704, 1199800, 1236578, 1265216, 1338661, 1338472, 1389084, 1420028.

1. U. S. P. 1136462, 1156894, 1181857, 1181858, 1181859, 1181860, 1185514, 1191801, 1217722, 1242783, 1263119, 1265216, 1268172, 1275884, 1339728, 1355976, 1357447, 1363763, 1394890, 1397103, 1420028, 1421288, 1421289, 1421290, 1429295, 1431845, 1457131, 1458505, Re-14338.

2. U. S. P. 1133385, 1146391, 1173931, 1195040, 1199798, 1236578, 1236579, 1244107, 1244108, 1244347, 1244348, 1244349, 1245476, 1338661, 1339728, 1386576, 1488608.

3. U. S. P. 1181858, 1181859, 1181860, 1184257, 1188800, 1195673, 1242783.

4. U. S. P. 1136248, 1244107, 1244108, 1244347, 1244348, 1244349.

5. U. S. P. 1244107, 1244108, 1244347, 1244348, 1244349.

6. U. S. P. 1136248, 1216581, 1244107, 1244108, 1244347, 1244348, 1244349.

7. U. S. P. 1128468, 1143979, 1226340, 1226342, 1226343, 1244107, 1244108, 1244347, 1244348, 1244349, 1265217, 1309980, 1440006, 1463864, 1488294.

8. U. S. P. 1181859, 1188798, 1188799, 1188800, 1193178, 1195673, 1203756, 1217722, 1226340, 1226343, 1229485, 1229486, 1229487, 1242783, 1342603, 1347801, 1354726, 1440006, 1454959, 1454960, 1454961, 1505043.

9. U. S. P. 1165179, 1180704, 1241738, 1388824, 1388825, 1388827, 1388828, 1389084, 1453764.

with sulfur and chlorine[1], or oxides of sulfur and chlorine[2] or with phosgene[3]. Dimethyl ether may be converted into methoxyacetic acid and diethyl ether into *b*-ethoxypropionic acid[4], by passing it with excess of CO_2 at 100-200 atms. over a catalyst (phosphoric acid on coke or graphite) at 300-400°.

In order to increase the reactivity the cellulose may be treated, prior to the acylation, with formic or acetic acids, or methyl or ethyl glycollate, the process being carried out as shown in the examples following:

1. 100 parts linters are introduced into a mixture, precooled to 0-5°, of 700 parts methoxyacetic acid, 480 parts methoxyacetic anhydride and 10-12 parts sulfuric acid. Cooling is continued until nearly all the cellulose passes into solution, when it is allowed to rise to 30-35°, complete solution taking place inside of 10 hrs. The cellulose methoxyacetate is precipitated by addition of water or petroleum ether, washed and dried. Soluble in methoxyacetic acid (of course), acetic acid and in chloroform-alcohol. The ester may be partially hydrolyzed as in acetylcellulose manufacture.

2. 100 parts linters are steeped 6-10 hrs. at 30° in a mixture of 400 parts methoxyacetic acid and 5 parts sulfuric acid. The whole is then cooled to 0-10° and introduced into a mixture of 1500 benzene, 500 methoxyacetic anhydride and 5 sulfuric acid. Temperature is allowed to slowly rise to 20-25° in 6 hrs. time. The cellulose methoxyacetate is precipitated with water and washed free from reactants.

3. Linters 100, ethoxyacetic acid 700, ethoxyacetic

1. H. Dreyfus, E. P. 313233; abst. C. A. 1930, **24**, 865; J. S. C. I. 1929, **48**, 671-B; Chem. Zentr. 1929, II, 1590.
2. *Ibid.* E. P. 313235; abst. C. A. 1930, **24**, 865; J. S. C. I. 1929, **48**, 671-B; Chem. Zentr. 1929, II, 1590.
3. *Ibid.* E. P. 313234; abst. C. A. 1930, **24**, 865; J. S. C. I. 1929, **48**, 671-B; Chem. Zentr. 1929, II, 1590.
4. *Ibid.* E. P. 313651; abst. C. A. 1930, **24**, 1120; J. S. C. I. 1929, **48**, 671-B; Chem. Zentr. 1929, II, 1590.

anhydride 560 and sulfuric acid 10-12 are acetylated together as in Ex. 1, cellulose ethoxyacetate being formed[1].

Alkacyl-alkoxyalkacyl cellulose derivatives may be formed by combining the process above with that of acetylation[2], alkoxy aliphatic substitution being effected before simple aliphatic substitution, or the reverse procedure may be adopted, as to a fatty acid cellulose ester as cellulose formate or acetate, but of low ester content. In the following example, alkoxyalkacylation precedes alkacylation:

1. Linters 100, precooled to 0-5° are introduced into methoxyacetic acid 600, methoxyacetic anhydride 400, sulfuric acid 0.4, the temperature being gradually allowed to rise to 15°. After about 20 hrs., and before solution of the cellulose has taken place, the mass is removed from the mixture, squeezed and washed, then introduced into a mixture of 500 glacial acetic acid, 150 acetic anhydride and 7 sulfuric acid and acetylated in the usual manner, solution becoming complete after several hours stirring. The mixed cellulose acetomethoxyacetate is precipitated by water and washed until neutral. The ester is soluble in acetic acid and in chloroform-alcohol. The solubility may be modified by submission to a partial hydration treatment as in the normal acetylation of cellulose. Cellulose acetoethoxyacetate is similarly formed, of analogous properties.

Cellulose Chloracetate is a representative of an ester group obtained by acylating cellulose with chlor- or bromacetate anhydrides, the halogen being subsequently displaced if desired, by amino-, alkylamino- or other groups[3], to form cellulose aminoaliphatic esters or cellulose hydroxyaliphatic acids. H. Rudy[4] has shown that cellulose does not react with chloracetyl chloride in presence of zinc chlo-

1. H. Dreyfus, E. P. 314918; abst. C. A. 1930, **24**, 1507; J.S.C.I. 1929, **48**, 714-B. F. P. 671921; abst. C. A. 1930, **24**, 2290. F. P. Addn. to F. P. 671921; abst. C. A. 1931, **25**, 1082.
2. *Ibid.* E. P. 314919; abst. C. A. 1930, **24**, 1508; J. S. C. I. 1929, **48**, 714-B. F. P. 671103; abst. C. A. 1930, **24**, 1867.
3. *Ibid.* E. P. 320842; abst. C. A. 1930, **24**, 2599; J. S. C. I. 1930, **49**, 379-B.
4. Cellulosechem. 1932, **13**, 49; abst. J. S. C. I. 1932, **51**, 502-A.

ride or pyridine; with chloracetic anhydride and sulfuric acid, cellulose trichloracetate, sintering at 85°, is formed. Similarly, di- and tri-chloracetic anhydride with hydrocellulose afford cellulose didi- and ditri-chloracetate, sintering at 160° and 198-200° respectively. All three esters are hydrolyzed by ethyl alcohol-ammonia to a cellulose chloracetamide and a reducing cellulose. Chlorination of cellulose triacetate with large excess of phosphorous pentachloride gives cellulose trichloracetate, unaffected by concentrated alkali or sodium ethylate. Starch trichloracetate is similarly formed.

Cellulose chloracetates are also prepared by heating cellulose or its transformation products with chloracetic anhydride in the presence of esterification catalysts as sulfuric acid[1]. The esters are isolated by precipitation with water or ether.

W. Barnett[2] has investigated the chlor-cellulose esters and the action of chloracyl chlorides on cellulose, and has prepared upwards of 50 preparations from cellulose and chloracetyl chloride under different conditions, the reaction being so rapid in general, that high dilution was required in order to stop the reaction at the desired point, and isolate the products in a condition susceptible of purification. At no stage in the entire series of cellulose esters produced was there an abrupt change in properties, but throughout, as the magnitude of the cellulose complex diminished, so the physical constants as solubility and melting point became more clearly defined, and also followed a general order, the solubilities increasing and melting points decreasing with diminution in number of cellulose units left in the esters.

An invention has been described[3] based on the observation that when cellulose is esterified in the presence of potassium acetate or the potassium salt of other weak acid,

1. Soc. des Usines Chim. Rhone-Poulenc, F. P. 672220; abst. C. A. 1930, **24**, 2290.

2. J. S. C. I. 1921, **40**, 253-T; abst. Bull. Soc. Chim. 1922, **32**, 250; J. C. S. 1921, **120**, i, 847; Chem. Tech. Uebers. 1922, **46**, 243; Paper Makers' Monthly J. 1922, **59**, 57.

3. Society Chemical Industry, Basle, E. P. 353978.

the reaction progresses without previous conversion to alkalicellulose or the use of an acid catalyst. The details are indicated in the following:

1. 100 parts regenerated cellulose from the rayon industry are immersed in 1000 parts 60% aqueous solution of potassium acetate until equilibrium of concentration has been established, centrifuged, then dried at 70°. The cellulose thus treated is introduced into 600 parts chloracetic anhydride dissolved in 4000 parts xylene, and the solution then boiled for 1 hr. under reflux. The material is then removed, washed with glacial acetic acid, then with water and dried. There is obtained about 220 parts cellulose chloracetate of 22.25% Cl, insoluble in the usual solvents.

2. 100 parts regenerated cellulose are immersed in 1000 parts 60% aqueous potassium acetate solution 1 hr. at 70°, removed, washed and dried, then immersed in 400 parts chloracetic anhydride and 1400 parts benzene and boiled 1 hr., washed and dried. Yield 170% on the cellulose, the ester containing 1.5 acyl groups on C_6 cellulose.

Cellulose Acetonitrate (Nitroacetate).[1] These double esters, containing both an inorganic and organic acid residue, are usually prepared by acetylating an incompletely nitrated cellulose, and not the reverse operation. Their

1. According to the method of I. G. Farbenindustrie (E. P. 319285; abst. C. A. 1930, **24**, 2600) cellulose acetonitrate is formed when cellulose is treated with acetic acid and acetic anhydride in the presence of a nitrate of a weak inorganic or organic base as the nitrate of ammonium, zinc, aniline or urea, with the addition of about 0.3-1% sulfuric acid at 50-100°. The nitroacetates are hydrolyzed and then employed for film manufacture. U. S. P. 1819397; abst. C. A. 1930, **24**, 5769, is similar.

A. Weihe, K. Thinius and Deutsche Celluloid-Fabrik (D. R. P. 550240, 550427; abst. C. A. 1932, **26**, 4173. U. S. P. 1867123) form mixed esters of cellulose containing nitric acid by treating cellulose esters still containing free OH groups, with diacetyl-*o*-nitric acid and a dehydrating agent. Thus, a solution of cellulose acetate, propionate or butyrate in diacetyl-*o*-nitric acid may be treated with acetic anhydride to give a cellulose aceto-, propiono- or butyro-nitrate (nitroacetate, nitropropionate, nitrobutyrate). They are soluble in acetone, methyl ketone, diacetone alcohol or a mixture of benzene-acetone-alcohol.

F. Becker (D. R. P. 550119, 550120; abst. C. A. 1932, **26**, 4172, 4173) prepares mixed nitric esters of cellulose by treating cellulose with nitric acid and aliphatic acids in the presence of a catalyst as

properties and technical applications have been touched upon in the historical development of the cellulose esters in Chaper II in a more or less comprehensive manner, as indicated by the methods of manufacture proposed, as shown on pages 349, 367, 410, 432, 455, 476, 490, 557, 585, 594, 598, 666, 684, 781, 782, 791, 871, 872, 877, 878, 887, 888, 929, 948, 949, 979, 1013, 1014, 1019. For other phases of the subject, consult the Index.

Cellulose Propionate. Many of the methods applicable for cellulose acetate formation are suitable for propionyl-cellulose manufacture, as the processes of C. Weber and C. Cross[1], Knoll & Co.[2], C. Claessen[3], and A. Polotsky[4], free HCl[5], monochloracetic acid[6] and sulfuric acid[7], being the

sulfuric acid, and a diluent preferably an organic acid, and adding to the mixture at a later stage an aliphatic acid anhydride. Or C. Malm and C. Fletcher (Can. P. 322870; abst. C. A. 1932, **26**, 4173) partially acetylate cellulose with less than 2 parts acid anhydride to 1 part cellulose, afterwards treating with nitrogen di-, tri-, tetra- or pent-oxide, nitric acid or fuming nitric acid, and then further acylate.

1. U. S. P. 632605. E. P. 22029, 1898; abst. J. S. C. I. 1899, **18**, 756. Can. P. 63101. D. R. P. 112817. Russ. P. 3264, 1900. Belg. P. 137577, 1898. Dan. P. 2558, 1899. Port. P. 2930, 1899. Belg. P. 137577 to Guido Henckel Donnersmarck covers the same ground, i.e., using nitrobenzene, epichlorhydrin or dichlorhydrin as solvents. Belg. P. 138462 is an addition to it.

2. D. R. P. 203178; abst. Jahr. Chem. 1905-08, 984; Chem. Zentr. 1908, II, 1549; Chem. Zts. 1909, **8**, 1053; Mon. Sci. 1912, **77**, 97; Zts. ang. Chem. 1908, **21**, 2426; Wag. Jahr. 1908, **54**, 366. D. R. P. 206950, being Addn. to D. R. P. 203178; abst. Chem. Zts. 1909, **8**, 1183; Zts. ang. Chem. 1909, **22**, 656; Chem. Ind. 1909, **32**, 153; Wag. Jahr. 1909, **55**, II, 397; Mon. Sci. 1912, **77**, 96. E. P. 2026-A, 1907; abst. J. S. C. I. 1908, **27**, 353.

3. D. R. P. 222450; abst. J. S. C. I. 1910, **29**, 811; Zts. ang. Chem. 1910, **23**, 1389; Chem. Zentr. 1910, II, 48; Wag. Jahr. 1910, **56**, 434; Chem. Zts. 1910, **9**, 1902; C. A. 1910, **4**, 2875.

4. U. S. P. 1296847.

5. E. Knoevenagel and H. Lebach, U. S. P. 891218; abst. J. S. C. I. 1908, **27**, 765; Mon. Sci. 1909, (4), **70**, 116. E. P. 2026-B, 1907; abst. J. S. C. I. 1908, **27**, 353. F. P. 373994; abst. J. S. C. I. 1907, **26**, 776; Mon. Sci. 1908, (4), **68**, 83; Chem. Tech. Rep. 1907, **31**, 302. D. R. P. 201233; abst. Chem. Zts. 1908, **7**, 993; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, II, 994; Chem. Ind. 1908, **31**, 587; Jahr. Chem. 1905-08, 982. D. R. P. 203178; abst. Chem. Zts. 1909, **8**, 1053; Zts. ang. Chem. 1908, **21**, 2426; Chem. Zentr. 1908, II, 1837; Jahr. Chem. 1905-08, 984; Chem. Ind. 1908, **31**, 741. Aust. P. 41831.

6. Actien-Gesellschaft fur Anilin-Fabrikation, E. P. 14255, 1906; abst. J. S. C. I. 1907, **26**, 220; C. A. 1907, **1**, 1341. F. P. 368738; abst. J. S. C. I. 1907, **26**, 30. D. R. P. 198482; abst. Mon.

usual catalysts employed in conjunction with propionic acid, propionic anhydride or propionyl chloride. Other methods of manufacture are stated on pages 360, 495, 621, 642, 667, 700, 773, 811, 865, 918, 928, 942, 949. Data on the properties (p. 700), solubility (949), saponifying (744, 747), bleaching (1014), dyeing (413, 607, 750, 934), carbonizing (767), delustering (774) and relustering (135) are stated elsewhere herein.

The indicated uses of cellulose propionate are for film manufacture[1], laminated glass[2], plastics production[3], filament manufacture[4], as a thickening paste[5], and in producing warp effects on textiles[6]. The uninflammable celluloid substitute of H. Dreyfus[7], the rot-proofing of fabrics by B. Wolcott and C. Jennison[8] and the airplane wing coating composition of Leduc, Heitz & Co.[9], all utilize cellulose propionate. The waterproofing composition of A. St. Armande[10] and the airplane wing tautening lacquer composition of F. Cumbers[11] employ propionylcellulose. The manu-

Sci. 1911, (5), **74**, 54; Zts. ang. Chem. 1908, **21**, 1760; Chem. Zentr. 1908, II, 118; Jahr. Chem. 1905-08, II, 982; Chem. Ind. 1908, **31**, 378.

7. L. Lederer, U. S. P. 999236; abst. J. S. C. I. 1911, **30**, 1050. E. P. 3103, 1907; abst. J. S. C. I. 1907, **26**, 889. F. P. 374370; abst. J. S. C. I. 1907, **26**, 776; Mon. Sci. 1908, (4), **68**, 84; Chem. Zts. 1907, **6**, 139.

1. British Celanese, Ltd., E. P. 274841; abst. J. S. C. I. 1928, **47**, 782-B. Compare F. P. 563785; abst. Ann. Rep. S. C. I. 1924, **9**, 166; Kunst. 1924, **14**, 41. Can. P. 273367.

2. W. Moss, U. S. P. 1831462.

3. G. Schneider, Can. P. 317330. A. Dubosc and A. Luttringer, Bull. soc. ind. Rouen, 1920, **48**, 91; abst. C. A. 1921, **15**, 171.

4. British Celanese, Ltd., E. P. 341148; abst. C. A. 1931, **25**, 5029.

5. *Ibid.* E. P. 313885; abst. C. A. 1930, **24**, 1218; J. S. C. I. 1930, **49**, 1146-B; Silk J. 1929, **6**, #65, 78. In E. P. 316521, C. Dreyfus and G. Schneider saponify yarns and fabrics made of cellulose acetate, propionate or butyrate with caustic soda in paste form, using as a thickener the cellulose ethers because they are unaffected by the alkali, materials treated in this manner possessing higher safe ironing properties.

6. C. Dreyfus, E. P. 317455; abst. C. A. 1930, **24**, 2309. See also E. P. 306534; abst. C. A. 1929, **23**, 5048.

7. U. S. P. 1181860.

8. U. S. P. 1474574; abst. J. S. C. I. 1924, **43**, 90-B.

9. E. P. 6798, 1911.

10. E. P. 106375.

11. E. P. 131384.

facture of cellulose propionic acid has been described[1], and its application advocated as a gelatin substitute in the form of its alkali salt.

Methods for the production of cellulose propionitrate (nitropropionate)[2], propio-benzoate, -butyrate, -cinnamate, -crotonate, -cyclohexanecarboxylate, -hydrocinnamate, -laurate, -myristate, -palmitate, -palmitostearate, -stearate, -undecylenate, and -valerate[3] have been described, as have those of cellulose propio-phthalate (phthalyl-propionate)[4].

C. Dreyfus and G. Schneider[5] pretreat linters with a lower fatty acid and propionic anhydride in the absence of a catalyst, and then add sulfuric acid to induce propionylation, the ester being afterwards partially hydrolyzed.

Cellulose Lactate. Cellulose Hydroxypropionate. According to H. Heimann and A. Bayerl[6], when cotton 1 is introduced with stirring into 80% lactic acid 20, and heated for 3 hrs. at 80°, with removal of excess lactic acid, the cellulose is changed and a cellulose lactate (?) results. L. Lilienfeld specifies cellulose lactate as an initial material for cellulose ether manufacture[7]. The manufacture of cellulose lactate is carried out by treating cellulose with lactic acid, or the potassium or sodium salts of the acids with thionyl chloride[8], and mixed esters as cellulose formyl-lactate (lactyl-formate) by reacting upon cellulose with an alkoxyacetic acid in the presence of a catalyst, and then

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. Norw. P. 31018; abst. Chem. Tech. Uebers. 1921, **45**, 13. Swiss P. 85075; abst. Kunst. 1921, **11**, 39.
2. British Celanese, Ltd., E. P. 338745; abst. C. A. 1931, **25**, 2566.
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.
4. R. Stinchfield, U. S. P. 1704306; abst. C. A. 1929, **23**, 2033; Plastics, 1930, **6**, 91.
5. U. S. P. 1824877; abst. J. S. C. I. 1932, **51**, 595-B.
6. U. S. P. 1728206; abst. J. S. C. I. 1929, **48**, 894-B.
7. U. S. P. 1188376.
8. H. Dreyfus, E. P. 316160. F. P. 672235.

formylating[1]. A cellulose aceto-lactate[2], and acetotartryl-lactate[3] are known.

Cellulose Butyrate. The butyrocelluloses may be prepared by the action of butyric acid, butyric anhydride or chloride and a catalyst as zinc chloride[4], ethylsulfuric acid[5], or aliphatic sulfonic acids as methanesulfonic acid[6]. Diluents as benzene or butyric acid aid in the smoothness of esterification[7]. The C. Cross and C. Weber method is to evaporate to dryness a mixture of cellulose 162 and magnesium butyrate 198, then add 213 parts butyryl chloride and 25 parts butyric anhydride[8].

L. Lederer first hydrolyzes cotton with an equal weight of glacial acetic acid and 2.5% sulfuric acid esterified with 5.6 parts butyric anhydride which has been diluted with an equal volume of carbon tetrachloride[9]. In the presence of a tertiary base as pyridine[10], the amount of butyryl chloride required for butyration can be reduced to but little more than that theoretically required. The cellulose butyrate is separated by ketones of high molecular weight as dipropylketone.

1. H. Dreyfus, E. P. 314918. F. P. 671921.
2. *Ibid.* E. P. 314919. F. P. 671103.
3. C. Webber and C. Staud, Can. P. 321129.
4. Soc. Anon. D'Explosifs et de Produits Chim., F. P. 385179; abst. Mon. Sci. 1909, (4), **70**, 105; Bull. Soc. Chim. 1909, (4), **6**, 557; J. S. C. I. 1908, **27**, 589; C. A. 1909, **3**, 2383. F. P. 385180; abst. Mon. Sci. 1909, (4), **70**, 106; Bull. Soc. Chim. 1909, (4), **6**, 557; J. S. C. I. 1908, **27**, 589; C. A. 1909, **3**, 2383.
5. C. Dreyfus, F. P. 430606; abst. J. S. C. I. 1911, **30**, 1375.
6. Soc. des Usines Chim. Rhone-Poulenc, F. P. 684273; abst. C. A. 1930, **24**, 5495.
7. *Ibid.* U. S. P. 1543310; abst. Chem. Zentr. 1925, II, 1826. F. P. 596802.
8. C. Weber and C. Cross, U. S. P. 632605. E. P. 22029, 1898; abst. J. S. C. I. 1899, **18**, 756. Can. P. 63101. D. R. P. 112817; abst. Jahr. Chem. 1900, 843; Wag. Jahr. 1900, II, 450. Russ. P. 3264. Belg. P. 137577. Dan. P. 2558. Port. P. 2930. Cf. D. R. P. 105347; abst. Wag. Jahr. 1899, 1064.
9. U. S. P. 999236; abst. J. S. C. I. 1911, **30**, 1050. E. P. 3103, 1907; abst. J. S. C. I. 1907, **26**, 889. F. P. 374370; abst. J. S. C. I. 1907, **26**, 776; Mon. Sci. 1908, (4), **68**, 84; Chem. Zts. 1907, **6**, 139. For sebacic esters of hydrocellulose, see A. Stein, Dissertation, Dresden, 1911, p. 71.
10. E. Desparmet, F. P. 664932; abst. C. A. 1930, **24**, 961.

Cellulose tributyrate or tri*iso*butyrate may be made by treating either cellulose or hydrocellulose with butyric anhydride in the presence of sulfonic salts as of methane- or ethane-sulfonic acid[1], and may be made in the fibrous or physically unaltered condition[2] by the introduction of alcohol or tetrachlorethane into the butylating bath. In the method of G. Esselen and H. Mork[3], the cellulose is given a pretreatment with sulfuric acid 0.4-0.6% and butyric acid 92-94%, then esterified in the usual manner. W. Bonner prepares cellulose butyrate, benzoate or palmitate[4], by first reacting upon cellulose with dry ammonia, resulting in the formation of a dry powder which is very reactive. This is then esterified in the usual way.

Cellulose butyrates soluble in methyl alcohol result when the ester containing a small amount of free butyric acid is heated with water until the saponification which ensues has reached the degree indicated by the solubility results desired[5]. By first feebly formylating cellulose, then butylating, a cellulose formylbutyrate (butyryl-formate) results containing but little formic acid[6], and of solubility in a wide range of organic solvents. After esterification, the ester is submitted to a partial saponification to increase its solubility. Both cellulose butyrates and *iso*butyrates may be prepared by using chlorinated acetic acid, especially trichloracetic acid as catalyst, preferably in the presence of a solvent as acetone or butyric acid, esterifying at 15-25° in the presence of a dehydrating agent (as 66° Be. sulfuric acid).

Cellulose butyrate giving on hydrolysis 65-68% butyric

1. Soc. des Usines Chim. Rhone-Poulenc, E. P. 323869; abst. C. A. 1930, **24**, 3368.
2. H. Mork and C. Coffin, U. S. P. 1421288, 1421289, 1421290.
3. U. S. P. 1425580, 1425581.
4. U. S. P. 1173336.
5. Soc. des Usines Chim. Rhone-Poulenc, E. P. 328259; abst. C. A. 1930, **24**, 5496.
6. R. Herzog and G. Frank, F. P. 700165; abst. C. A. 1931, **25**, 3481.

acid[1], and therefore intermediate in composition between the di- and tri-ester, is obtained by first steeping cellulose in 80-95% aqueous formic acid for 24 hrs. at ordinary temperature, then esterifying with butyric anhydride, butyric 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°, and dissolves in the usual solvents forming highly viscous solutions.

Cellulose tributyrate and tri*iso*butyrate[2] are prepared by submitting cellulose to the regulated action of a chlorine derivative of acetic acid in the presence of a suitable solvent as butyric acid or acetone at a low temperature, and then esterifying at 15-25° in the presence of a dehydrating agent as sulfuric acid and an appropriate solvent. Cellulose acetobutyrates result in proceeding as above[3], then esterifying with a mixture of butyric anhydride and acetic anhydride in presence of oil of vitriol.

Higher cellulose esters in this group as cellulose angelate, hexanoate, hypogaete, oleate, phenylacetate, phenylpropionate, heptylate[4] have been described, being produced by the general method of esterifying modified cellulose by the anhydride and the chloride of the respective acid in the presence of the magnesium salt of the acid, and preferably in the presence of a diluent as benzene.

The cellulose butyrates have been proposed for the manufacture of artificial filaments[5], mildewing and rotproofing canvas by a superficial butylation of the cellu-

1. G. v. Frank and H. Cohn, Cellulosechem. 1931, **12**, 68; abst. C. A. 1931, **25**, 5554.
2. Soc. des Brevets Etrangers Lefranc et Cie, F. P. 686906; abst. C. A. 1931, **25**, 812; Addn. 38980; abst. C. A. 1932, **26**, 1782. D. R. P. 550322; abst. C. A. 1932, **26**, 4173.
3. *Ibid.* F. P. 687169; abst. C. A. 1931, **25**, 813.
4. C. Weber and C. Cross, U. S. P. 632605. G. Henckel-Donnersmarck, D. R. P. 112817.
5. W. Whitehead and C. Dreyfus, E. P. 313971.

lose[1], as a pipe mending composition[2], phenol-aldehyde condensate composition[3], and as an anti-fouling paint[4].

Cellulose Higher Fatty Acid Esters. The higher cellulose esters of the aliphatic acid and allied groups have assumed prominence only within about the last ten years, and nowhere, insofar as aware, has there appeared a comprehensive discussion of these bodies as a whole, together with their indicated technical usefulness. This, coupled with their peculiar and desirable properties, not only as adjuncts to the cellulose ethers and esters in physical admixture, but also in combination chemically with the cellulose ethers, is the reason for a detailed statement of these cellulose derivatives herein.

In 1921 A. Gruen and F. Wittka[5] described esters of stearic acid with cellulose, cellulose distearate being obtained by the action of 6 parts stearyl chloride upon 1 part cellulose in a mixture of benzene and pyridine. It is scarcely distinguishable from the original cellulose, melts at 220° with decomposition, is insoluble in practically all the usual solvents including cuprammonium solution, but dissolves in fatty acids and glycerides at 200°, the solubility increasing with the molecular weight of the glyceride. When dissolved in olive oil, there is some exchange of oleic for stearic radical. Cellulose dilaurate, also prepared by using 6 parts lauryl chloride, melts at about 250°. This is more soluble than the distearate, dissolving to a considerable extent in tri*iso*valerin. Methyl acetate and ethyl alcohol precipitate it from solutions, but not ethyl ether. Acetylcellulose heated with alcohol in an autoclave at 270° for 5 hrs. gave cellulose lauro-monoacetate. Cellulose monostearate is said to be best prepared by the action of 1 mol. stearyl chloride upon 1 mol. cellulose. It is slightly soluble in chloroform,

1. B. Wolcott and C. Jennison, U. S. P. 1474574; abst. J. S. C. I. 1924, **43**, 90-B.
2. L. Wilson, U. S. P. 1389084.
3. W. Bonner, U. S. P. 1173337.
4. L. Collardon, U. S. P. 1105619. E. P. 1600, 1912. F. P. 453395. D. R. P. 274875. Swiss P. 63580, 63821.
5. Zts. ang. Chem. 1921, **34**, 645-A; abst. C. A. 1922, **16**, 1566.

carbon tetrachloride and tetrachlorethane, decomposing without melting.

The second year afterwards, H. Gault and P. Ehrmann[1] obtained higher fatty acids of cellulose of increased solubility, especially in those organic solvents normally employed in the cellulose ether and cellulose ester art. It was found that when hydrocellulose is treated with 5 parts of higher acid chloride in the presence of an excess of pyridine, using benzene as a solvent, and heating at 110-120° for 2-3 hrs., soluble cellulose esters result. The distearate, dipalmitate and dilaurate were prepared, amorphous substances, soluble in most organic solvents, and giving colloidal solutions. No soluble palmitic ester could be prepared from normal cellulose[2]. The di-esters are obtainable by this method in 80% yields, dissolving in aromatic hydrocarbons, chloroform and halides of ethylene, insoluble in alcohol and acetone. The benzene and chloroform solutions give translucid films, remarkably flexible, non-inflammable and water-resistant. The reaction is applicable to the chlorides of either the pure acids or the crude commercial mixtures obtained by saponifying oils or fats. The pure cellulose esters of lauric, palmitic and stearic acid were prepared, and also those from the solid fatty acids of copra and tallow. The m. pt. varied from 85-90° for cellulose distearate to 110° for cellulose dilaurate. Cellulose nitrolaurate (lauronitrate) and cellulose acetolaurate (lauroacetate) were prepared of definite composition, soluble in aromatic hydrocarbons, and yielding strong and flexible films, slightly more inflammable than those from straight fatty acids. Esterification of starch without preliminary solution gives di-esters quite similar to the corresponding cellulose derivatives, but films prepared therefrom are less plastic.

The method of preparation may be improved by intro-

1. Compt. rend. 1923, **177**, 124; abst. C. A. 1923, **17**, 3249; J. S. C. I. 1923, **42**, 826-A. U. S. P. 1553924. F. P. 566124.

2. H. Gault and P. Ehrmann, Chim. et Ind. May, 1924, Spec. No. 574; abst. C. A. 1925, **19**, 251.

ducing sulfur chloride in the reaction mixture[1], yields of 80-90% with lauryl chloride and 50-70% with palmityl or stearyl chloride being obtained. K. Hess and E. Messmer[2] prepared these esters by adding the acid chloride to a suspension of cellulose in pyridine and chloroform, obtaining a 300% yield on the cellulose of laurate, resembling the original cellulose and insoluble in ordinary solvents. Substituting hydrocellulose for cellulose in the esterification, the tripalmitate was obtained.

In 1927, were prepared[3] cellulose laurodinitrate and palmitodinitrate, both fibrous, and much less inflammable than the nitrocellulose from which they were prepared. They are soluble in chloroform, carbon tetrachloride, and pyridine, wholly insoluble in ethyl alcohol, alcohol-ether, ether, acetone and acetic acid, and in general, more resistant to chemical reagents than nitrocellulose. Cellulose palmitodiacetate has similar properties. In general, the introduction of higher fatty acid rests in cellulose nitrate or acetate, reduces the inflammability, renders them more soluble in organic solvents, and increases resistance to hydrolyzing agents.

Cellulose monolaurate has been obtained in fibrous granules, m. pt. 190-200° with decomposition, insoluble in the usual organic solvents, but swelling to a transparent gel in chloroform, ethyl ether or aromatic hydrocarbons, from which it may be precipitated as a fine powder by ethyl alcohol, acetone or acetic acid. The dilaurate melts indefinitely at 85-90° with decomposition, particularly soluble in benzene, toluene and xylene, from which it may be precipitated by ethyl alcohol, acetone or acetic acid[4].

The cellulose caproates[5] are prepared by methods sim-

1. H. Gault and P. Ehrmann, Caout. et Gutta. 1926, **23**, 13312, 13888; 1927, **24**, 13453; abst. C. A. 1927, **21**, 1350.
2. Ber. 1921, **54**B, 499; abst. C. A. 1921, **15**, 2422.
3. H. Gault and P. Ehrmann, Caout. et Gutta. 1927, **24**, 13748, 13824; 1928, **25**, 13868; abst. C. A. 1928, **22**, 1038.
4. *Ibid.* Caout. et Gutta. 1927, **24**, 13532, 13603; abst. C. A. 1927, **21**, 2794.
5. *Ibid.* Caout. et Gutta. 1927, **24**, 13706; abst. C. A. 1927, **21**, 4062.

ilar to those outlined above. The monocaproate forms a tough, fibrous mass, insoluble in all solvents, and softening around 250°. The dicaproate is precipitated from a benzene solution as very fine fibers, dissolving in all the solvents of cellulose laurate, particularly in aromatic hydrocarbons. Softens at 140° and melts at 180°. Cellulose tricaproate forms a very hard granular mass and cannot be precipitated in fibrous form. It softens at 100° and melts at 230°.

In general, when the reaction of preparation is carried out at 110°, the solubility of the esters formed *decreases* with increase of number of C atoms in the acid radical, while the solubility *increases* proportionately to the copper number of the hydrocellulose employed. The thermoplasticity of these esters depends, in a large degree, upon the amount of degradation of the cellulose molecule. When normal or un-modified cellulose is esterified with these acids, the products are insoluble, but with modified cellulose, the esters are characterized by a ready solubility in aromatic hydrocarbons, even if a portion of the fatty acid molecule has been replaced by cellulose acetate or nitrate, both of which are insoluble in benzene, toluene or xylene[1].

P. Karrer, J. Peyer and Z. Zega in connection with their investigations on cork substance[2], prepared cellulose hexapalmitate (on a C_{12} cellulose) by reacting upon cellulose precipitated from Schweitzer's reagent with palmityl chloride in quinoline for 4 hrs. at 120°. It melted about 78°. A cellulose ricinoleate has been described by A. Luttringer[3], and a cellulose palmitate established with 1 mol. palmitic acid and 4 mols. C_6 cellulose.

Cellulose naphthenates have been described[4], prepared from naphthenic acid fractions having acid values of 199-250. Cellulose esters are obtained with naphthenic acid

1. H. Gault and P. Ehrmann, Bull. Soc. Chim. 1926, **39**, 873; abst. Plastics, 1927, **3**, 126.
2. Helv. chim. Acta, 1922, **5**, 863; abst. C. A. 1923, **17**, 988.
3. Caout. et Gutta. 1923, **20**, 11960.
4. G. Kita, T. Mazume, T. Nakashima and I. Sakurada, Cell. Ind. Tokyo, 1926, **2**, 31; abst. Caout. et Gutta. 1927, **24**, 13424. See Kunst. 1926, **16**, 41, 69; abst. C. A. 1926, **20**, 3079.

anhydrides, but the degree of esterification is low. With the acid chlorides in the presence of pyridine, esters containing up to 2.5 mols. naphthenic acid per mol. cellulose have been obtained, unmodified cellulose reacting less avidly than hydrocellulose. Those with high naphthenic acid content show definite melting points. The cellulose naphthenates prepared from normal cellulose are substantially insoluble in the usual solvents, although a portion dissolves in benzene. The degree of solubility depends not only upon the naphthenic acid content, but also upon the relative degradation of the cellulose. Cellulose dinaphthenate prepared from modified cellulose is completely soluble in benzene, chloroform, carbon tetrachloride and ether. The originally insoluble ester also becomes soluble in these liquids after fusion.

It has been established that only a slight degree of etherification takes place upon heating cellulose with palmitic anhydride in the presence of pyridine and chloroform[1], but if the cellulose is heated with palmityl chloride and pyridine, preferably diluted with ether or benzene, cellulose tripalmitate, soluble in ether or benzene, results. The esters may be purified by washing with alcohol, and then extracting with ether or benzene. The monopalmitate is still fibrous and only slightly swollen. The tripalmitate from hydrocellulose is soluble in benzene, but that from normal cellulose partially only. The monopalmitate is insoluble in benzene, but becomes transparent in it. The m. pts. ranging from 180-220° are lower in the hydrocellulose esters than from normal cellulose with the same palmitic acid content[2].

According to the conclusions reached by G. Kita, T.

1. G. Kita, T. Mazume, I. Sakurada and S. Nakajima, Cell. Ind. Tokyo, 1925, **1**, 227; abst. J. S. C. I. 1926, **45**, 45-B; Can. Pulp & Paper Mag. 1927, **25**, 356; Cell. Ind. 1925, **1**, 23-A. G. Kita, T. Mazume, J. Sakrada and T. Nakashima, Kunst. 1926, **16**, 41, 69; abst. J. S. C. I. 1926, **45**, 870-B; Chem. Zentr. 1926, II, 1266; C. A. 1926, **20**, 3079.

2. I. Sakurada and T. Nakashima, Sci. Papers Inst. Phys. Chem. Research (Tokyo), 1927, **6**, 197; abst. C. A. 1928, **22**, 683.

Nakashima and I. Sakurada[1], all of the cellulose tri-esters of lauric, palmitic or stearic acids are soluble in benzene, carbon tetrachloride, chloroform or ether. If there is a deficiency in solubility, it may be overcome by heating the cellulose fatty acid with acids. Inasmuch as these esters are represented by long hydrocarbon residues[2], they are therefore much less polar than cellulose acetate, and their solubility relationships are basically different. Whereas cellulose distearate is insoluble in triacetin (a solvent for cellulose triacetate), the solubility in triglycerides increases with the size of the alkyl groups. This progressively increasing solubility is shown in tributyrin, tri-*iso*-valerin, and tricaprylin, while it dissolves freely in triolein.

In an X-ray study of certain cellulose and dextrose esters by the Debye-Scherrer method[3], the microcrystalline cellulose dilaurate and distearate show that the internal structure of the cellulose is completely destroyed by fixation of the long aliphatic chains. Dextrose *α*-penta-acetate, -laurate and -palmitate have also been studied[4].

Manufacture of Cellulose Higher Fatty Acid Esters[5]. The details of commercial production of these higher cellulose esters are primarily to be found in the patented processes of the I. G. Farbenindustrie, comprised in the processes represented by the succeeding thirteen examples:

(1) Soluble esters of the higher fatty acids may be made from unaltered cellulose[6] by conducting the esterification exceeding a certain value. The temperature mini-

1. J. S. C. I. Japan, 1927, **30**, 475; abst. C. A. 1928, **22**, 499.
2. G. Whitby, Fourth Colloid Symposium Monograph, 1926, **4**, 203; abst. C. A. 1927, **21**, 3293; J. S. C. I. 1928, **47**, 17-A; Chem. Zentr. 1928, II, 856.
3. A. Nowakowski, Compt. rend. 1930, **191**, 411; abst. J. S. C. I. 1930, **49**, 1352-A.
4. G. Druce, Rayon Record, 1930, **4**, 841.
5. Anon., Chem. Age, (London), 1932, **26**, 26.
6. I. G. Farbenindustrie, E. P. 283181; abst. C. A. 1928, **22**, 3988; Silk J. 1928, **4**, #48, 64; J. S. C. I. 1928, **47**, 637-B. F. P. 699217; abst. C. A. 1931, **25**, 3482. D. R. P. 539470; abst. C. A. 1932, **26**, 1783. I. G. Farbenindustrie, M. Hagedorn and G. Hingst, D. R. P. 515106; abst. C. A. 1931, **25**, 1671. See E. P. 201510; abst. J. S. C. I. 1924, **43**, 128-B. I. G. Farbenindustrie, E. P. 306132, 319001, 325512, 326502, 334897. D. R. P. 487011, 511978, 519457.

mum varies with different acids, being 110° for lauric acid, 140° for stearic, and not below 100° in the case of any fatty acid. The cellulose is heated with the desired acid chloride at 100-140°, usually in the presence of a diluent which is a solvent for the ester to be obtained. In order to ensure a smooth course of reaction, the mixture is heated as rapidly as possible, and is finished as soon as no more fiber can be detected in the mixture, usually in 1.25-2 hrs. The formed ester is then precipitated by methyl or ethyl alcohol or acetone, washed and dried. According to the proportion of reactants used, a di- or tri-ester results. The cellulose esters obtained as above have the solubilities of those made using a modified cellulose, and, in addition, have considerably better mechanical properties, especially in tensile strength.

For example, 800 cc. pyridine and 160 gms. cellulose are introduced into a mixture of 4 liters xylene and 960 gms. stearyl chloride, the temperature being then raised to 135-140°. After 1.5-2 hrs. no more fibers are observable, when the mass is poured into alcohol, and the precipitated ester washed with water and dried. A cellulose di-stearate is obtained, soluble in aromatic and in chlorinated hydrocarbons. Pyridine may be replaced by quinoline.

(2) However, in the above process, if a temperature under 100° be employed, cellulose esters of the fatty acids are obtained which are not dissolvable in the solvents customarily employed in the technology of cellulose ester plastics. This solubility may be greatly increased by heating the formed ester in a liquid medium and in the absence of water, to the action of an acid, acid anhydride, or a salt, as exemplified in the following five examples[1]:

(a) 100 gms. insoluble cellulose tristearate are thoroughly moistened with 500 cc. tetrachlorethane and after addition of 5 gms. trichloracetic acid, the mixture is heated

1. I. G. Farbenindustrie, E. P. 284298; abst. C. A. 1928, **22**, 4815; J. S. C. I. 1929, **48**, 593-B. D. R. P. 515107; abst. C. A. 1931, **25**, 1671; Chem. Zentr. 1931, I, 1544.

to 145°. After about 1.5 hrs. there is produced a clear, transparent solution in which no fibers are observable. The mixture is precipitated by ethyl alcohol, washed with water and dried, and will then be found soluble in benzene, chloroform, and tetrachlorethane.

(b) 100 gms. insoluble cellulose trilaurate are moistened with 500 cc. tetrachlorethane and 10 gms. pyridine hydrochloride, then heated to 145°. After 1 hr. the previously insoluble ester has completely dissolved, is then precipitated as above, and has the solubilities mentioned under (a).

(c) 100 gms. insoluble cellulose tristearate are moistened with 500 cc. toluene, 2 gms. ferric chloride added, and the mixture heated to 90-100°. After 10-15 min. the ester has become completely dissolved, and may be isolated as above. Solubilities same as in (a).

(d) A sparingly soluble hydrocellulose dipalmitate is mixed with benzene to form a 20% solution, and with 0.1-2% (calculated on the weight of the solvent) of aluminum chloride, zinc chloride, pyridine hydrochloride, benzenesulfonic acid or sulfuric acid, heated to 80-145° until the ester shows the desired solubility. The ester is precipitated in the form of white, amorphous flocks, and differs in its solution in chloroform, methylene chloride or benzene from the parent material in a smaller viscosity and absence of gelatinous character.

(e) 100 gms. sparingly soluble hydrocellulose trilaurate are dissolved in 200 gms. lauric anhydride at 200°. After the mixture has been cooled it is poured into ethyl alcohol to separate the ester, which is then boiled several times with ethyl alcohol while stirring, filtered and dried. The viscosity has been so reduced that easily flowable solutions may be obtained up to 70% concentration. The softening point is about 70°.

(3) If cork meal is suspended in chlorbenzene and

treated with lauryl chloride in presence of pyridine[1], esters result possessing the typical appearance of cork, but are insoluble in the usual solvents. However, they are indicated for plastics manufacture by virtue of being moldable under pressure and when heated.

(4) The solubility of the higher cellulose esters as laurate or palmitate may be increased[2] by the use of an acid halide as phosphorous oxychloride coupled with heat.

(5) Processes (1) and (2) above may be combined in a single operation[3], by first conducting the esterification at a temperature lower than 100°, and then, without isolating the insoluble ester thus produced, the mixture is heated at a temperature above 100° until the solubility desired has been attained.

(6) If a mixture of 450 cc. xylene, 85 cc. pyridine, 53 gms. lauryl chloride and 20 gms. cotton are heated to 110-120° 6 hrs., and for a further 2 hrs. at 140-145°, until no more dissolved particles are present, and then 6 gms. phosphorous oxychloride in 10 cc. pyridine added, and the mixture stirred during 2 hrs. at 110-120°, a cellulose laurophosphate (phospholaurate) is obtained, containing 65.5% bound lauric acid and 4.2% phosphoric acid, dissolving in chloroform, methylene chloride, benzene and xylene[4].

1. I. G. Farbenindustrie, E. P. 291773. According to Kodak Pathe (F. P. 667557; abst. C. A. 1930, **24**, 1217) cellulose esters containing halogen substituted fatty acid groups are prepared by submitting cellulose to the simultaneous action of a halogen substituted fatty acid containing more than 5 C atoms, and an organic acid anhydride. Thus, cellulose heated with chloracetic anhydride and chloracetic acid in the presence of magnesium perchlorate with addition of *α*-bromstearic acid in acetic acid, gives cellulose aceto-*α*-bromstearate.

2. *Ibid.* E. P. 292929; abst. C. A. 1929, **23**, 1504; Silk J. 1928, **5**, #52, 80. F. P. 644636; abst. C. A. 1929, **23**, 2033. F. P. 35460, Addn. to F. P. 644636; abst. C. A. 1930, **24**, 3901. See D. R. P. 515107; abst. Chem. Zentr. 1931, I, 1544. D. R. P. 533593, Addn. to D. R. P. 515107; abst. Chem. Zentr. 1931, II, 3178. For methods of manufacture of cellulose laurate, cellulose naphthenate and cellulose phenylacetate, see I. G. Farbenindustrie, F. P. 664770. Can. P. 294939.

3. *Ibid.* E. P. 297766, Addn. to E. P. 283181; abst. J. S. C. I. 1929, **48**, 51-B; Chem. Zentr. 1929, I, 817. F. P. 644480; abst. C. A. 1929, **23**, 1749. F. P. 38195, Addn. to F. P. 644480; abst. C. A. 1931, **25**, 5556.

4. *Ibid.* E. P. 300942; abst. C. A. 1929, **23**, 4071; J. S. C. I. 1929, **48**, 126-B. F. P. 34859, Addn. to 629861; abst. C. A. 1930,

(7) Process (5) is modified in that after the reactants have been added[1], the temperature is allowed to slowly rise to around 145°, depending upon the acid radical to be attached to the cellulose, and the maximum temperature maintained until the formed ester goes entirely into solution in the diluent used in the acylation.

(8) In the preparation of mixed esters of the higher fatty acids[2], the higher fatty acid chlorides may be used in admixture with each other or in several stages in succession, or there may be used a halide of a cyclic substituted fatty acid or an alicyclic carboxylic acid as cyclopentane- or cyclohexane-carboxylic acid. The general methods of preparing these mixed cellulose esters is indicated by the following eight examples:

(a) *Cellulose Phenylacetate.* Into a mixture of 480 cc. pyridine bases (b. pt. 115-145°) and 1500 cc. chlorbenzene is gradually poured a mixture of 700 cc. phenylacetic acid chloride and 200 cc. chlorbenzene. Into this mixture, heated to 80°, are introduced 100 gms. linters and the whole heated with stirring 1 hr. at 115-120°, the cotton meanwhile dissolving. The ester is precipitated by pouring into methyl alcohol, washed and dried. The ester contains 77% combined phenylacetic acid, is hard and brittle when cold but softens at 80-100°, melting at about 140°. Soluble in benzene hydrocarbons and aliphatic halogenated hydrocarbons.

(b) *Cellulose Naphthenate.* 100 gms. cotton linters

24, 1216. I. G. Farbenindustrie, M. Hagedorn, O. Reichert and E. Gühring, D. R. P. 511208; abst. C. A. 1931, **25**, 1379. D. R. P. 533126, Addn. to D. R. P. 511208; abst. C. A. 1932, **26**, 598. D. R. P. 535253, Addn. to D. R. P. 511208; abst. C. A. 1932, **26**, 1119.

1. I. G. Farbenindustrie, E.P. 305661; abst. C.A. 1929, **23**, 4818.

2. *Ibid.* E. P. 305947, Addn. to E. P. 283181, 297766; abst. C. A. 1929, **23**, 5041; J. S. C. I. 1930, **49**, 814-B; Br. Plastics, 1930, **2**, 229; Chem. Zentr. 1929, II, 112. F. P. 699217; abst. C. A. 1931, **25**, 3482. D. R. P. 483999; abst. C. A. 1930, **24**, 961; Chem. Zentr. 1930, I, 146. Can. P. 304212. M. Hagedorn and E. Gühring (D. R. P. 516882; abst. C. A. 1931, **25**, 3167) purify cellulose laurate dissolved in chlorbenzene, pyridine or other appropriate solvent, by means of steam at 120°, which precipitates the ester as a white flocculent powder, easily separated by filtering or centrifugalization.

are heated 3 hrs. on the steam-bath with 700 cc. chlorbenzene, 400 cc. naphthenic acid chloride (b. pt. 95-120° at 12 mm. pressure) and 200 cc. *a*-picoline at 80-90°. The insoluble ester formed is solubilized by a further heating at 135° for 20 min. Precipitated by acetone and purified by extraction with methyl alcohol. Soluble in benzene, methylene chloride (dichlormethane), chloroform, ether and ethyl acetate, and swells strongly in benzine.

(c) *Cellulose Butyro-ricinoleate (Ricinoleo-butyrate).* Into a mixture of 700 cc. butyryl chloride, 350 cc. ricinoleic acid chloride and 550 cc. pyridine bases, are introduced 100 gms. cellulose in the form of wadding. The mixture is maintained at 85-90° for 12 hrs. In order to convert the insoluble ester into soluble form, there are added to the mixture 100 cc. butyl chloride and heating continued 1 hr. at 135°. The ester formed is precipitated by addition of ethyl alcohol and purified by extraction with methyl alcohol. Soluble in aromatic hydrocarbons and in halogenated aliphatic hydrocarbons.

(d) *Cellulose Lauro-naphthenate (Naphtheno-laurate).* Into a mixture of 409 gms. lauryl chloride, 265 gms. commercial pyridine bases and 2300 cc. chlorbenzene, are added 100 gms. cotton, the whole being heated 12-20 hrs. at 90°. There are then added 270 gms. naphthenic acid chloride and 180 gms. pyridine bases, and the whole heated with stirring for 1-3 hrs. at 110-120°. The pasty solution thus produced is mixed with ethanol and the purified mass extracted with the same. The ester softens at above 50°, dissolves in benzene, toluene and xylene and in halogenated aliphatic hydrocarbons.

(e) *Cellulose Acetonaphthenate.* 100 parts acetone-insoluble cellulose acetate (36% combined acetic acid) are swollen in a heated mixture of 1500-2000 parts chlorbenzene and 120 parts commercial pyridine bases, and after addition of 400 parts naphthenic acid chloride, the mass is further esterified at 110-120° until the mixture has attained the desired solubility in chloroform and in benzene. It is precipitated by alcohol.

(f) *Cellulose Acetopalmitate.* 100 gms. linters are impregnated with a mixture of 1180 cc. chlorbenzene or xylene, and 235 gms. pyridine bases, then heated to 50° and mixed with 47 cc. acetyl chloride. After the mixture has been heated several hours on the steam-bath there are added 70 gms. pyridine bases and 424 gms. palmityl chloride, and heating continued 20 hrs. on the water-bath. In order to convert into soluble form, the reaction mixture is heated at 120°, and the ester then isolated. It is soluble as in (c).

(g) *Cellulose Lauro-phenylacetate.* (Laurate- phenylacetate). To a mixture of 2500 cc. xylene and 513 cc. pyridine bases is added a mixture of 1083 cc. lauryl chloride and 253 cc. phenylacetic acid chloride (phenylacetyl chloride). Into this liquid, heated to 80°, are introduced 100 gms. linters and the whole kept at 130° for 2 hrs. It is then poured into methyl alcohol and extracted 4 times with boiling methyl alcohol. The ester is soluble as in (c) above.

(h) 100 gms. linters are introduced into a mixture of 1500 cc. chlorbenzene and 400 cc. distilled lauryl chloride and 800 cc. whale oil acid chloride. Whale oil is composed primarily of palmitic, palmitoleic, stearic and oleic acids. The mixture is heated to boiling for 3 hrs. in an oil-bath at 135°. The combined ester formed is soluble as in (c).

(9) Cyclohexanecarboxylic acid may be substituted for phenylacetic acid, double esters as cellulose lauro-cyclohexanecarboxylate being produced.

(10) Esters as cellulose oleo-naphthenate (naphthenate-oleate, or[1] starch naphthenate-oleate-stearate may like-

1. I. G. Farbenindustrie, E. P. 318967; abst. C. A. 1930, **24**, 2469. D.R.P. 539470. To increase the solubility of the higher fatty acid cellulose esters (F. P. 644636; abst. C. A. 1929, **23**, 2033) they are heated in a liquid medium to a high temperature with acids, acid anhydrides or salts of strong acids with feeble bases. Thus, cellulose tristearate in tetrachlorethane, when heated to 145° with the addition of trichloracetic acid or toluene with ferric chloride at 90-100°, becomes soluble in benzene, chloroform and tetrachlormethane. Similarly, cellulose dipalmitate is heated in benzene with the addition of aluminum

wise be produced, as indicated in the following four examples:

(a) Into a mixture of 180 gms. technical cocoanut oil acid purified through vacuum distillation, 64 gms. pyridine bases and 700 cc. chlorbenzene, there are introduced 40 gms. cotton, the mass being then heated 6 hrs. at 90-100°. The insoluble cellulose ester first formed gradually goes into solution, and as soon as the desired solubility is reached, is precipitated by alcohol, washed and dried. The ester is soluble in benzene, toluene and xylene, and contains 80% fatty acid in combination with the cellulose.

(b) 50 gms. cotton are placed in a mixture of 180 gms. distilled stearyl chloride, 46 gms. technical pyridine bases and 500 cc. chlorbenzene and heated 18 hrs. at 80-100°. There results a thin solution of a cellulose monostearate, which is precipitated with ethyl alcohol and purified. The ester dissolves in aromatic hydrocarbons and haloid aliphatic hydrocarbons, and contains 65% stearic acid in ester form.

(c) A mixture of 280 gms. distilled lauryl chloride, 88 gms. pyridine and 600 cc. chlorbenzene is heated with 40 gms. wood pulp 12 hrs. at 90-100°, then heated to the boiling point of the chlorbenzene until the solubility required has been reached. After about 1 hr. the ester has completely gone into solution. About 84% lauric acid in chemical combination.

(d) 20 gms. starch are placed in a mixture of 120 gms. lauryl chloride, 39 gms. pyridine and 300 cc. chlorbenzene, heated 12-15 hrs. at 90-100° while stirring, the starch laurate being isolated through precipitation with ethyl alcohol, purification and drying. Soluble in the solvents mentioned in (b).

(11) By shaking the fatty acid chloride with pyri-

chloride or zinc chloride or benzenesulfonic acid. It is stated that the resistance to acids of these esters (F. P. 668048) is increased by chlorinating them suspended in a neutral medium, as the formation of cellulose chlortrilaurate by treatment of cellulose laurate in benzene with phosphorous pentachloride.

dine bases at 30°, then adding cellulose and chlorbenzene and heating 0.5-1 hr. at 120-130°, bodies like cellulose laurate, cellulose naphthenate or cellulose phenylacetate[1] are produced, being soluble in the usual organic solvents except acetone and the aliphatic alcohols.

(12) If the carbohydrate is previously swelled by treatment with alkali hydroxide solutions of at least 30%, soaked with water and one or more halides of higher fatty acids, the cellulose esters thus produced, as cellulose stearate, laurate or oleate, or the cocoanut fatty acid ester of agar-agar, become soluble in the usual organic reagents[2].

(13) In the formation of starch esters, as the palmitate, stearate and undecylenate, unmodified starch is treated with the chloride of the fatty acid in the presence of a tertiary base and a diluent[3], the reaction mixture being heated for some time at the boiling point of the diluent, which may be benzene, chloroform or toluene. The esters formed are odorless and non-inflammable, and soluble in benzene, toluene, xylene and other solvents.

Somewhat similar to the above process is the method of P. Berthon[4], the starch esters formed being precipitated by alcohol, washed and dried at a low temperature. These esters are suitable for film formation. If 100 gms. dinitrocellulose (11.3% N) be dissolved in 200 gms. pyridine, and there is added 300 gms. lauryl chloride dissolved in 300 gms. toluene, and the mixture heated 0.5-1 hr. at 40-45°, a starch lauryl-dinitrocellulose results of diminished inflammability and wide solubility[5].

It has been found[6] that an organic acid anhydride will

1. I. G. Farbenindustrie, E. P. 327165; abst. C. A. 1930, **24**, 5043; J. S. C. I. 1930, **49**, 602-B.
2. *Ibid.* E. P. 353193; abst. J. S. C. I. 1931, **50**, 1089-B. F. P. 668686; abst. C. A. 1930, **24**, 1650. D. R. P. 515109; abst. C. A. 1931, **25**, 1671.
3. *Ibid.* D. R. P. 484242; Addn. to D. R. P. 483080; abst. C. A. 1930, **24**, 962.
4. U. S. P. 1651366; abst. C. A. 1928, **22**, 881.
5. Soc. de Stearinerie et Savonnerie de Lyon, F. P. 581160.
6. Kodak, Ltd., H. Clarke, C. Malm and R. Stinchfield, E. P. 287880; abst. C. A. 1929, **23**, 512; J. S. C. I. 1930, **49**, 279-B; Chem. Zentr. 1928, II, 304; Br. Plastics, 1930, **1**, 498; Plastics, 1929, **5**, 334.

behave as an impeller in causing an organic acid, containing a higher number of carbon atoms in the molecule than is contained in the molecule of the acid corresponding with the anhydride, to esterify with cellulose. The method is especially applicable for the preparation of cellulose acetopropionate, stearopalmitate, acetopalmitate, butyromethoxyl-benzoate, and acetopalmito-stearate. The method may also be applied to cellulose ethers still containing esterifiable hydroxyls.

Uses of Cellulose Esters of Higher Fatty Acids. Cellulose laurate, elaidate, acetostearate, and similar esters are indicated for plastics and molded or otherwise shaped masses[1], the ester being first ground to a fine powder, a plasticizing agent added if desired, and the mass submitted to combined heat and pressure. Cellulose laurate with a solvent as chlorbenzene or benzene[2] and a resin as dammar, with or without fillers as talc or lithopone, is said to make an excellent plastic for billiard balls, poker chips and similar articles.

For the coating of surfaces as a varnish or enamel[3], 10 parts cellulose dilaurate and 8 parts gutta percha are dissolved in a mixture of benzene 30, xylene 30 and chlorbenzene 20. The gutta percha may be substituted by a suitable resin. Or, 8 parts cellulose monoacetate-distearate with 4 parts rubber are dissolved in a mixture of methylene chloride 50, chlorbenzene 28 and benzene 10. They are best applied with a brush and are nonhygroscopic and free from blushing.

As an anti-rust paint the cellulose higher fatty acid esters as cellulose trilaurate appear to be indicated[4] on

1. I. G. Farbenindustrie, E. P. 289063; abst. C. A. 1929, **23**, 704; Br. Plastics, 1930, **1**, 447; J. S. C. I. 1930, **49**, 185-B. F. P. 648154; abst. C. A. 1929, **23**, 2822. F. P. 35906, Addn. to F. P. 648154; abst. C. A. 1930, **24**, 4159.
2. *Ibid.* E. P. 326952; abst. C. A. 1930, **24**, 4932; Chem. Zentr. 1931, I, 1859; J. S. C. I. 1930, **49**, 452-B. Can. P. 304211.
3. *Ibid.* E. P. 317987; abst. J. S. C. I. 1929, **48**, 863-B; Br. Plastics, 1929, **1**, 234. D. R. P. 542633; abst. C. A. 1932, **26**, 3345.
4. *Ibid.* F. P. 667205.

account of the acid portion forming an insoluble compound with the metal upon dissociation. Cellulose trilaurate dissolved in a mixture of benzene and xylene is applied, naphthenic acids being added in relatively small amounts[1]. As a plastic or mastic[2] cellulose laurate or acetolaurate has been advocated, combined with natural or synthetic resins, dissolved in the aromatic hydrocarbons. Cellulose trilaurate or cellulose naphthenate, alone or admixed[3], have been described as desirable for the fabrication of shaped objects, being rolled or calendered at about 70° and then shaped under high pressure as by hydraulic extrusion. The preliminary rolling treatment increases the elasticity of the material, and permits of shaping and bending without decrease in pliancy.

In the production of threads by the viscose process[4], the spinning solution comprises the usual cellulose xanthate and a xanthate of a water-insoluble higher alcohol, as lauryl-, stearyl- or oleyl-xanthate. The threads are said to be softer and more pliable, and to give higher wet strength test. As an impregnation mass, there has been brought forward cellulose trilaurate or laurate of starch[5], especially desirable for wood impregnation. Air is exhausted from the wood, and a 10% solution of the ester in methylene chloride or chloroform, introduced under pressure.

In the insulation of cables[6], cellulose butyro-laurate, swollen in transformer oil or propylnaphthalene is applied in alternate layers with porous non-swelling materials, the composite coating being then subjected to a swelling treatment. As a rust-proof coating[7], cellulose trilaurate in

1. I. G. Farbenindustrie, Can. P. 293807.
2. *Ibid.* F. P. 671053; abst. C. A. 1930, **24**, 1947.
3. *Ibid.* E. P. 315275; abst. C. A. 1930, **24**, 1739. F. P. 678254; abst. C. A. 1930, **24**, 3646.
4. *Ibid.* E. P. 365982; abst. J. S. C. I. 1932, **51**, 336-B.
5. *Ibid.* F. P. 661435; abst. C. A. 1930, **24**, 483.
6. *Ibid.* E. P. 367817; abst. J. S. C. I. 1932, **51**, 518-B.
7. I. G. Farbenindustrie, H. Schladebach and H. Haehle, D. R. P. 542925; abst. C. A. 1932, **26**, 3125. Holl. P. 24895; abst. Chem. Zentr. 1932, I, 2101.

conjunction with drying oils, pigments and softening agents is recommended on account of the high permanency of the cellulose laurate to normal atmospheric influences.

Benzine or other organic liquids containing water in suspension[1] may be dried by treatment with cellulose stearate, palmitate or laurate. The ester must be insoluble in the organic liquid, and may be used in such a form that the organic liquid may filter through it. Textiles such as cotton, artificial silk and wool are rendered water-repellent by a superficial esterification with stearic or palmitic acid, under such mild conditions that no NaOH and little condensing agent is required[2]. The superficial stearated or palmitated cellulose is neutral and of high stability.

In the production of laminated or safety glass cellulose laurate or butyrolaurate has been advocated[3], constituting the middle layer between the glass sheets. These esters are fast to light and unaffected by water, and permit of very clear solutions being obtained in filtrations of the cellulose ester dissolved in benzene or toluene. Adhesion may be increased by the addition of polymerized vinyl acetate, and softness by the use of resorcinol monoacetate. If it is desired to impart a tackiness to the laurate layer, a proportion of cellulose naphthenate with vinyl acetate and resin may be used spread on the glass surface, and the two surfaces contacted with the cellulose laurate film.

Cellulose Glycollic Acid. Cellulose Glycollate. In 1921 the Deutsche Celluloid Fabrik[4] described the treatment of

1. W. Koreska, E. P. 350976; abst. Chem. Zentr. 1931, II, 2821. Aust. P. 120875; abst. C. A. 1931, **25**, 2436; Chem. Zentr. 1931, I, 2149.

2. A. Nathansohn, E. P. 355256; abst. J. S. C. I. 1931, **50**, 1047-B; Textile Mfr. 1932, **51**, 77.

3. I. G. Farbenindustrie, E. P. 315667; abst. Brit. Plastics, 1930, **2**, 229. F. P. 678320; abst. C. A. 1930, **24**, 3620. For production of antifouling paint containing cellulose palmitate, see E. P. 1598, 1912; 1600, 1912. F. P. 453393. D. R. P. 274875. Belg. P. 252906. Holl. P. 1380. Swed. P. 40613. Swiss P. 63580, 63821.

4. E. P. 138116. D. R. P. 332203. Their method of procedure is indicated in the following two examples:

a. 10 gms. cellulose are moistened with water and mercerized 2 hrs. with 30% alcoholic NaOH solution. After removal of excess of alkali, a solution of 10 gms. monochloracetic acid in 5 cc. water is slowly introduced and the mixture allowed to stand 36 hrs. at room

alkalicellulose with chloracetic acid or its homologues in the presence of alkali hydroxides to produce esters which they designated as cellulose acetic acid (see p. 449, n. 1), but more appropriately are to be termed cellulose hydroacetic acid (glycollic acid). The product obtained was a white, fibrous substance, insoluble in water but soluble in alkaline solutions, the alkali salts, however, being soluble in water to viscous solutions, suitable as substitutes for gelatin. By the use of chlorpropionic acid, cellulose lactic acid results. The conclusion that the product of chloracetic acid or sodium chloracetate upon modified cellulose is celluloseglycollic acid, that is an ether-acid, is based upon the analogous reaction between sodium ethylate and chloracetic acid in which ethylglycollic acid is formed, the reaction between cellulose and chloracetic acid being formulated upon one molecule alkalicellulose with 1 mol. chloracetic acid, giving 1 mol. celluloseglycollic acid and 1 mol. NaCl.

The action of chloracetyl chloride upon cellulose has been examined by W. Barnett[1], who advances the opinion that in addition to degradation and decomposition products of cellulose (as cellobiose hepta-acetate), a glycollic ester of cellulose is formed, the initial reaction between chloracetylchloride and cellulose in the presence of pyridine giv-

temperature. Excess of alkali is neutralized, and the solution poured into alcohol, where a white, flocculent precipitate forms, readily filterable.

b. 200 gms. air-dry mercerized cellulose are moistened with 1000 gms. 20% NaOH solution, and allowed to stand 2 hrs. Then 345 gms. monochloracetic acid in the form of sodium salt are added suspended in 440 cc. alcohol, and the mixture kneaded 1 hr. As soon as the product becomes entirely water-soluble, lye is pressed off, and the product washed with 90% alcohol to remove salts.

1. J. S. C. I. 1921, **40**, 253; abst. Bull. Soc. Chim. 1922, **32**, 250. For preparation of monochloracetic acid, see C. Torres and L. Socias, Anales soc. espan. fis. quim. 1930, **28**, 490. H. Brueckner, Zts. ang. Chem. 1928, **41**, 226. D. R. P. 506280. J. Marques, Quimica e industria, **1**, 59; Chem. Zentr. 1924, II, 2159. O. Magidson, I. Zilberg and N. Preobrazhenskii, J. Chem. Ind. Moscow, 1928, **5**, 58. H. Doughty and A. Black, J. A. C. S. 1925, **47**, 1091. For utilization of chloracetic acid waste liquors, consult W. Calcott, U. S. P. 1547201. For acetic anhydride manufacture, see C. Strosacker and C. Schwegler, U. S. P. 1713104. The I. G. Farbenindustrie (E. P. 312915) add a halogen fatty acid to the viscose precipitating bath to improve tensile strength, extensibility and luster of filaments.

ing a chloracetyl ester, which, reacting with water forms cellulose glycollate[1].

I. Sakurada[2] prepares celluloseglycollic acid best by soaking cellulose in 20% NaOH solution and then treating with concentrated sodium monochloracetate solution, in this way obtaining a sodium salt soluble in water, but precipitated by acetone or alcohol. Mineral acids precipitate the free acid in a finely-divided form, flocculated by alcohol. Analysis indicated one glycollic acid residue per C_6 cellulose could be introduced. Celluloseglycollic acid is not hydrolyzed by heating with acid or alkali.

In a study of ethers of polysaccharides with oxy-acids, J. Chowdhury[3] found that upon treatment of alkalicellulose with chloracetic acid and alkali, excess of NaOH is required to cause the reaction to run smoothly, and that when the reaction mixture is neutral or slightly acid, no water-soluble product was produced, even when the time and temperature was varied. The following generalizations were established by him: Differences between using 30% alcoholic NaOH solution (50:50) and aqueous NaOH solution with regard to yield is very small. With increasing

1. W. Heintz, Monatsber. 1860, 26; Ann. 1860, **58**, 247; J. Prakt. Chem. 1860, **79**, 233; Zts. Gesammt. Naturw. 1860, **15**, 221; Pogg. Ann. 1860, **109**, 331.

2. Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 96; abst. J. S. C. I. 1929, **48**, 430-A. He found (Cellulosechem. 1928, **9**, 86; J. S. C. I. Japan, Suppl. **31**, 190) that 0.5 equivalents of chloracetic acid, when allowed to act for a day upon cellulose which has previously been soaked in 40-50% NaOH solution, and pressed, the free celluloseglycollic acid may be precipitated therefrom. The acid is not hydrolyzed by boiling acids and alkalis. The sodium salt may be salted out by means of ammonium chloride and sodium chloride. Otherwise it is insoluble. He also demonstrated (Cellulosechem. 1929, **10**, 145; abst. Zts. ang. Chem. 1929, **42**, 640) that when monochloracetic acid is allowed to react upon alkalicellulose at room temperature and the reaction product dissolved in dilute NaOH, then by addition of alcohol, sodium celluloseglycollate separates. It is soluble in water, more so in alkaline solutions. From 5-10% NaOH solutions celluloseglycollic acid transparent and tenacious threads and films may be obtained. He established the product as a compound of cellulose with a carboxyl group. At room temperature the acid is readily transformed into a soluble compound, which is similar in structure and properties to viscose, and with which it may be mixed in any proportion.

3. Biochem. Zts. 1924, **148**, 76; abst. C. A. 1925, **19**, 640; J. C. S. 1924, **126**, i, 1029; Chem. Zentr. 1924, II, 622.

NaOH concentration the yield rises. The yield as well as the content of glycollic acid increases when the ratio of chloracetic acid to NaOH solution becomes greater than the ratio 3:4, a higher chloracetic acid content having but little influence upon the yield and sodium content. Temperature has no influence upon the reaction, and concentrated alkali is more favorable in yield of ester than is dilute alkali. It has also been demonstrated that the mercerization and action of chloracetic acid may proceed simultaneously, and not by a two-stage process.

In a series of seven different patents issued to L. Lilienfeld, the methods of manufacture and technical indications of these cellulose derivatives have been exhaustively covered. He superficially or incompletely "glycollates" cellulose in the form of fabrics[1] with a monohalogen fatty acid or salt (as sodium glycollate) in the presence of an alkali, the goods being first treated in the spun or woven condition with 20-40% NaOH solution, then squeezed until the fabric has increased by 2.5-3 times its original weight. Sodium monochloracetate is then added, the goods kept at 50-60° for a length of time depending upon the depth of effect desired. By using a thickening medium as British gum, differential printed and pattern effects may be produced, or the thickened product may be used as a size, cement, or thickening agent for pigments[2]. These cellulose derivatives may also be produced by carrying out the conversion of cellulose into glycollic ester without the use of alcohol[3], or with not more than 20% as much alcohol as water. Monochloracetic acid, *a*-brompropionic acid, bromsuccinic acid and *a*-brom*iso*butyric acid give cellulose glycollate, lac-

1. E. P. 231803; abst. C. A. 1925, **19**, 3600; J. S. C. I. 1925, **44**, 709-B; Chem. Zentr. 1926, I, 782. Aust. P. 105039.
2. E. P. 231805; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 985-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, I, 796. Aust. P. 122076.
3. E. P. 231809; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 914-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, I, 275. D. R. P. 516461; abst. C. A. 1931, **25**, 1993. U. S. P. 1682292; abst. C. A. 1928, **22**, 3988; J. S. C. I. 1928, **47**, 744-B.

tate, malate (hydroxysuccinate) and *a*-hydroxy*iso*butyrate (acetonate, dimethyloxalate)[1].

The use of a cellulose hydroxy-paraffin monocarboxylic acid (cellulose glycollic acid, cellulose lactic acid)[2] insoluble in hot or cold water, but soluble in aqueous alkalis, is advocated for the formation of films, filaments and plastic masses, on account of their chemical resistance and indifference, not changing appreciably on boiling for several hours with lye up to 20% strength; stable both in the solid and dissolved state; are colorless as well as their solutions; and even in the crude reaction mixture obtained in their preparation, contain no by-products which render purification difficult. Furthermore, they are of a high degree of purity when isolated from the reaction mixture, and easily precipitated in the form of technical articles.

Some of their indicated uses are as follows:

Films. 100 parts celluloseglycollic acid or cellulose-lactic acid, insoluble in water but soluble in dilute alkalis, are dissolved while kneading or stirring in 900-1200 parts NaOH solution of 5-8%, the solution, after filtering if necessary, being distributed in a layer from a hopper and coagulated by 10-20% sulfuric acid, 25% acetic acid, 30% ammonium chloride solution, 20% tannin, or 40% formaldehyde solution, or by the usual viscose precipitating bath. The solidified film is washed with water and dried. Flexibility may be increased by incorporating therein 10% glycerol.

Artificial Filaments. A solution as in Ex. 1 is forced through fine orifices into a coagulating or setting bath, washed with water and dried. The filament may be toughened by treatment with formaldehyde or other toughening agent. Filaments may also be obtained by mixing viscose

1. U. S. P. 1682294; abst. C. A. 1928, **22**, 3988; J. S. C. I. 1928, **47**, 744-B. Aust. P. 61132. E. P. 231810; abst. J. S. C. I. 1925, **44**, 914-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, I, 540.

2. E. P. 231811; abst. J. S. C. I. 1925, **44**, 914-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, I, 275. U. S. P. 1682293; abst. C. A. 1928, **22**, 3988. D. R. P. 535393; abst. C. A. 1932, **26**, 1120.

ripened to the optimum point for filament formation with celluloseglycollic acid, and treated as in Ex. I, the same precipitant being equally applicable to both. This filament requires an additional treatment with sodium sulfide or other desulfurizing agent and a bleaching treatment.

Textile Finishes. Cotton or other woven fabric is coated with a unitary or plurality of celluloseglycollic acid layers. After drying between each coat, and preferably also steaming after the last or top coat, the cloth is led into a precipitating bath, washed and dried, all under tension.

Textile Printing. 100 parts celluloseglycollic acid, mica 6-10, or lampblack 4 or zinc oxide 8-10 are printed with suitable printing rollers on cotton material, the printed fabric in the dry condition being then treated with a precipitating solution to set the deposited layer.

Book Cloth. Porous textile material as calico is provided with one or more coatings of celluloseglycollic acid or cellulose lactic acid until the pores of the textile are completely filled and the deposited solution is firmly anchored in the interstices of the cloth. The material is then calendered and embossed. Pigments, lakes and dyes may be incorporated, according to the methods used in the pyroxylin artificial leather industry.

H. Dreyfus[1] prepares derivatives of hydroxy-aliphatic acids by treating cellulose with anhydrides of glycollic, lactic or hydracrylic acids which may be prepared, for instance, by treating the sodium or potassium salt of the respective acid with thionyl chloride. Mixed esters may be prepared by employing another anhydride as acetic anhydride in addition to the hydroxyaliphatic anhydride, producing, for example, cellulose aceto-glycollate, aceto-lactate, aceto-hydracrylate, in addition to the formation of cellulose glycollate, lactate and hydracrylate.

1. E. P. 316160; abst. C. A. 1930, **24**, 1739; J. S. C. I. 1929, **48**, 848-B. F. P. 672235; abst. C. A. 1930, **24**, 2290.

Or[1], cellulose glycollic acid or cellulose glycollate still containing free hydroxyls in the cellulose may be etherified to produce a methylcellulose glycollate (an ether) or an ester of celluloseglycollic acid, i.e. methylcellulose glycollate. The following example is illustrative:

162 parts cellulose are treated with 300 parts 50% NaOH solution, kneaded for 2 hrs., during which period a further 180 parts powdered NaOH are added, and then 200 chloracetic acid added, the temperature rising to 35-40°. After about 6 hrs. further quantities of caustic soda and chloracetic acid are worked in (250 NaOH, 200-300 chloracetic acid), this addition repeated once more and after another 6 hrs. during which the temperature rises to 50-55°, the cellulose glycollate is precipitated by aqueous HCl and alcohol. The precipitated product is then cautiously washed with hot aqueous alcohol. To this product are added 200-300 parts 50% NaOH solution and 80-100 parts powdered NaOH, after which 500 parts methyl sulfate are added gradually, and the mass kneaded. A higher etherification results upon a further addition of 80-100 parts powdered NaOH and 200-300 parts methyl sulfate. The finished product may be thoroughly washed with water to remove products of reaction, and may then be dissolved in an organic solvent as acetone, acetic acid or chloracetic acid. By the use of ethyl sulfate, an ethylcellulose glycollate results.

H. Dreyfus[2] prepares cellulose glycollate and cellulose glycollic acid substitution compounds as indicated by the following details:

1. Celluloseglycollic acid or oxyethylcellulose or other oxyalkylated cellulose[3] is dissolved or suspended in 10 times its weight of benzene and treated with 1.25 times its weight of thionyl chloride in the case of an ether containing

1. H. Dreyfus, E. P. 343521; abst. C. A. 1931, **25**, 5557; J. S. C. I. 1931, **50**, 480-B; Silk J. 1931, **8**, #85, 54; Brit. Plastics, 1931, **3**, #28, 63. F. P. 703650; abst. C. A. 1931, **25**, 4705.
2. E. P. 344529; abst. C. A. 1932, **26**, 304.
3. See E. P. 166767, 277721, 343521.

2.5-3 ether groups, or a correspondingly smaller quantity with a lower ether. The mixture is at first gently warmed, and maintained at 25-35°. After 20-30 min. the excess of thionyl chloride and benzene is removed under vacuum, and the cellulose derivatives cautiously washed with ligroin.

2. Cellulose malonate, phthalate, malate, or maleate, obtained by the action of the corresponding acid on cellulose in presence of chloracetic anhydride, is treated with thionyl chloride as in Ex. 1.

Cellulose derivatives containing one or more free OH groups may be esterified or etherified with a compound containing the cyanogen group[1]. The products may be converted by reduction or hydration into other cellulose derivatives containing nitrogen. Appropriate agents include chloracetonitrile, cyanoacetyl chloride, *A*- or *B*-chlorpropionitrile or their homologues, the products formed having affinity for wool dyes. According to E. Correns[2] new cellulose derivatives result from the treatment of cellulose or its conversion products with chloracetic anhydride and a higher homologue of acetic acid in the presence of acetic anhydride and its higher homologues. The solubility properties of the esters may be varied by changing the proportion of acetic anhydride in the mixture. The formation of cellulose aceto-glycollate, propiono-glycollate, and butyro-glycollate are examples.

Cellulose Oxalate. In 1911, J. Briggs[3] prepared oxalic esters of cellulose by heating cotton saturated with oxalic acid. The esterification, however, is represented by only about 1 mol. oxalic acid to a C_{60} cellulose, and hence the solubility of the ester formed was very inferior.

G. v. Frank and W. Caro[4] have found that the more recent practice of esterifying in the presence of a chloride of a dibasic acid, as oxalyl chloride, is not suitable for the

1. H. Dreyfus, F. P. 704872; abst. C. A. 1931, **25**, 4705.
2. D. R. P. 550475; abst. C. A. 1932, **26**, 4173; Addn. to D. R. P. 516250; abst. C. A. 1931, **25**, 1993.
3. J. S. C. I. 1912, **31**, 520.
4. Ber. 1930, **63B**, 1532; abst. C. A. 1930, **24**, 4270.

preparation of cellulose oxalic esters on account of low solubility, but that if the Cl atom in oxalic chloride be replaced by an alcohol radical, thus producing an ester-half-chloride of oxalic acid, then in the presence of pyridine, cellulose may be esterified with comparative ease, forming products of excellent solubility, even when the operation is conducted at little above room temperature. The products formed appear to be mixed esters of oxalic acid with cellulose and alcohols, a tri-ester being obtained of the general formula $C_6H_7O_5(CO.COOR)_3$. If R is C_2H_5, for example, then cellulose tri-ethyl-oxalate results, and not tri-ethylcellulose oxalate, the latter a cellulose ether-ester.

Through the action of various ester-chlorides upon cellulose, have been obtained cellulose allyl-oxalate, *iso*-amyl-oxalate, menthyl-oxalate and cetyl-oxalate, with a degree of esterification lying between a di- and tri-ester. The properties of these bodies are determined by the ratio of cellulose residue to hydrocarbon residue; the resistance to tearing of the films decreases with increasing size of the alcohol radical, the plasticity increases, and at the same time the softening temperatures decrease. Likewise, the density falls, the solubility augments in non-polar solvents and falls in polar solvents, and the resistance to tearing in film form drops. With increasing size of hydrocarbon substituted group, the solubility in hydrocarbon-like solvents increases, with use of solvent mixtures in the direction of an increasing content of hydrocarbon, ether or chloroform in the mixture. Technically, these esters are of little present significance on account of their low resistance to hydrolyzing agents. Patent protection has been granted[1].

Cellulose Crotonate. Crotonylcellulose may be prepared by treating cellulose or its near transformation products with crotonic anhydride in the presence of esterification catalyst as sulfuric acid[2], with or without the presence

1. G. Frank, D. R. P. 499053; abst. C. A. 1930, **24**, 4156.
2. Soc. des Usines Chim. Rhone-Poulenc, F. P. 684550; abst. C. A. 1930, **24**, 5306.

of diluents as benzene or crotonic acid. A crotonic acid pre-treatment of the cellulose is said to be beneficial in the production of cellulose crotonate[1], and subsequently esterified with crotonic anhydride in the presence of the usual catalysts.

The use of hydrated or partially hydrated cellulose for the initial cellulosic material forms the basis for another method of cellulose crotonate formation[2], crotonic acid being heated together with the cellulose in the presence of chlorbenzene to lower the boiling point of the mixture. The manufacture of mixed esters as cellulose aceto-crotonate (crotonyl-acetate) or cellulose stearo-crotonate (crotonyl-stearate)[3] has been described, obtained by partially esterifying cellulose with one acid radical, and completing the esterification by the introduction of the other acid. In the formation of cellulose aceto-crotonate it is preferable to acetylate a partially crotonated cellulose. A phthalyl-crotonate (crotonyl-phthalate) has been described[4], preparable in an analogous manner.

In a manner similar to the partial hydration of the cellulose acetates, cellulose tricrotonate may be subjected to the saponifying action of hot water in the presence of catalysts as mineral acids, whereby the solubility range is materially increased[5].

Cellulose Acetocrotonate. The manufacture of mixed esters as cellulose acetocrotonate or cellulose acetocinna-

1. Soc. des Usines Chim. Rhone-Poulenc, E. P. 328588; abst. C. A. 1930, **24**, 5496; J. S. C. I. 1930, **49**, 655-B; Chem. Zentr. 1930, II, 1803. Can. P. 305507. F. P. 684759; abst. C. A. 1930, **24**, 5496.
2. Kodak-Pathe, F. P. 655803; abst. C. A. 1929, **23**, 4071.
3. H. Clarke and C. Malm, U. S. P. 1739210; abst. C. A. 1930, **24**, 962; J. S. C. I. 1930, **49**, 943-B; Brit. Plast. 1930, **2**, #18, 278.
4. R. Stinchfield, U. S. P. 1704306; abst. C. A. 1929, **23**, 2033; Plastics, 1930, **6**, #2, 91.
5. Soc. des Usines Chim. Rhone-Poulenc, F. P. 684759; abst. C. A. 1930, **24**, 5496. H. Gault and M. Angla (U. S. P. 1882554) have assigned to the same firm a method for the preparation of cellulose acetocrotonates by the treatment of hydrocellulose with acetic acid at ordinary temperature, followed by the crotonation with a mixture of crotonic acid, crotonic anhydride and zinc chloride. See D. R. P. 203642, 206950. U. S. P. 891218. F. P. 532146.

mate[1] may be effectuated with comparatively large and uniform yields, by proceeding as indicated in the following examples:

1. Tissue paper 5 is added to a mixture of crotonic acid 15, chloracetic anhydride 30 and magnesium perchlorate 0.5. The reaction mass is kept at 60-65° until the fibers nearly disappear which is in about 5 hrs. The cellulose crotonate obtained may be precipitated by water, washed with 50% methyl alcohol and dried, when it is solvable in acetone, chloroform, benzene or mixtures of these, and from which transparent films result. The ester may be directly acetylated into an acetocrotonate.

2. Tissue paper 5, crotonic acid and acetic anhydride 15 each, 0.2 parts copper perchlorate and 22 parts chloroform are admixed, warmed to 60-65° until a translucent dope is obtained, e.g. after about 65 hrs. The double ester is precipitated with methyl alcohol, washed with the same liquid and dried. Soluble in either acetone or chloroform.

3. 20 parts rayon fibers (regenerated cellulose) are mixed with 300 parts crotonic acid and 50 parts chlorbenzene, heated 48 hrs. at 155-157°. The rayon fibers which are now lower cellulose esters of crotonic acid are filtered off, washed with methyl alcohol, and acetylated in a mixture of acetic acid 30, acetic anhydride 20, zinc chloride 1 at 60-65° until a homogeneous dope is obtained. The cellulose acetocrotonate is then precipitated with water, washed and dried. It is soluble in chloroform or acetone.

Cellulose Furoate. The similarity of furoic acid[2] to benzoic acid, and the excellent properties of the cellulose benzoates, if their cost of production is not taken into consideration, has led to the preparation of cellulose esters of furoic acid (pyromucic acid)[3]. These esters may be prepared by a modified Schotten-Baumann reaction such as

1. H. Clarke and C. Malm, U. S. P. 1690620.
2. P. Frankland and F. Aston, J. C. S. 1901, **34**, 515. E. Baum, Ber. 1904, **37**, 2949.
3. 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.

has been employed in the preparation of cellulose benzoates[1], fibrous esters in 65% yield of theory and 2.5-3 furoate residues per C_6 unit being formed. Fibrous cellulose furoates are insoluble in all the usual cellulose ester solvents, one acid residue being much more firmly bound than are the other two.

Cellulose di- and tri-furoate may be prepared by treating standard cellulose with pyridine and furoyl chloride with tetrachlorethane by heating at about 100° for 3 hrs., filtered, washed with alcohol and chloroform, boiled in water and dried at 100°. Excess of pyridine causes the fibers to lose tensile strength, and to become dark brown in color; excess furoyl chloride diminishes the yield. When butyl acetate is used as diluent, a horn-like mass having a low saponification value, is obtained. Heating for longer periods of time causes decrease in yield of fibers, and increased amount of soluble portion. Cellulose furoate (cellulose pyromucate, cellulose furfurancarboxylate) is a white, odorless, light powder.

The I. G. Farbenindustrie[2] have described cellulose esters, which instead of substituting for the halides of cyclic substituted fatty acids and of alicyclic carboxylic acids[3], employ halides of saturated or unsaturated heterocyclic carboxylic acids or heterocyclic substituted fatty acids, as the carboxylic acids of furane (furoic or pyromucic acid), coumarone, thiophene, pyrrol, pyrrolidine, indole, piperidine, methylpiperidine, pyrazine, piperazine, methylpyridine, quinoline, *iso*quinoline, and their derivatives, corresponding acids being such as picolinic, nicotinic, *iso*nicotinic, methylpyridinecarboxylic, quinolinic and cinchomeronic acids.

The cellulose esters obtainable are said to possess the desirable properties of the aliphatic and dicarboxylic cellulose esters, those cellulose esters with nitrogen in the ring

1. C. Cross and E. Bevan, Ber. 1901, **34**, 1514; Chem. News, 1890, **61**, 87. D. R. P. 139669.
2. E. P. 347451; abst. C. A. 1932, **26**, 2862.
3. E. P. 283181, 305947.

forming salts with acids and addition products with halogen-alkyl groups. In the combinations obtained from esters of halogen hydrides, ethylsulfonic acid or methyl sulfate, the changed solubility is remarkable in that a much larger number of organic solvents shows a dissolving action upon these cellulose esters.

Cellulose Isonicotinate. As an example of carrying the invention into effect, 200 gms. cotton linters are covered with 4 liters anhydrous chlorbenzene, 1050 gms. isonicotinic acid prepared from the hydrochloride by removal of the acid radical, and 900 gms. pyridine are then added, and the mixture heated 3-5 hrs. at 105-115° while stirring. Cellulose isonicotinate is obtained in a mass softened by the action of chlorbenzene used, and can be redissolved in chloroform or pyridine after the chlorbenzene has been removed. The cellulose ester is soluble in chloroform, dichlormethane (methylene dichloride), tetrachlorethane, pyridine and glacial acetic acid, and becomes soluble in water upon addition of methyl iodide (iodomethane). Similarly, cellulose picolinate, cellulose nicotinate, cellulose methylpyridinecarboxylate, cellulose quinolinate, and cellulose cinchomeronate may be prepared. Some of these cellulose esters have pharmaceutical, bactericidal and narcotic properties.

Cellulose Isatoate. When cellulose or related substance is treated with isatoic anhydride (a solid melting at 233-240°), a compound containing the characteristic isatoic group is formed, which probably is a cellulose isatoate[1]. This ester may be diazotized and coupled with the usual components. When diazotized and coupled with *b*-naphthol an orange color is produced. Treatment of cellulose with *p*-sulfobenzeneazoisatoic anhydride (prepared by phosgenation of *p*-sulfobenzeneazoanthranilic acid), followed by diazotization and coupling with *b*-naphthol, gives a red.

1. I. G. Farbenindustrie and F. Gunther, D. R. P. 433147; abst. J. S. C. I. 1927, **46**, 215-B.

The Society of Chemical Industry[1] prepare a solution of 8 parts cellulose to 160 parts of a mixture of benzylpyridinium chloride and pyridine, and introduce at 110° 20 parts well dried isatoic anhydride, the mixture being then stirred at this temperature for 20 hrs., after which it is poured into considerable water. The product separates as a slowly solidifying yellowish mass, which is comminuted and dissolved in cold sulfuric acid of 5-10% strength, whereupon cellulose anthranilate (cellulose *o*-amidobenzoate) separates and is washed with water and dried. The cellulose ester thus obtained is insoluble in organic solvents, but dissolves in dilute aqueous mineral acids to solutions which are opaque and foam strongly. Such solutions may be diazotized and coupled with suitable components for producing azo-dyestuffs.

Cellulose Veratroate. Veratroyl-carboxylic acid, m. pt. 138°, has been produced by the oxidation of anethol, isoeugenolmethyl ether and isosafrol[2]. K. Freudenberg and W. Dürr[3] have described a veratroylcellulose (cellulose veratroate), containing 18.6% of methoxyl, and which absorbs 12.5% nitrogen dioxide almost without loss of methyl alcohol. So far as aware, it has no technical usefulness.

Cellulose Benzoate results from the action of benzoyl chloride on cellulose, preferably after modification to alkalicellulose, or the cellulose regenerated from viscose. C. Cross, E. Bevan and C. Beadle[4] and E. Baumann[5] have shown that the benzoates may be obtained by the above method, but of varying composition. Benzoates from hydrocellulose[6] or from "soluble starch"[7], or cellulose precipi-

1. E. P. 359249, Ex. 13.
2. Ber. 1891, **24**, 3488. 3. Ber. 1930, **63B**, 2713.
4. J. C. S. 1893, **26**, 837; Chem. News, 1890, **61**, 87. C. Cross, E. Bevan and R. Jenks, Ber. 1901, **34**, 2496.
5. Ber. 1886, **19**, 3218.
6. A. Girard, Compt. rend. 1875, **81**, 1105; abst. Chem. Zentr. 1876, 83; Jahr. Chem. 1875, 786; Bull. Soc. Chim. 1876, **26**, 190; J. C. S. 1876, **30**, 696.
7. H. Brown and G. Morris, J. C. S. 1889, **55**, 449; abst. Jahr. Chem. 1889, 2063; Mon. Sci. 1889, (4), **3**, 1284; Chem. Zentr. 1889, 124; Bull. Soc. Chim. 1889, **2**, 682.

tated from zinc chloride solutions[1] yield a higher benzoylation than does unmodified cellulose.

O. Hauser and H. Muschner[2] have been unable to corroborate the work of C. Cross and E. Bevan[3] in obtaining a structureless cellulose dibenzoate and a fibrous monobenzoate by the action of benzoyl chloride and NaOH on cellulose, attributable by J. Briggs[4] to steeping the cellulose first in benzoyl chloride, then with NaOH, whereas the reverse is the proper method. Z. Skraup[5] has shown that for maximum esterification, the ratio per hydroxyl in cellulose should be 7 NaOH and 5 benzoyl chloride. H. Ost and F. Klein[6], using finely chopped cotton, obtained a maximum yield of 218%, when using in 22% solution, 30 of NaOH and 22 benzoyl chloride per cellulose molecule.

The A. Wohl process of manufacture involves heating cellulose to 150° with benzoyl chloride in the presence of pyridine, and nitrobenzene as solvent[7]. By the action of benzoyl chloride in basic solution upon alkalicellulose[8], a tribenzoate was obtained, completely soluble in chloroform. A mixture of chlorine and sulfur dioxide has been advo-

1. C. Cross and E. Bevan, Chem. News, 1891, **63**, 66; abst. J. C. S. 1891, **60**, 890; Chem. Zentr. 1891, **62**, 620; Jahr. Chem. 1891, 2181.

2. Zts. ang. Chem. 1913, **26**, 137; J. S. C. I. 1913, **32**, 357; Chem. Zentr. 1913, I, 1412; Jour. Dyers and Col. 1913, **29**, 194; Kunst. 1913, **3**, 330; C. A. 1913, **7**, 2854; J. C. S. 1913, **104**, i, 363.

3. Ber. 1901, **34**, 1514; J. C. S. 1901, **80**, i, 452; Chem. Zentr. 1901, II, 94; Jahr. Chem. 1901, 891.

4. Zts. ang. Chem. 1913, **26**, 255; Chem. Zentr. 1913, I, 2110; Jour. Dyers Col. 1913, **29**, 194; Kunst. 1913, **3**, 330; C. A. 1913, **7**, 2855; J. S. C. I. 1913, **32**, 595; J. C. S. 1913, **104**, 594.

5. Monatsh. 1889, **10**, 389.

6. Zts. ang. Chem. 1913, **26**, 437; abst. J. S. C. I. 1913, **32**, 823; Kunst. 1913, **3**, 331; C. A. 1913, **7**, 3661; J. C. S. 1913, **104**, i, 1043; Chem. Zentr. 1913, II, 1293.

7. D. R. P. 139669; abst. Jahr. Chem. 1903, 1014; Chem. Ind. 1903, **26**, 167; Wag. Jahr. 1903, **49**, II, 418; Zts. ang. Chem. 1903, **16**, 285; Chem. Zentr. 1903, I, 744. See also D. R. P. 243581, 1908; abst. J. S. C. I. 1912, **31**, 381; C. A. 1912, **6**, 2316; Chem. Tech. Rep. 1912, **36**, 196; Wag. Jahr. 1912, II, 17; Zts. ang. Chem. 1912, **25**, 654; Chem. Ind. 1912, **35**, 190; Chem. Zentr. 1912, I, 695. E. P. 2527, 1912. See also Akt. Ges. f. Anilin-Fabrikation, E. P. 22237, 1911; abst. J. S. C. I. 1912, **31**, 379. F. P. 435507, 1911; abst. J. S. C. I. 1912, **31**, 329. Belg. P. 239564, 1911.

8. E. Knoevenagel and H. Busch, Cellulosechemie, 1922, **3**, 52; abst. Caout. et Gutta. 1923, **20**, 11751.

cated as catalyst in cellulose benzoylation[1]. Cellulose dibenzoate may be prepared by warming cellulose mercerized with 35% NaOH and aged for 24 hrs., with benzoyl chloride at 50-60° for 1-2 hrs.[2]. It gives a clear solution in chloroform or acetone. Cellulose monobenzoate may be nitrated to cellulose mononitrate-mononitrobenzoate, or dinitrate-mononitrobenzoate, both similar to the cellulose nitrates, but less hygroscopic and less soluble in ether-alcohol[3]. Cellulose mono-*p*-chlorbenzoate has been prepared. A relatively lower temperature may be employed in the benzoylation of cellulose[4], if the esterification is carried out in the presence of ββ′-dichlordiethyl ether. By esterifying with a mixture of acetyl chloride and benzoyl chloride, mixed cellulose acetobenzoates (benzoylacetates) may be formed.

The inflammability of cellulose benzoate may be diminished by brominating[5], forming a cellulose brombenzoate. Cellulose is said to benzoylate more readily when pretreated with dry, liquid ammonia[6].

Under the trade name of "Benzoale" has been patented an explosive[7] in which the brisant effect of the cellulose nitrate is toned down by the presence of other cellulose esters as benzoate. Cellulose benzoates have been proposed for the insulation of wire, protection of metal surfaces[8], as plastic bodies in conjunction with chloral and amyl lac-

1. W. Barnett, J. S. C. I. 1921, **40**, 61-T; abst. J. C. S. 1921, **120**, i, 308; Chim. et Ind. 1921, **6**, 771.
2. K. Atsuki and K. Shimoyama, Cellulose Ind. Tokyo, 1926, **2**, 336; abst. C. A. 1927, **21**, 4062.
3. M. Sendo and J. Kondo, Cellulose Ind. Tokyo, 1930, **6**, 150; abst. C. A. 1931, **25**, 1668.
4. C. Webber and C. Staud, U. S. P. 1831274; abst. C. A. 1932, **26**, 844.
5. H. Clarke, U. S. P. 1687060; abst. Plastics, 1929, **5**, 142. See E. Geinsperger, Monats. Chem. **26**, 1459.
6. W. Bonner, U. S. P. 1173336.
7. A. Luck, E. P. 24662, 1898; abst. J. S. C. I. 1900, **19**, 375. See Soc. D'Exploitation des Brevets Dolter, F. P. 375092; abst. J. S. C. I. 1907, **26**, 877.
8. E. Thomson and J. Callan, U. S. P. 695127, 1902; Reissue 11997, 1902. E. P. 2264, 1902; abst. J. S. C. I. 1903, **22**, 303.

tate[1], as a lacquer[2], and plastic body in conjunction with the phenol-aldehydes, and for the impregnation of cables[3].

The cellulose benzoates would be entensively employed in the arts were it not for the comparatively high cost of the acid radical (benzoic) in comparison with acetic acid.

Cellulose Phthalate may be prepared according to the method of H. Levey[4] by heating to 70° a mixture of 10 gms. modified cellulose, 30 phthalic anhydride and 2.5 fused zinc chloride containing a small amount of diethyl phthalate. After 24 hrs. heating, the ester is washed free from reactants and dried. The ester is insoluble in cold or boiling acetone, chloroform, ethyl acetate, benzene, carbon tetrachloride, toluene, pyridine, acetic acid, the xylenes, tetrachlorethane, aniline, ether, nitrobenzene or diethyl phthalate, alone or admixed with ethyl alcohol. By heating to 75° with zinc chloride in 50% acetic acid, the solubility is not increased. Amount of phthalic acid introduced is equal to 1 mol. per C_{48} cellulose.

R. Stinchfield has described mixed esters of phthalic acid with acetic, propionic, butyric, crotonic, lauric, palmitic or stearic acids, as cellulose acetophthalate[5], obtained by "inactivating" one of the carboxyl groups of phthalic acid by esterifying it, and causing the other carboxyl to react with the cellulose, using magnesium perchlorate as catalyst. The esters are soluble in acetone, chloroform, benzene or mixtures of them, insoluble in ligroin, ether or carbon tetrachloride.

1. C. Ellis, U. S. P. 999490; abst. J. S. C. I. 1911, **30**, 1051.
2. R. Grueter, U. S. P. 1195673. See Paint & Varnish Mfr. Assoc. Circ. No. 338, 1928, p. 657; abst. Plastics, 1929, **5**, 339. G. Druce, Rayon Record, 1930, **4**, 841. G. Kita, T. Mazume, T. Nagashima and I. Sakrada, Cellulosechemie, 1926, **7**, 125; abst. C. A. 1927, **21**, 1705; Can. Pulp and Paper Mag. 1927, **25**, 314.
3. W. Bonner, U. S. P. 1173337. See Societe Debauge, F. P. 453564.
4. Ind. Eng. Chem. 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.
5. U. S. P. 1704306; abst. C. A. 1929, **23**, 2033; Plastics, 1930, **6**, #2, 91.

A cellulose phthalyl-dinitrate has been described[1], obtained when an acetylcellulose, containing etherifiable OH groups, is treated with the chloride of an acid ester of a polybasic acid. Thus, a mixture of cellulose dinitrate, monobutyl phthalate, ethyl acetate and sulfuryl chloride, when allowed to react, the chloride of the acid ester is formed and reacts with the cellulose compound, forming cellulose phthalyl-dinitrate. When cellulose phthalate reacts with thionyl chloride dissolved in benzene at 25-35°, excess of reactants removed under vacuum, and precipitating, aminated cellulose ethers result[2].

It has been found that by the treatment of cellulose admixed with tertiary bases as pyridine and treated with phthalic anhydride cellulose compounds are produced having a strong affinity for basic dyestuffs[3]. If 15 parts cellulose are mixed with 100 parts pyridine and 10 parts phthalic anhydride, and allowed to stand for 4 hrs. at 60°, a white mass forms which is insoluble in dilute alkalis.

Cellulose phthalate may also be formed by introducing into a solution of 8 parts cellulose in 160 parts of a mixture of benzylpyridinium chloride and pyridine[4], 20 parts phthalic anhydride at 100°, the mixture being stirred for 1 hr. at 100-105°. The light yellowish brown mass thus obtained is poured into 1000 cc. water containing 5% pyridine, whereby the powder which at first separates becomes completely dissolved. By acidifying the solution, cellulose phthalate is precipitated out in the form of a feebly yellowish flocculent mass, which is suction filtered and washed with water. After drying, it is extracted with acetone, the cellulose phthalate remaining undissolved. It dissolves readily in weak alkalis as sodium carbonate or weak ammonia, and is freely soluble in aqueous pyridine. Insoluble in organic solvents as acetone, alcohol, tetrachlorethane or benzene.

1. Deutsche Celluloid Fabr., E. P. 355172; abst. J. S. C. I. 1931, **50**, 968-B. F. P. 709958.
2. H. Dreyfus, E. P. 344529; abst. J. S. C. I. 1931, **50**, 626-B. F. P. 704872.
3. Soc. Chem. Ind. Basle, Swiss P. 142173.
4. *Ibid.* E. P. 359249.

Cellulose Cinnamate. The tricinnamate, softening at 180° and becoming transparent at 200° in chloroform, is readily prepared from cellulose, cinnamyl chloride and pyridine in nitrobenzene, at 100-120°, and yields a cellulose tris(dibromhydrocinnamate)[1], decomposing about 210°. Of great thermal stability, it is hydrolyzed with difficulty. Partial hydrolysis by means of phenol or the chloracetic acids (particularly trichloracetic acid) yields secondary cinnamates, soluble in cold benzene or hot acetone. If these solutions are cooled, a portion of the material (20% if trichloracetic acid is used), separates as minute crystals. Purification of the crystalline and amorphous fractions leads to products of a similar degree of esterification and approximately the same specific rotation, but varying softening points and reducing powers.

Hydrolysis of crystalline cellulose cinnamate yields a product resembling Hess' cellulose *A*, insoluble in water and organic media, soluble in NaOH, and giving the Roentgen diagram of hydrocellulose. Cryoscopic experiments with cellulose cinnamate indicate the presence of a tetrosan. Reesterification of the di-cinnamate appears to result in the formation of the tri-cinnamic ester.

Where hydrated or partially hydrated cellulose is heated with cinnamic acid at a temperature below that at which harmful degradation takes place[2], cellulose 2.5-cinnamate is formed. Cellulose acetocinnamate and acetochlorcinnamate have been described[3].

Cellulose Mixed Esters. In attempts to raise or lower the melting point, increase the solubility range, and the solvent action of feeble plasticizing bodies upon cellulose acetate, primarily, and to a lesser degree other cellulose esters, double or mixed esters have been proposed in the hopes of introducing new and desirable technical properties.

1. G. v. Frank and H. Mendrzyk, Ber. 1930, **63**B, 875.
2. Kodak-Pathe, F. P. 655803; abst. C. A. 1929, **23**, 4071.
3. H. Clarke and C. Malm, U. S. P. 1698048. E. P. 304278. F. P. 653742.

C. Webber and C. Staud[1] have described double esters of acetic acid with tartaric, racemic, malic, glycollic, glyceric, pyruvic, α-ketobutyric, α-ketovaleric, α-ketocaproic, levulinic, toluic, benzoic, mandelic and cinnamic acids. Cellulose acetate containing less than 44.8% acetyl is utilized, and this ester is further esterified by treatment with the corresponding acid, extracted, washed to neutrality and dried. The double esters (cellulose aceto-mandelate for example) are soluble in chloroform, acetone, chloroform-alcohol (85:15) and mixtures of ethylene chloride and methyl alcohol.

They have also described the preparation of a series of mixed cellulose esters obtained by reacting upon cellulose formate, acetate, butyrate or benzoate incompletely esterified[2], with oxalic, glyceric, pyruvic, maleic, lactic, tartaric, and levulinic acids, the following example indicating the preferred formation of these 28 different cellulose mixed esters: 5 grams cellulose tribenzoate are dissolved in a solution containing 25 cc. pyruvic acid and 25 cc. ethylene chloride at 100° and digested 67 hrs. Upon precipitation in ether and washing with alcohol to neutrality, cellulose pyruvylbenzoate (benzopyruvate) is obtained, soluble in chloroform, ethylene chloride, ethylene chloride-chloroform, and insoluble in 1.4-dioxane, acetone, benzene and benzene-ethanol.

Cellulose acetopropionate and cellulose acetobutyrate may also be produced[3] when acetylcellulose (about 36% acetyl content) is propionated with a mixture of propionic acid, propionic anhydride and magnesium perchlorate trihydrate. These esters are soluble in ethylene chloride, acetone and ethyl acetate. Ethylene chloride and alcohol are

1. U. S. P. 1785466; abst. Plastics, 1931, **7**, 234; C. A. 1931, **25**, 592; J. S. C. I. 1931, **50**, 877-B. E. P. 338202; abst. C. A. 1931, **25**, 2289; J. S. C. I. 1931, **50**, 242-B; Br. Plastics, 1931, **2**, 529. Can. P. 312806; abst. C. A. 1931, **25**, 4401. Soc. Kodak Pathe, F. P. 687996, 690458; abst. C. A. 1931, **25**, 813, 1082.
2. U. S. P. 1861200; abst. C. A. 1932, **26**, 3919.
3. C. Staud and E. McLean, U. S. P. 1880515.

said to constitute a good solvent combination for film and filament formation.

Cellulose aceto-propionate results upon treating cellulose with chlorbenzene, pyridine bases, acetyl chloride and propionyl chloride[1], and aceto-butyrate and butyropropionate[2] in an analogous manner. Cellulose aceto-butyrate is also formed when cellulose, chloracetic acid and a mixture of acetic and butyric acids are allowed to react together[3]. Methylene chloride or ethylene chloride may be used as diluents and solvents in their manufacture[4]. If 400 gms. cellulose acetate (56% acetic acid) and 130 gms. butyric acid are heated together during 3 hrs. at low temperature in the presence of thionyl chloride[5], a cellulose butyrodiacetate is formed. Liquid sulfur dioxide is recommended for the preparation of cellulose aceto-butyrate[6], the inclusion of butyric anhydride in conjunction with butyric acid being recommended where the butyryl content is desired of a relatively high degree in comparison to the acetyl residue[7].

The use of zinc chloride as catalyzer in the formation of cellulose aceto-propionate, -butyrate or -valerate[8] is said to result in yields nearly theoretical. If the cellulose is pretreated with formic or acetic acids, no esterification results, but the cellulose is transformed into an unusually receptive state for further double esterification[9], especially for cellulose propionate and butyrate formation. If a maximum acetylation has been effected with the cellulose, the

1. I. G. Farbenindustrie, Can. P. 306968.
2. *Ibid.* F. P. 691031; abst. C. A. 1931, **25**, 1260. See also F. P. 668686; abst. C. A. 1930, **24**, 1650.
3. Soc. Des Brevets Etrangers Lefranc et Cie., F. P. 687169; abst. C. A. 1931, **25**, 813.
4. I. G. Farbenindustrie, E. P. 337366; abst. C. A. 1931, **25**, 2288; J. S. C. I. 1931, **50**, 197-B.
5. *Ibid.* F. P. 717623. Methods are described in the patent for the formation of cellulose acetocarbonate, acetochromate, acetobutyrosulfite and acetococinate.
6. *Ibid.* F. P. 664459; abst. C. A. 1930, **24**, 961.
7. Soc. des Usines Chim. Rhone-Poulenc, E. P. 321575; abst. C. A. 1930, **24**, 2882.
8. C. Ruzicka, E. P. 303432; abst. C. A. 1929, **23**, 4571.
9. H. Dreyfus, E. P. 325231; abst. C. A. 1930, **24**, 4156; Chem. Zentr. 1930, II, 2333; J. S. C. I. 1930, **49**, 414-B. See E. P. 325224; abst. J. S. C. I. 1930, **49**, 414-B. Ital. P. 276675.

ester may be subjected to a partial saponification or deacetylation treatment, and then further esterified by a radical different from acetic acid. Cellulose aceto-oleate has been made in this manner[1], chloracetic anhydride and oleic acid being employed.

Cellulose chlorstearate, chloracetate, aceto-palmitate and aceto-stearate[2] may be obtained by admixture of the respective anhydrides in desired proportions, esterifying in the presence of magnesium perchlorate, or[3], if it is desired to reduce the inflammability, chloracetic acid, chloracetic anhydride and *a*-bromstearic acid may be simultaneously esterified in the presence of magnesium perchlorate, a cellulose aceto-*a*-bromstearate resulting. Operating upon acetone-soluble cellulose acetate (36.6% acetyl) in the above indicated manner[4], cellulose, plus chlorine or bromine substituted butyric, valeric, caproic, heptylic, caprylic, pelargonic, lauric, myristic, palmitic, crotonic, cyclohexanecarboxylic, benzoic, *o*-methoxybenzoic, *o*-chlorbenzoic, acetylsalicylic, phenylacetic, cinnamic, or hydrocinnamic acids, forms the corresponding chlor or brom substituted double ester as cellulose aceto-dibromstearate, aceto-*a*-bromstearate, acetotetrachlorstearate, aceto-*a*-bromhexoate. In a similar manner have been prepared cellulose aceto-laurate, -myristate, -palmitate and stearate[5]. Cellulose aceto-*o*-chlorbenzoate, soluble in chloroform, insoluble in acetone, has also been synthesized[6].

1. H. Clarke and C. Malm, U. S. P. 1698048; abst. C. A. 1929, **23**, 1268.
2. *Ibid.* U. S. P. 1735159; abst. C. A. 1930, **24**, 723; Plastics, 1930, **6**, 336. See U. S. P. 1716422; abst. C. A. 1929, **23**, 3807. F. P. 667556.
3. *Ibid.* U. S. P. 1698049; abst. C. A. 1929, **23**, 1267; J. S. C. I. 1929, **48**, 594-B; Plastics, 1929, **5**, 512. F. P. 667557. E. P. 304279; abst. J. S. C. I. 1930, **49**, 655-B; Br. Plastics, 1930, **2**, 135.
4. *Ibid.* U. S. P. 1968048; abst. C. A. 1929, **23**, 1268; J. S. C. I. 1929, **48**, 594-B; Plastics, 1929, **5**, 573. E. P. 304278; abst. C. A. 1929, **23**, 4818. F. P. 653742; abst. C. A. 1929, **23**, 3807. See E. P. 287880; abst. C. A. 1929, **23**, 512.
5. *Ibid.* U. S. P. 1704282; abst. C. A. 1929, **23**, 2033; Plastics, 1930, **6**, 91.
6. *Ibid.* U. S. P. 1704283; abst. C. A. 1929, **23**, 2033; Plastics, 1929, **5**, 515.

When an arylcellulose as cellulose acetate is digested with an aliphatic or mono- or di-basic ester containing an OH group in the α-position, as lactic, tartaric, racemic, glycollic, glyceric or malic acids[1], the corresponding cellulose aceto-lactate, -tartrate, -racemate, -glycollate, -glycerate, or malate results. If the cellulose is previously treated with a tertiary organic base as dimethyl-α-hexylamine or methylpiperidine[2], double esters are readily formed where the corresponding chlorides, acids and anhydrides are brought in contact with the cellulose at elevated temperatures.

The I. G. Farbenindustrie[3] have given detailed directions for the preparation of cellulose phenylacetolaurate (laurophenylacetate), butyroricinoleate (ricinoleobutyrate), lauronaphthenate (naphthenolaurate), acetonaphthenate (naphthenoacetate), acetylpalmitate (palmitylacetate). Methods for the manufacture of cellulose acetostearate, ethylcellulose myristate and ethylcellulose benzoate have also been published[4], as has ethylcellulose silicate, and cellulose acetostearate[5].

By causing the esterification to take place in the presence of chloracetic acid (which does not enter into the cellulose esterification)[6], cellulose esters as aceto-propionate, acetobutyrate and propionobutyrate may be prepared. By esterifying in the presence of chlorbenzene or chlornaphthalene[7], mixed esters as cellulose acetopropionate and acetocrotonate result.

The Society of Chemical Industry[8] have described a method for mixed ester formation in which cellulose is dis-

1. Soc. Kodak Pathe, F. P. 690115; abst. C. A. 1931, **25**, 1082. See F. P. 688601; abst. C. A. 1931, **25**, 813.
2. H. Dreyfus, E. P. 325822; abst. C. A. 1930, **24**, 4156; J. S. C. I. 1930, **49**, 504-B. Ital. P. 278348.
3. E. P. 305947. See E. P. 284298, 292929, 297766.
4. I. G. Farbenindustrie, D. R. P. 533126, Addn. to D. R. P. 511208.
5. *Ibid.* F. P. 629861. See D. R. P. 332203. F. P. 581160.
6. *Ibid.* E. P. 285858. The products are soluble in benzene.
7. M. Hagedorn and O. Reichert, U. S. P. 1832381; abst. C. A. 1932, **26**, 1438.
8. E. P. 359249; abst. J. S. C. I. 1932, **51**, 224-B.

solved in the additive products of alkylating or aralkylating agents with heterocyclic tertiary bases, optionally in the presence of diluents, and given basic methods for the preparation of cellulose acetyl (or butyryl or benzoyl or acetylbenzoyl)-phthalate or -anthranilate, and also by the combination of the above eight mixed acid radicals with triphenylmethyl to form the corresponding cellulose ether-esters, as triphenylcellulose acetylbenzoylanthranilate[1].

Cyanogen Cellulose. When cyanogen chloride or bromide is allowed to act upon alkalicellulose, cellulose derivatives containing nitrogen are obtained, the cyanogen halide being previously dissolved in an indifferent solvent as ethyl ether or carbon tetrachloride. The use of such solvents is advisable, though not necessary, for it is possible to produce these derivatives by leading a cyanogen halide in the vapor phase over alkalicellulose. The reaction begins at about —10° and quickly rises by self-heating. The following two examples are self-explanatory[2]:

1. 20 parts cotton are treated at ordinary temperature with a mixture of alcohol 60, 60 of 33% NaOH and 30 of water for 0.5 hr. The alkalicellulose thus obtained is pressed off and treated with a solution of 6 parts of cyanogen bromide in 20 parts carbon tetrachloride. Spontaneous reaction ensues and after 30 min. the reaction product may be pressed off, rinsed, acidified, washed and dried. The product has a nitrogen content of 1.9%.

2. 10 parts of cotton are mercerized as in Ex. 1, and stirred, while cooling to about —10°, into 150 parts ether in which 2% cyanogen chloride has been dissolved. As soon as no further reaction takes place, the reaction product is washed and dried. Nitrogen content 1.7%.

Cellulose containing nitrogen chemically combined and

1. For resume of cellulose mixed esters, refer to Freitag, Kunst. 1932, **22**, 110.
2. J. Haller, U. S. P. 1813619; abst. C. A. 1931, **25**, 5287; J. S. C. I. 1932, **51**, 501-B.

unresponsive to direct-acting vat and acid dyestuffs[1] may be obtained as indicated in the following three examples:

1. The cellulose (sulfite cellulose or linters) is impregnated with 10% KOH solution, excess alkali removed by pressing, and then treated with a solution of cyanogen chloride in xylene 2 hrs. at 25-40° in presence of powdered chalk. On 10 parts cellulose, 3-5 parts cyanuric chloride are used. The amount of solvent required depends upon the type of apparatus, the main point to be observed being that the material must be uniformly saturated with the solution. After the reaction subsides, the mass is washed with water containing salt, then with pure water and dried.

2. Alkalicellulose as in Ex. 1 is treated with 5 parts cyanuric chloride to 10 parts cellulose with agitation for 0.5 hr. at room temperature, and in the presence of a small amount of chalk. Excess of chloride is then rinsed off, the product washed with acetone, then water and dried.

3. 100 parts cellulose are impregnated with a solution of 600 parts NaOH of 38°, 600 parts alcohol and 300 parts water for 40 min., centrifuged to 2.5-3 fold weight of cellulose, and treated with a warm solution of 50 parts cyanuric chloride in 1500 parts xylene for 1-1.5 hrs. During this time the temperature gradually rises to 30°. It is then completely rinsed in cold water and dried.

Or[2], the alkalicellulose may be impregnated with cyanuric bromide, using 3-5 parts per 10 parts cellulose.

Alkalicellulose is treated with a heterocyclic compound containing one or more C:N group as cyanuric chloride, cyanuric bromide, or a compound of the triazine series having at least one exchangeable halogen atom as dichlorquinazoline, dichlorphthalazine, tribrompyrimidine or dichloride of maleic acid hydrazide, the new cellulose derivatives being characterized as a class by valuable dyeing prop-

1. Soc. Chem. Ind. Basle, E. P. 343748; abst. J. S. C. I. 1931 **50**, 480-B; C. A. 1932, **26**, 304. Belg. P. 366720. F. P. 689557; abst. C. A. 1931, **25**, 1082. Swiss P. 142175; abst. C. A. 1931, **25**, 2288. Belg. P. 367534.

2. *Ibid.* Swiss P. 144228, Addn. to Swiss P. 142175; abst C. A. 1931, **25**, 4124.

erties, and containing nitrogen chemically fixed with cellulose[1]. The following two examples indicate the quantitative relations of the process:

1. 10 parts cotton are impregnated in 10% alcoholic KOH and pressed. The cotton is then immersed in a boiling solution of 10 parts of dichloride of maleic acid hydrazide in 200-300 parts xylene in presence of some powdered chalk for 1-2 hrs., washed hot, rinsed in dilute HCl, washed until neutral and dried.

2. Alkalicellulose produced as above is treated with 10 parts dichlorquinazoline in 200-300 parts xylene heated to gentle boiling until the fiber is uniformly immune to direct dyestuffs. It is then washed as above.

After the cellulose has been etherified by treatment with cyanuric halide[2], the cellulose may be further treated with either 5-10% strength piperidine, or 5% sodium hydrosulfide, which augments the affinity for acid dyestuffs. Condensation products from cellulose and cyanuric halides still containing reactive halogen[3] may be further condensed with compounds having reactive hydrogen and at least one chromophore or group capable of dye formation. Thus, when cellulose is condensed with cyanuric chloride, and then with 4.4′-diaminodiphenylmethane, diazotized and developed with *b*-naphthol (yellow-red) is formed; similarly H-acid, developed with diazotized *p*-nitroaniline (dark brick-red), or *m*-4-xylidine (red); S-acid, developed with diazotized anthranilic acid (brown); xyleneazo-*m*-aminobenzoyl-J-acid (red); *p*-nitroaniline reduced with *b*-naphthol (red); and pararosaniline (red).

Cellulose and Cyanides. The Society Chemical Industry in Basle[4] have described cellulose derivatives containing nitrogen which may be obtained by treating cellulose, pref-

1. Soc. Chem. Ind. Basle, E. P. 342167; abst. C. A. 1931, **25**, 5030. Swiss P. 146541. Belg. P. 377253.
2. *Ibid.* E. P. 347926, Addn. to E. P. 342167; abst. Silk J. 1931, **8**, #89, 54. Swiss P. 142175; abst. C. A. 1931, **25**, 2288. F. P. 687301; abst. C. A. 1931, **25**, 812.
3. *Ibid.* E. P. 363897, Addn. to E. P. 342167.
4. E. P. 370355; abst. J. S. C. I. 1932, **51**, 543-B.

erably in the form of alkalicellulose, with a cyanide as KCN, and after removal of excess of salt, the cellulose is submitted to the action of dilute chlorine or bromine in carbon tetrachloride. The product has a high affinity for acid colors and for some basic dyes.

In the H. Dreyfus process[1], nitrogen derivatives of cellulose are prepared by treating cellulose or its conversion products as hydrocellulose or oxycellulose, with either alkalis or mineral acids, washed, and then with hydrocyanic acid. The products obtained may be hydrogenated, hydrolyzed, alkylated or acylated, and are distinguished by their affinity for acid wool dyes.

Cellulose Cyanoacetate. Cyanoacetic cellulose esters, either alone or admixed with cellulose acetate and rich in nitrogen may be prepared, the cyanogen groups being transformed into CONH groups by treating at 40-50° with alkali and hydrogen dioxide under conditions in which the triacetate is not altered[2]. The esters with cyanogen groups have a greater affinity for colors, principally for those with CONH groups. By hydrolysis further preparations are obtained with free carboxyl groups without saponifying the cellulose esters that keep all the physical properties of the cellulose triacetate intact.

Another class of cellulose compounds containing nitrogen chemically combined therein is obtained by submitting cellulose to the action of phosphonitrile halides in the presence of agents, neutralizing acids[3], suitable compounds including treating cellulose with $P_3N_3Cl_6$, $P_4N_4Cl_8$, $P_5N_5Cl_{10}$, $P_6N_6Cl_{12}$ or $P_7N_7Cl_{14}$ and products in which one or more of the Cl atoms are replaced by OH, NH_2 or NHR groups, R being any organic radical. This new class of cellulosic bodies may be obtained, for example, by heating on the water bath for 4 hrs. 100 gms. alkalicellulose with 30 gms.

1. F. P. 714061; abst. C. A. 1932, **26**, 1782.
2. G. Levi, Boll. assoc. Ital. Chim. e col. 1930, **6**, 80; abst. C. A. 1930, **24**, 4387.
3. Soc. Anon. pour L'Ind. Chim. Basle, F. P. 708945; abst. C. A. 1932, **26**, 1438. See F. P. 709122; abst. C. A. 1932, **26**, 1119.

nitrile of phosphorous chloride and 500 cc. dry pyridine. The product is then pressed and washed with cold water. Analogous results are obtainable by using the corresponding chloramide, $P_3H_3Cl_4(NH_2)_2$, or a compound in which the ammonia group has been replaced by an amine, as aniline or monomethylamine. Or, one may take a mixture of 20 gms. nitrile of phosphorous chloride, 60 cc. pyridine dry, add 40 gms. powdered dry chalk and 40 gms. alkalicellulose, heating the mixture to 90-95° during 3 hrs. These compounds have not the usual affinity of cellulose for cotton dyes.

Another class of cellulose compounds containing nitrogen therein is prepared by acting upon alkalicellulose in the presence of acid-binding agents, with 1-*b*-haloethylpiperidines, the products being useful for the treatment of textiles[1], possessing an affinity for most acid dyestuffs. As an example of the preparation of a member of this family, alkalicellulose is first produced by acting upon 15 parts of cellulose with 25% NaOH solution, pressing excess alkali out, and adding a solution in acetone of 15 parts chlorethylpiperidine. After allowing to stand 5 hrs. at 40-60°, the mass is washed with water and dried. Yield, 17 gms. of the cellulose derivative. Analogous compounds are obtained by acting upon cellulose with chlorethyldiethylamine[2].

H. Dreyfus has announced a new series of cellulose derivatives[3], obtained by treating cellulose substances with organic acid esters in the presence of organic bases such as alkylpiperidines or dimethylhexylamine, at 140-200°. The products obtained may afterwards be etherified or esterified. Those esters susceptible of treatment include acetates of methyl, ethyl, amyl, benzyl and *m*- and *p*-xylenyl; ethyl laurate, dimethyl and diethyl malonate and succi-

1. Soc. Anon. pour L'Ind. Chim. Basle, Swiss P. 145053, Addn. to 141556; abst. C. A. 1931, **25**, 5287.
2. *Ibid.* Swiss P. 141556; abst. C. A. 1931, **25**, 2288. F. P. 680956; abst. C. A. 1930, **24**, 4156.
3. F. P. 685333; abst. C. A. 1930, **24**, 6013.

nate; and ethyl ethoxy-acetate. Among the organic bases suitable may be mentioned dialkylaniline, dialkylnaphthylamine, dimethyl-*n*-hexylamine, and *iso*-amyldiethylamine. The process is exemplified by introducing into a flask with reflux condensation, 100 parts linters and 600 parts dimethyl-*n*-hexylamine, which are boiled together for 1-2 hrs. Then *iso*-isoamyl acetate is introduced in vapor form, and the boiling operation continued for 5-12 hrs. more. A dimethylaminocellulose appears to be formed, which may be acetylated into the corresponding dimethylaminocellulose acetate. Or, 100 parts linters are introduced into an autoclave containing 200 parts methyl acetate and 600 parts methylpiperidine and heated 8-20 hrs. at 140-170°. The product is then precipitated with water, washed and dried.

A class of cellulose compounds which preserves the original structure of the fiber[1] is prepared by treating alkalicellulose with a mixture of carbon bisulfide and alkylating or aralkylating agents, then treating the products thus obtained with organic amines containing at least one NH group. The N-containing reagents include aniline, dimethylamine, mono- and di-ethylamine, dimethyl-*p*-phenylenediamine, piperidine, piperazine, ethylenediamine, diethylethylenediamine asymmetric and similar bodies. The following two examples explain the process:

1. Cellulose is impregnated with cold 20% NaOH solution, and the alkalicellulose obtained treated in one of the two following ways:

a. The alkalicellulose is mixed with 100 parts ethyl monochloracetate and 600 parts carbon bisulfide and left for 1-2 days. The mixture is then treated with a 10% aqueous solution of piperazine or diethylethylenediamine for 1-2 hrs. on the water bath, the product washed 0.5 hr. with hot water and dried. The finished cellulose compound is readily dyed by tartrazine, or benzyl violet 10 B.

b. The alkalicellulose is treated for one or more hours with a mixture of 100 gms. allyl bromide (or benzyl chlo-

1. Soc. Anon. pour L'Ind. Chim. Basle, F. P. 686575; abst. C. A. 1931, **25**, 591.

ride) and 600 parts carbon bisulfide, the material rinsed to remove the yellow color, then treated as in (a) above.

2. Cotton is treated with 5-20% alcoholic KOH, excess alkali removed, and then mixed with allyl bromide and carbon bisulfide for 1.5 hrs., and afterwards warmed on the water bath with 3% piperazine. The cellulose product obtained contains chemically fixed N and S, and has a pronounced affinity for acid colors. Instead of piperazine, benzylamine may be used. An etherized cellulose compound results in each instance.

When alkalicellulose is dissolved with a strong organic base as a quaternary ammonium compound (tetraethylammonium hydroxide, tetramethylammonium hydroxide, phenyltrimethylammonium hydroxide) or guanidine, preferably with cooling to —10°, a solution of the cellulose results, which may be precipitated out by the addition of acids, salts, alcohol, steam or by heating, and is useful for the preparation of films or plastic masses[1]. The conduct of the process is quite simple. It consists substantially in dissolving the alkalicellulose in an aqueous solution of the base at a low temperature, and precipitating therefrom when all of the cellulose has passed into solution.

Other somewhat analogous cellulose compounds are producible by treating cellulose in the presence of an organic derivative of ammonia in which at least 1 H atom is reactive, and in which one or both of the other H atoms may be replaced by an alkyl, or aralkyl group, e.g. alkylamines or arylamines as aniline; acid amides as acetamide, benzamide or phthalamide; amino acids as aminoacetic acid; amidines, urea, cyanamide, dicyanodiamide, dicyanamide, guanidine or thiourea[2]. Transparent films of unusual strength are said to be obtainable.

Cellulose, either in the normal or modified state[3], is

1. L. Lilienfeld, E. P. 217166; abst. C. A. 1925, **19**, 398. Aust. P. 101001.
2. W. Harrison, E. P. 286332; abst. C. A. 1929, **23**, 155. D. R. P. 497240; abst. C. A. 1930, **24**, 3645.
3. H. Dreyfus, E. P. 345989; abst. J. S. C. I. 1931, **50**, 626-B.

capable of yielding N-containing derivatives when treated with primary and secondary amines or organic ammonium bases or their salts as methylamine, dimethylamine, ethylamine, diethylamine, methylaniline, tetramethylammonium iodide, trimethylethylammonium iodide or methyltriethylammonium iodide. Thus, regenerated cellulose is introduced into an autoclave together with about 10 times the weight of mono- or di-methylamine or -ethylamine, the autoclave closed, and the contents raised to 180-220°, and maintained at that temperature for 2-6 hrs. After cooling, the treated material is well washed and dried, and will be found to have a strong affinity for acid dyestuffs.

Esters of cellulose as the acetate, formate, propionate, butyrate or benzoate[1] may be converted into cellulose ethers or cellulose ether-esters by treatment with such bodies as sodium or potassium methylate, ethylate or benzylate, giving rise to mixed ether-esters as methyl (or ethyl or benzyl) formate, acetate, propionate, butyrate or benzoate (example, methylcellulose acetate), which are then treated with certain tertiary organic bases such as dialkylanilines, dialkylnaphthylamines, pyridine, piperidine, quinoline, dimethyl-*n*-hexylamine, *iso*-amyldiethylamine or similar bodies, to form compounds of undetermined composition, but which may be regarded as mixed cellulose ether-esters containing nitrogen chemically fixed therein.

Hydrazinecellulose, ethylenediaminecellulose, tetramethylenediaminecellulose, addition compounds of cellulose with hydrazine, ethylenediamine and tetramethylenediamine have been described by C. Trogus and K. Hess[2], and by X-ray methods, proof has been established of a simple relation between the dimensions of the basic molecule entering into the cellulose lattice and the equatorial interference. The lattice change of cellulose by the diamine is considered as an expression of the formation of a compound between diamine and cellulose. The amount of hy-

1. H. Dreyfus, F. P. 713700.
2. Zts. Physikal. Chem. 1931, **14**B, 387; abst. J. S. C. I. 1932, **51**, 149-A.

drazine chemically combined with the cellulose is between 0.5-1.5 mol. per C_6 cellulose[1]. These diamine compounds of cellulose are not decomposed on several days standing over phosphorous pentoxide at 760 mm., but on treatment with water are decomposed regenerating the original cellulose. They have no technical interest at the present time.

Organic substitution derivatives of cellulose containing nitrogen chemically combined[2] are obtainable by treating cellulose with etherifying or esterifying agents containing the nitrile group -CN, cellulose compounds resulting which may be reduced or hydrated into other compounds of technical usefulness. When cellulose is treated with nitrile-containing etherifying or esterifying agents as chloracetonitrile, cyanacetyl chloride, *a*- or *b*-chlorpropionitrile, in the presence of such bases as N-methylpiperidine, dimethyl-*n*-hexylamine or dimethylaniline, cellulose ethers or esters result. An exemplification of the process is clarified by the following examples:

1. 162 parts linters are suspended in a mixture of 500 dimethyl-*n*-hexylamine, 300 nitrobenzene and a solution of 350 parts cyanacetyl chloride in 1000 parts nitrobenzene, and the temperature raised to 80-90° for 1-2 hrs., after which time there is no more evolution of heat. The celluloss derivative is separated, washed with alcohol and dried. Soluble in glacial acetic acid and acetylene tetrachloride, insoluble in alcohol, ether or water.

2. There are mixed cotton 162, cyanacetyl chloride 100, dimethyl-*n*-hexylamine 120, and glacial acetic acid 1000. When the reaction is complete without heating, a mixture of 250 parts acetic anhydride, 200 parts acetic acid and 16-20 parts sulfuric acid are added, the reaction mixture being cooled to maintain a temperature of 15-25°. When solution is complete, the mixed cellulose derivative is precipitated by water or ether and dried.

1. O. Schwartzkopf, Cellulosechem. 1931, **12**, 33.
2. H. Dreyfus, E. P. 344488; abst. C. A. 1931, **25**, 4705.

3. Cotton 162 is impregnated with 320 parts 50% NaOH solution, the whole being kneaded for 2 hrs. At the end of this time 150-225 parts chloracetonitrile are added, the mass being kneaded for a further 2-3 hrs. at a temperature up to 60°. A further 240 parts NaOH are then worked in, and subsequent 250 parts chloracetonitrile, the temperature being then carried to 50-100°. The cellulose ether formed is soluble in glacial acetic acid, insoluble in ether.

4. The cellulose ether from Ex. 3 is suspended in 10 times its weight of amyl alcohol and the whole heated until just short of boiling. Sodium in the form of a 10% amalgam is then gradually added during 2 hrs. until the total sodium added is 0.5-0.75 times the weight of cellulose ether used. The liquor is then boiled 30 min., and the cellulose compound separated, washed and dried. It has a pronounced affinity for acid dyestuffs.

Amidocellulose. *Aminocellulose. Cotton, Amidated.* Back in 1882, when the nitration of cotton was considered as producing a nitro-derivative called nitrocellulose, and not an ester (cellulose nitrate as we now know to be the case), H. Aron[1] described amidocelluloses obtained by reducing nitrocellulose, the product being employed in secondary galvanic batteries and cells under the name "metallodion." In 1913, J. Briggs[2] described a soluble compound under the name cellulose diaminobenzoate (aminocellulose benzoate), not definitely characterized.

According to P. Karrer and W. Wehrli[3] cellulose may be amidated in general by treating it first with a sulfonyl chloride and then with aqueous ammonia or aliphatic or aromatic amine, the type of sulfonyl chloride or amine used influencing the dyeing properties of the amidated cellulose.

1. E. P. 2943, 1882.
2. Zts. ang. Chem. 1913, **26**, 255; abst. Chem. Zentr. 1913, I, 2110; J. Soc. Dyers Col. 1913, **29**, 194; Kunst. 1913, **3**, 330; C. A. 1913, **7**, 2855; J. S. C. I. 1913, **32**, 595; J. C. S. 1913, **104**, 594.
3. Zts. ang. Chem. 1926, **39**, 1509; abst. C. A. 1927, **21**, 1015.

It appears that the amidation is superficial or incomplete, the inner portions of the fiber remaining un-esterified.

It has been shown by I. Sakurada[1] that esters of *p*-toluenesulfonic acid react with amines by replacement of the hydroxyl group of the alcohol with the amino group. With cellulose yarn esterified with *p*-toluenesulfonic acid (1.8% acid content) Sakurada obtained on treatment with ammonia and other amines, preparations with a low N-content (0.8-1% N), but with 24-60 hrs. heating of cellulose mono-*p*-toluenesulfonate with strong, aqueous ammonia in a closed tube at 100°, he obtained a preparation of the composition 1 aminocellulose plus 1 cellulose plus ½ ester. With alcoholic ammonia solution after 90 hrs. a solution was obtained of about the same composition as before.

By treatment of cellulose toluenesulfonate with aniline or methylaniline on the water bath for 20 hrs., 2 cellulose aniline plus ½ cellulose plus 1 ester results. To obtain aminocellulose, cellulose toluenesulfonate is hydrolyzed and the unchanged cellulose removed by solution in copper ammonia. When the unaltered cellulose toluenesulfonate is saponified and the cellulose dissolved, an aminocellulose and an anilinocellulose are obtained. G. Payras[2] has described the preparation of cellulose benzenesulfonate and its application, and A. Sachs[3] its reduction to aminocellulose, and the dyeing properties of the products so produced.

In the opinion of C. Mullin and R. McGee[4], the behavior of amidocellulose confirms the theory that the dyeing of wool and silk with acid dyestuffs comprises a chemical reaction between the acid dyes and the basic groups in the fibers.

1. Cellulosechemie, 1929, **10**, 145; abst. J. S. C. I. Japan, Suppl. Binding, 1929, **32**, 11-B; Bull. Inst. Phys. Chem. Res. Japan, 1929, **8**, 31; Chem. Zentr. 1929, I, 1678.
2. Rev. gen. mat. Plastiques, 1930, **6**, 3, 5.
3. Textile Colorist, 1926, **48**, 601.
4. Textile Colorist, 1931, **53**, 834; abst. Chem. Zentr. 1932, I, 2095. Textile Recorder, 1931, **49**, #578, 59; #579, 59; abst. C. A. 1931, **25**, 5996; Chem. Zentr. 1931, I, 2284; II, 3057.

In the patented method of P. Karrer[1], it is stated that when cotton which has been partially esterified with an arylsulfonic acid as *p*-toluenesulfonic acid, is treated under pressure at an elevated temperature with ammonia or an amine, hydrazine or hydrazine derivative, an amidocellulose is formed readily colored with such dyestuffs as Orange II, Sulforhodamine, Lanofuchsine or Tartrazine. If, after treatment of cellulose *p*-toluenesulfonate with a heterocyclic nitrogen compound as pyridine, quinoline or acridine[2], increased affinity for acid dyes results. In order to produce more uniform and controllable results in the formation of amidocellulose[3], it is advised to first form the cellulose sulfonate, then while still in the wet state, to treat the esterified fibers for several hours with ammonia or an amine at a low temperature, instead of a shorter time treatment at an elevated temperature. Instead of ammonia, piperidine may be used, the material being heated not above 90°.

The process of H. Dreyfus varies from the above in several fundamental respects[4]. Cellulose derivatives containing hydroxy groups are treated so as to replace one or more OH groups by amino or substituted groups, the cellulose ester or ether as cellulose glycollate, cellulose glycollic acid (carboxymethyl cellulose) being treated directly with a body as thionyl chloride, either directly or in presence of a solvent for the cellulose ether or ester, or in presence of a non-solvent diluent. The nitrogen derivatives obtained according to the process are characterized by a strong affinity for acid wool dyestuffs. Derivatives containing primary or secondary amino groups may be alkylated or aralkylated by treatment with ethyl chloride or other etherifiant to obtain alkylated amidocellulose as ethylamidocellulose (amidoethylcellulose), or may be acylated or both (if

1. U. S. P. 1650989. E. P. 249842. D. R. P. 438234. See also F. P. 648026.
2. P. Karrer, U. S. P. 1673627.
3. *Ibid.* E. P. 263169, Addn. to E. P. 249842. D. R. P. 466937. D. R. P. 467585, Addn. to D. R. P. 438324.
4. E. P. 344480; abst. J. S. C. I. 1931, **50**, 626-B; Silk J. 1931, **8**, #86, 53. F. P. 704280; abst. C. A. 1931, **25**, 4705.

a primary amine be used, an example being ethylaminocellulose acetate). The general scope of the invention, which is susceptible to a number of modifications, is indicated in the following examples:

1. Cellulose glycollic acid is dissolved in 10 times its weight of benzene, treated with 1.25 times its weight of thionyl chloride for an ether containing 2.5-3 groups, the mixture being first gently warmed, maintained at 25-35° for 20-30 min., excess of thionyl chloride and benzene removed under vacuum, and the cellulose derivative washed cautiously with ligroin. The chlorinated product is then heated with excess of ammonia solution in a closed container at 100-110°. The product, which contains nitrogen, is soluble in acetone or acetic acid, insoluble in ether or ligroin.

2. Oxyethylcellulose is treated as in 1 above.

3. Cellulose malonate, phthalate, malate or maleate is treated with thionyl chloride as in Ex. 1, then heated with excess of aniline in a reflux condenser for 30 min., cooled, and the cellulose derivative (an amidocellulose malonate, (?) for example) precipitated and washed. It has a pronounced affinity for acid dyestuffs, and depending upon the acid radical attached.

4. Ammonium celluloseglycollate, cellulose oxalate or maleate is powdered and suspended in 5-10 times its weight of distilled anthracene oil, heated to 180-220° for 4-7 hrs., then separated from the anthracene oil and washed with ligroin.

The formation of aminocellulose compounds by the methods of the I. G. Farbenindustrie is exemplified in the following five processes:

Alkalicellulose is esterified with benzene- or toluenesulfonyl chloride, then acetylated or alkylated and treated with an amine as aniline, diethylamine, pyridine or *iso*-amylamine, as indicated herewith:

I. Cellulose acetate 100, acetone 240 are mixed with toluene-4-sulfochloride in acetone 80. After addition of

5.5 parts urea in 10 parts water, a solution of 3.75 parts NaOH in 10 parts water is slowly added, drop by drop. Stirring is continued 5 hrs. Then 50 parts *iso*amylamine (or a like quantity of diethylamine or triethylamine) are added, and the mass heated 1 hr. in an autoclave at 100° The reaction product is precipitated by water and washed 15 hrs. with hot water. The cellulose ester formed dissolves in acetone, glacial acetic acid and mixtures of *sym*-tetrachlorethane, or di- or tri-chlormethane (chloroform) containing 10% ethyl alcohol.

II. 100 parts alkalicellulose are esterified with benzenesulfonic acid chloride suspended in benzene, free benzene removed, and the ester washed with alcohol, then with water in succession, and finally acetylated. The precipitated cellulose acetobenzenesulfonate (?) formed is soluble in dichlormethane-alcohol 9:1, and in the dry condition when heated with aniline for 3 hrs. at 160°, forms an anilinocellulose acetate (?) soluble in acetone, glacial acetic acid, *sym*-tetrachlorethane and mixtures of di- and tri-chlormethane-methyl alcohol 9:1.

III. 100 parts cellulose aceto-toluene-4-sulfonate in Ex. I are dissolved in acetone and autoclave heated with 100 parts diphenylamine 3 hrs. at 120°. Then the cellulose ester is precipitated and washed free from reactants. It is soluble in di- or tri-chlormethane-ethyl alcohol 9:1.

IV. 100 parts cellulose *p*-toluenesulfonate are treated with pyridine 2000 and 280 of benzoyl chloride until solution takes place. The mass of cellulose benzoyl-*p*-toluenesulfonate is precipitated, washed with ammonia to remove small quantities of benzoic acid present and dried. The ester is soluble in pyridine and tetrachlorethane, and di- or tri-chlormethane-alcohol 9:1.

V. 100 parts cellulose aceto-*p*-toluenesulfonate (cellulose acetate toluene-*p*-toluenesulfonate) are dissolved in acetone and heated 3 hrs. in an autoclave at 140° with 100 parts dimethylaniline. The reaction mass is separated by

pouring into dilute HCl, washed until neutral and dried. Soluble as in Ex. IV[1].

In another method[2], 10 gms. cellulose dicrotonate are treated for 10 hrs. at 100° in a closed pressure vessel with ammonia gas. There is obtained a reaction mass consisting of about equal parts aniline and a water-insoluble product of 2.1% N content, which contains cellulose aminopropionate.

Soluble derivatives of amidocellulose are obtainable from cellulose esters derived from organically substituted inorganic acids by either esterifying or etherifying them and then reacting with an amine, or by causing them to react with acid chlorides or acid anhydrides in presence of a tertiary amine. The composition of the product depends on the kind of cellulose ether, ether-ester, ester or mixed ester and the amine brought into reaction, and is explained by the following examples:

I. 33 parts linters are soaked 4 hrs. in excess of 40% NaOH solution at 0°, pressed to 100 gms., disintegrated and mixed with 116 parts benzenesulfochloride in 495 parts benzene. The mixture is heated 1 hr. on the steam bath. The reaction product is washed successively with hot benzene, hot ethyl alcohol and water, dried and acetylated in the usual manner. The cellulose aceto-toluenesulfonate obtained is then boiled 3 hrs. with a mixture of 400 parts aniline and 650 parts alcohol, and the mass containing anilinocellulose aceto-sulfonate (?) precipitated by dilute HCl[3].

II. 100 parts cellulose toluene-4-sulfonate are boiled 2 hrs. with 250 parts diethylamine in 800 parts alcohol. The filtered solid matter is washed with alcohol, dried, and acetylated, forming a cellulose aceto-toluene-4-sulfonate.

1. M. Hagedorn and A. Ossenbrunner, U. S. P. 1833286. I. G. Farbenindustrie, E. P. 279801; abst. J. S. C. I. 1929, **48**, 167-B.
2. I. G. Farbenindustrie, D. R. P. 542004; abst. Chem. Zentr. 1932, I, 2791.
3. *Ibid.* E. P. 279801; abst. J. S. C. I. 1929, **48**, 167-B; Silk J. 1928, **4**, #46, 68; Chem. Zentr. 1928, I, 977. F. P. 641043; abst. C. A. 1929, **23**, 1266; Chem. Zentr. 1929, I, 2925.

III. 100 parts cellulose toluene-4-sulfonate are boiled with 2000 parts pyridine and 172 parts benzoyl chloride until complete dissolution ensues, when the mass containing cellulose benzoyl-toluenesulfonate (cellulose toluenesulfo-benzoate) is filtered, washed with ammonia to remove benzoic acid and dried.

IV. 100 parts cellulose toluene-4-sulfonate are boiled 2 hrs. with 250 parts *iso*amylamine in 800 parts alcohol, the solid matter separated by filtration, washed with alcohol and dried, then ethylated, forming probably an amidoethylcellulose.

Where products entirely soluble in water are desired, and which are desirable fire-proofing additions to fabrics and textiles[1], 18 parts of alkalicellulose are agitated 2 hrs. with 100 parts 20% NaOH solution, and 22.8 parts sodium 1-chlor-1-methylbenzenesulfonate-4 (or 46 parts sodium 1-chlor-1-methylbenzenesulfonate-2 or 24.1 parts sodium 1-chlor-1.3-dimethylbenzenesulfonate-4) in 100 vols. 96% alcohol added, and the mixture stirred until a water solubility results.

P. Karrer and S. Kwong[2] produce an amidocellulose by treatment of yarn with ammonia, the product containing 0.71% N. This yarn fixes on the average about 0.05 gms. equivalent of the following acids, sulfuric, hydrochloric, perchloric, oxalic, acetic, phosphoric and *p*-toluenesulfonic. In conjunction with W. Wehrli[3], P. Karrer finds that when cellulose, especially cotton, which has been partially esterified with *p*-toluenesulfonyl chloride is treated with ammonia and an amine or hydrazine, the cellulose takes on one amido group where the amidation is effected in several weeks with aqueous ammonia in the cold, or it is complete in one hour at 100°. Aromatic amines may also be used but the affinity for acid dyes in the product formed is not so strong as with the ammonia.

1. I. G. Farbenindustrie, Aust. P. 117056.
2. Helv. Chim. Acta. 1928, **22**, 3049.
3. Helv. Chim. Acta. 1926, **9**, 591; abst. C. A. 1926, **20**, 3819.

M. Munch[1] has found that although amidocellulose (amidated cotton) is completely immune to the substantive dyes, weakly aminated cotton has a weak affinity for cotton colors, the amidated yarn being dyed with acid dyestuffs preferably in the presence of 1-4% acetic acid. Upon dyeing aminocellulose with wool in the same dyebath, the latter has been found to take up less color, fastness to washing and soaping, in general, being better on cotton than on wool. It is possible to produce local immunization effects on cotton goods by printing the same with a thickened mixture of alcohol, NaOH, and *p*-toluenesulfonyl chloride, washing the fabric, and then dyeing with dyestuffs to give the color effects desired[2]. If a mixture of ordinary direct dyed cotton and amidocellulose be heated together with water, all of the dyestuff in the cotton will gradually transfer onto the aminized cellulose. If the ester group be removed, as by treatment with potassium cyanide solution, immunity towards direct dyes is destroyed.

According to Society of Chemical Industry Basle[3], new derivatives of cellulose which preserve the original structure of the fiber may be prepared by treating alkalicellulose with a mixture of carbon bisulfide and alkylating or aralkylating agent, then treating the products thus obtained with organic amines containing at least one NH group. Thus, alkalicellulose is treated with a mixture of ethyl chloracetate and carbon bisulfide, and then treated with an aqueous solution of piperazine.

Cellulose Methane Esters. It has been discovered that new cellulose methane esters may be formed from alkalicellulose, or its dithiomethane (CS_2) derivatives or salts[4], by treating with a halogen methane derivative with four labile replaceable hydrogens, or in its place, its components. There can be used, for example:

1. Textile Mercury, 1927, **77**, 353.
2. Anon., Farben Ztg. 1928, **34**, 564.
3. F. P. 686575; abst. C. A. 1931, **25**, 591.
4. E. Hausheer, Swiss P. 139512.

Dichloroxymethane, $Cl_2C:O$; dichlorthiomethane, $Cl_2C:S$ or its components CS_2 and CCl_4; chloroxy- or thiomethane alcohol ester $Cl.C:O(O.R)$, $Cl.C:S(O.R)$, wherein O.R is alcohol or cellulose groups, or its components $Cl_2C:O$, or $Cl_2C:S$ plus alcohol or alcoholate; chlor-N-methane $Cl.C:N$; tetrachlormethane CCl_4; tetrachlormethylmethane $Cl_3C.CH_2Cl$, or $Cl_2CH.CHCl_2$; chlor-oxymethaneamide $Cl.C:O(NH_2)$, or its components $Cl_2C:O$, or $Cl.C:O(O.R)$ plus NH_3; chloroxymethamine, e.g. $Cl.C:O(NHC_6H_5)$, or its components $Cl_2C:O$, or $Cl.C:O(O.R)$ plus amine, e.g. $NH_2C_6H_5$; chloroxymethane-amidicarbonic acid, e.g. $Cl.C:O(NHCH_2COOH)$, or its components $Cl_2C:O$ plus NH_3-$[:Cl.C:O(NH_2)]$ plus monohalogencarbonic acid, e.g. $Cl.CH_2COOH$; chlorthiomethaneamide $Cl.C:S(NH_2)$, or its components CS_2 plus NH_3 plus Na and SH removing agents, e.g. CS_2 plus NH_3 plus $Cl.CH_2COONa$, or CS_2 plus $Cl.CH_2COONa$ plus NH_3, or CS_2 plus NH_3 plus $K_3Fe(CN)_6$ plus HCl, or $Cl.C:S(O.R)$, or $Cl_2C:S$ plus NH_3, or $Cl.C:N$ plus H_2S; chlorthiomethanamine, e.g. $Cl.C:S(NHC_6H_5)$, or its components CS_2 plus amine and NaSH removing agent, e.g. CS_2 plus $NH_2C_6H_5$ plus $ClCH_2COONa$, or CS_2 plus $NH_2C_6H_5CH_3$ plus $K_3Fe(CN)_6$ plus HCl, or $Cl.C:S(O.R)$, or $Cl_2.C:S$ plus amine, e.g. $NH_2C_6H_5$; chlorthiomethaneamidocarbonic acid, e.g. $Cl.C:S(NHCH_2COOH)$, or its components CS_2 plus NH_3 plus 2 $Cl.CH_2COONa$, or CS_2 plus $Cl.CH_2COONa$ plus NH_3 plus $Cl.CH_2COONa$, or CS_2 plus NH_3 plus $K_3Fe(CN)_6$ plus HCl plus $ClCH_2COONa$, or $Cl_2.C:S$ plus NH_3 plus $Cl.CH_2COONa$; furthermore as homologous combinations: CS_2 plus $Cl.C:O(NH_2)$, or its components CS_2 plus $Cl_2.C:O$ plus NH_3, or CS_2 plus NH_3 plus $Cl_2.C:O$; CS_2 plus $Cl.C:O(NHC_6H_5)$ and homologues or its components, e.g. CS_2 plus $Cl_2C:O$ plus amine, e.g. $NH_2C_6H_5$, or CS_2 plus amine, e.g. $NH_2C_6H_4CH_3$ plus $Cl_2C:O$.

Alkalicellulose may be treated with one or more of the above mentioned compounds and dilute inorganic acids in the presence of a halogen methane derivative. Ammonia or amines as phenylamine may be added thereto for the

production of a cellulose thiomethane-phenylamine or a cellulose dihydrodithiomethanephenylamine. The following example is indicative of the general method by which this class of compounds may be prepared:

100 parts cellulose are immersed in 100 parts 18% NaOH solution at 15-20° for 2-24 hrs., pressed to 350 parts, milled, ripened and treated for 6-24 hrs. with 25-60 parts dithiomethane (carbon bisulfide). The fresh, ultimately ripened cellulose xanthate is dissolved in 1000-5000 parts water or dilute NaOH solution, filtered, made weakly alkaline or faintly neutral by the addition of acetic acid, and then to the milky solution with stirring, are added 60-120 parts phenylamine (aniline) and after standing 1-8 hrs., 60-120 parts monochloracetic acid are added. After 6-72 hrs. the cellulose thiomethanephenylamine precipitates out, is washed with water and then alcohol. It is hardly soluble in water, alcohol or ether, but dissolves in 1% NaOH solution, and in moist condition in several aromatic and aliphatic bases.

Cellulose Carbamates. *Cellulose Phenylisocyanate.* P. Goissedet[1] has found that when cellulose or its derivatives, still containing replaceable hydroxyls, is treated with an aliphatic or aromatic isocyanate, cellulose aryl- or alkylcarbamates result. When, for instance, 1 part cellulose is admixed with 3 parts phenyl isocyanate diluted with dry pyridine and heated at 120° with stirring for 12-24 hrs., the cotton fibers gradually disappear, forming a colloidal solution from which the insoluble cellulose phenylisocyanate may be precipitated with water, washed and dried. At the same time small amounts of diphenyl urea are formed, which are separated from the ester by the solubility of the former in benzine.

1. U. S. P. 1357450; abst. C. A. 1921, **15**, 436; J. S. C. I. 1920, **39**, 817-A; Paper, 1921, **27**, 26; Caout. et Gutta. 1921, **18**, 11074. E. P. 130277; abst. J. S. C. I. 1919, **38**, 714-A; C. A. 1920, **14**, 122. F. P. 496526; abst. Chim. et Ind. 1920, **4**, 668; Textilber. 1921, **3**, 202; Paper, 1921, **28**, 38. Swiss P. 88193. Ital. P. 172228; abst. Chem. Ztg. 1922, **46**, 600.

The ratio of pyridine to cellulose may vary within wide limits. The former apparently aids in the reaction in addition to acting as a desirable diluent. Due to the fact that the process may be carried out in the presence of tertiary bases, either singly or admixed, products may be obtained of a wide range of insolubility and viscosity in the usual cellulose ester solvents. The formed ester is insoluble in water or alcohol, but dissolves in methyl or ethyl acetates, alcohol-ether, benzyl alcohol, furfural and tetrachlormethane. It is non-explosive and less inflammable than cellulose acetate.

In a more recent process[1], the method of manufacture does not change the outward appearance of the cellulose, although nitrogen is chemically combined. The product may be prepared by wetting cotton with phenylisocyanate under addition of a small amount of pyridine or zinc chloride at 80°. After 4 hrs., excess of phenylisocyanate is removed by vacuum distillation, and the cellulose derivative freed from residual pyridine and some diphenyl urea by washing with alcohol. The phenylisocyanation may be conducted in the absence of applied heat, by allowing the mixture to remain together for several (at least 4) days, then washing with hot alcohol. Cotton fibers thus treated are strongly colored by basic dyes without mordants, and have an affinity for cellulose ester and ether dyes.

Cellulose Xanthacetic Acid. Cellulose Xanthacetate. When viscose, after purification by treatment with acetic acid, is treated with sodium chloracetate, sodium cellulosexanthacetate separates slowly as a jelly and is precipitated by alcohol or salt solution[2]. The addition of dilute sulfuric acid to the aqueous solution precipitates cellulosexanthacetic acid, stable at 105°, but slowly decomposing in alkaline solutions. In contrast to cellulose xanthate (viscose) brief boiling with dilute sulfuric acid causes no de-

1. Soc. Anon. pour L'Ind. Chim. Basle, Swiss P. 142749; abst. C. A. 1931, **25**, 2288. Ital. P. 274021.

2. T. Nakashima, Bull. Inst. Phys. Chem. Research Tokyo, 1929, **8**, 103; abst. J. S. C. I. 1929, **48**, 430-A.

composition. The proportion of xanthacetate formed increases with the amount of sodium chloracetate used. A product of the approximate composition of $C_{12}H_{19}O_9.O.CS.S.CH_2CO_2Na$ results when 2 mols. sodium chloracetate are used. The sodium salt of the acid is soluble in water, but not the acid[1]. The copper, silver, mercury, barium and zinc cellulosexanthacetates have been prepared by adding a metallic salt solution to the free acid. The copper salt is blue, the others white.

J. Simonin[2] has reported upon a study of cellulose xanthacetate, the latter being prepared by first converting cellulose into viscose in the conventional manner. When in solution with carbon bisulfide, the dope is diluted with 10% acetic acid until neutral or faintly alkaline, when sodium chloracetate dissolved in water is added. Finally the solution is treated with weak sulfuric acid and the cellulose xanthacetate precipitated in shred-like form.

These esters are produced primarily according to the discoveries of (1) L. Lilienfeld and the investigations of (2) Society of Chemical Industry in Basle.

1. *Disclosures of L. Lilienfeld.* These cellulose xanthofatty acids and esters obtained therefrom may be arranged in three groups as follows: (a) Bodies which, particularly in the freshly prepared condition, are soluble in water, usually warm or hot. Their aqueous solutions leave on evaporation transparent pellicles insoluble or scarcely soluble in water at ordinary temperatures. (b) The solubility in water characteristic of the first group is lacking in the second group. The solubility of their members in aqueous ammonia or of numerous organic bases is common to both groups. Weak solutions of these reagents as 0.01-0.02% ammonia or 0.25-0.5% aniline solution suffices to dissolve most of the members of the first and second groups. The solutions yield on drying, transparent films insoluble in water. A further property of members of (a) and (b)

1. T. Nakashima, Zts. ang. Chem. 1929, **42**, 546; abst. C. A. 1929, **23**, 4451; J. S. C. I. 1929, **48**, 799-A.
2. Rev. gen. mat. Plastiques, 1929, **5**, 507.

groups is the solubility in dilute solutions of alkali. (c) To this group belong those cellulose derivatives insoluble or sparingly soluble in water and in aqueous ammonia, but which dissolve in aqueous solutions of alkalis to form solutions precipitable by acids, salts and alcohols. If such a solution be forced through a fine orifice into a suitable setting bath, it solidifies to a filament, which after washing and drying, is shiny and transparent[1].

These cellulose derivatives show the characteristic reactions of the xantho-fatty acids. When heated on the water bath in neutral or alkaline solution they decompose, yielding the respective thionhydroxyparaffin monocarboxylic acid, hydrogen sulfide, carbon dioxide and cellulosic body. Their solutions in alkali decompose, even at room temperature, splitting off the respective thionhydroxyparaffin-monocarboxylic acid. According to their mode of formation, behavior and reactions, these compounds are to be regarded as cellulose xanthofatty acids (cellulose thionthiolcarbonhydroxyparaffin monocarboxylic acids) and therefore compounds which are derived from fatty acids by substituting a cellulose xanthic acid residue for a hydrogen atom united to carbon.

The following illustrates but does not limit the invention: 1000 parts crude viscose suitable for viscose rayon manufacture are treated with 5-10% acetic acid while stirring, until the mixture reacts neutral or faintly alkaline. As soon as the hydrogen sulfide evolved in the neutralization has dissipated, the viscose, which has become light in color, is treated with a solution of sodium monochloracetate prepared by dissolving 60-100 parts of the salt in 480-800 parts water, and neutralized with powdered sodium carbonate or bicarbonate. As soon as the chloracetate has been incorporated with the viscose, the mixture is stirred and allowed to stand at room temperature for some time (6-48 hrs.)

1. L. Lilienfeld, E. P. 231800; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 913-B; Ann. Rep. S. C. I. 1925, **10**, 149; 1926, **11**, 618. D. R. P. 424560; abst. C. A. 1931, **25**, 4401. Belg. P. 325270. Holl. P. 17632. Aust. P. 102305, 116823.

and is then treated with 1-3% sulfuric acid until a strong acid reaction to Congo paper results, the product separating in flocks and shreds. The precipitate is separated from the mother liquor by decantation, washed with water until neutral, the product being soluble in warm water. Aqueous solutions upon evaporation to dryness form transparent films or skins, insoluble in water.

The product, glycol cellulose xanthacetic acid (cellulose-thionthiol-carbon-glycollic acid) when dried directly, consists of scales or laminae, and when previously freed from water by means of alcohol, is a white, flaky or powdery substance, dissolving to a clear solution in 0.01-0.05% ammonia solution. As the ammonium content of the solution increases, likewise does the tendency to jellify, a solution prepared with 0.5% ammonia gelating shortly after its preparation. Cellulose xanthacetic acid dissolves readily in aqueous solutions of organic amines, quaternary ammonium bases, urea, guanidine, pyridine, quinoline and dilute sodium carbonate solutions.

In the manufacture of cements, sizes and finishing and coating compositions[1], the cellulose xanthofatty acid is dissolved in a mixture of water and a phenylamine derivative as monomethylaniline.

Esters of cellulosexanthic acid are prepared by acting on a cellulose-xanthic acid or a cellulose xanthate with the ester of an inorganic acid, preferably in faint alkaline solution[2]. In etherifying a cellulosexanthic acid, the reaction usually takes place without the application of heat, but warming accelerates the reaction. The formation of the new cellulose compound is indicated by the precipitation of the final product, which tends to separate in jelly form where the mixture is stirred but slightly. If, however, the mixture is more dilute and is vigorously stirred, the prod-

1. L. Lilienfeld, E. P. 247223; abst. J. S. C. I. 1926, **45**, 783-B; Ann. Rep. S. C. I. 1926, **11**, 129. Dan. P. 36162. Norw. P. 42141. Belg. P. 355400. India P. 11143.

2. *Ibid.* E. P. 252654; abst. J. S. C. I. 1926, **45**, 1009-B; Chem. Zentr. 1927, I, 1090.

uct precipitates out as a coarse, flocculent mass. The ethyl cellulose xanthate may be isolated by separating the precipitate by filtration, comminuting and then washing with alcohol, then with ether or benzene. This ethyl ester is soluble in 10% aqueous alkali to a clear, viscous solution. By the use of methyl sulfate, a methylcellulose xanthate results.

The preparation of cellulose xantho-glycerophosphates has been described[1], obtained by acting upon cellulose xanthate with glycerophosphoric acid.

2. *Methods of Society of Chemical Industry.* Alkalicellulose is treated with a mixture of carbon bisulfide and alkylating or aralkylating agent, a change being produced in the cellulose accompanied by an increase in weight; but the products formed are not soluble in water and retain completely the original fibrous structure of the cellulose. They, however, have a very high capacity for undergoing reaction with organic bases containing at least one hydrogen atom linked to nitrogen as mono- or di-methylamine or -ethylamine, aniline, dimethyl-*p*-phenylenediamine, piperazine, ethylenediamine, and diethylethylenediamine, whereby further products, insoluble in aqueous alkalis are obtained, which have an outstanding affinity for acid dyestuffs, and to a lesser extent, for insoluble acetate silk dyestuffs[2].

Particularly valuable and easily accessible are the products, which, with retention of the original structure of the cellulose, are obtained on the one hand with aid of such halogen alkyls which do not contain more than 4 carbon atoms, and the *b*-carbon of which carried a double bond such as allyl halides, or chloracetic alkyl esters or bromacetic acid alkyl esters, and, on the other hand, with aid of

1. L. Lilienfeld, E. P. 357121; abst. J. S. C. I. 1932, **51**, 141-B. Addn. to E. P. 335906; abst. J. S. C. I. 1931, **50**, 153-B. See also E. P. 357154, 357526. This etherification of cellulose xanthate may take place in the complete absence of water (Cf. E. P. 362437).

2. R. Haller and A. Heckendorn (Soc. Chem. Ind. Basle), U. S. P. 1838038; abst. C. A. 1932, **26**, 1454. E. P. 341237. Swiss P. 141558.

aliphatic diamines as dialkylethylenediamines or piperazine. The following examples indicate the scope of the process:

1. *With Chloracetic Ester.* A solution of 100 parts chloracetic ester is allowed to act, in conjunction with 600 parts carbon bisulfide, on alkalicellulose in the cold for 1-2 days. The material is then rinsed for a short time in cold or warm water, and then, without previous drying, warmed 1-2 hrs. on the water bath with a 10% aqueous solution of piperazine or diethylethylenediamine, and finally rinsed 0.5 hr. in hot water. The product is nearly white and is readily dyed with such acid wool dyestuffs as Tartrazine and Benzyl violet 10B.

2. *With Alkylhalides or Aralkyl Halides.* 100 parts allyl bromide, or benzyl chloride or diethyl sulfate, or a mixture of allyl and benzyl bromides, in 10% solution in carbon bisulfide, are warmed for 1.5 hrs. with alkalicellulose and alcoholic KOH. It is then rinsed, and hydro-extracted, and in this condition, appears in part at least, to contain methylcellulose xanthate, ethylcellulose xanthate, allylcellulose xanthate and allylbenzylcellulose, depending upon the etherifiant used. It is then heated on the water bath with an aqueous 10% solution of piperazine, benzylamine or aniline. At the close of the reaction the material is rinsed with hot water. The chemical composition of the finished cellulose derivative is unknown, but chemically combined nitrogen and sulfur are present. It has retained the strength and appearance of the initial cellulose, and has strong affinity for acid dyestuffs.

Cellulose esters may be made by the action of an organic anhydride on a cellulose xanthate or cellulosexanthic acid[1] which is either soluble in water or has become insoluble in water owing to ripening. The esters produced are free from sulfur. The process finds application in several technical operations, the conversion of cellulose xanthate into ester being accomplished by impregnating a ma-

1. Soc. Chemical Industry in Basle, E. P. 349322; abst. Chim. et Ind. 1932, **27**, 656; Text. Mfr. 1931, **57**, #682, 381. Belg. P. 370566.

terial as a textile with viscose by a filling operation, by saturation, dressing or filling, and then the material thus prepared may be treated with the hot acid anhydride, the cellulose ester being formed in close union with the material, and by further treating the latter by a dyeing operation, portions of the fiber which have been covered or associated with the cellulose ester, are immune to substantive dyestuffs, so that multicolor and differential effects may be obtained.

The operation is carried out as follows: A cotton web is impregnated with a viscose solution, dried and treated with acetic anhydride in the presence of xylene for 0.5-2 hrs. During the treatment the temperature is raised to 140°. By this treatment the web acquires a durable dressing, stable against water, which gives it a stiff and thick character. From the fact that no sulfur is chemically combined, the final product would appear to be a simple cellulose acetate, obtained by the action of acetic anhydride on regenerated cellulose.

Cellulose Xanthamides. If cellulose xanthic acid (which see) is acted upon by ammonia or primary or secondary amines[1] at room temperature, the solution gelatinizes in the course of a few days, and the amide of cellulose xanthic acid is formed. The product contains about 1 amido group per C_6 cellulose molecule and is insoluble in water and the usual organic solvents of the cellulose ether industry. The amide dissolves in alkali and gradually decomposes in solution to regenerated cellulose, in this respect resembling viscose. Cellulose xanthamide, cellulose xanthanilid and mono- and di-ethyl cellulose xanthamide and xanthanilid have been prepared. Cellulose xanthamides may also be obtained by the interaction of sodium cellulose xanthate acetic acid upon ammonia or amines[2].

These amido bodies have been described in detail in a

1. T. Nakashima, Zts. ang. Chem. 1929, **42**, 643; abst. C. A. 1929, **23**, 5167; Chem. Zentr. 1929, II, 985; J. S. C. I. 1929, **48**, 799-A.
2. *Ibid.* J. S. C. I. (Japan) 1928, **31**, 629; Suppl. Bind. 1928, **31**, 155-B; abst. C. A. 1929, **23**, 3081.

series of three patents issued to L. Lilienfeld[1], in which viscose, prepared in the usual manner, and either in the freshly prepared or ripened stage suitable for spinning purposes, is treated with 5-10% acetic acid until the mixture shows a neutral or faintly alkaline reaction. As soon as the hydrogen sulfide has been liberated incident to neutralization, the mass may be treated with sodium monochloracetate to form a hydroxyalkylcellulose, and to this is added ammonia (forming xanthamide) or aniline (forming a cellulose xanthanilid, cellulose phenylthiourethane), which after several hours, separates as a flocculent precipitate, which when washed with alcohol, then with ether and dried at a low temperature under reduced pressure, forms a powder, insoluble in water, alcohol or ether, but dissolving in 1-10% sodium hydroxide solution, or 10-25% ammonia solution, or in ethylamine especially in presence of some water. Likewise soluble in diethylamine, ethylenediamine, guanidine, aniline, piperidine, pyridine, mono- or di-chlorhydrin, or in phenol and water. When heated 4-6 hrs. at 200° under pressure with 2% sulfuric acid, aniline and H_2S are split off. These bodies in alkaline solution are miscible with the alkylcelluloses soluble in or swelling in water, to a multiplicity of indicated uses.

In another process[2] N-substituted thiourethanes of cellulose are treated with basic substances and then etherified, as shown by the following example: 100 parts cellulose phenyl-(or tolyl-)thiourethane[3] is mixed with 4900 parts 10% NaOH solution, filtered, and etherified with 600-

1. E. P. 231800; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 913-B; Ann. Rep. S. C. I. 1925, **10**, 149; 1926, **11**, 618. D. R. P. 424560; abst. C. A. 1931, **25**, 4401. Belg. P. 325270. Holl. P. 17632. Aust. P. 102305, 116823. U. S. P. 1674401. Can. P. 259330; abst. C. A. 1926, **20**, 2411. E. P. 231801; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 955-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, II, 2190. D. R. P. 438918; abst. Chem. Zentr. 1927, I, 1770. Holl. P. 19083. Norw. P. 42811. Swiss P. 118235. Aust. P. 102306, 121030, 121031, 121032. U. S. P. 1674401. Swed. P. 61131. E. P. 231802; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 913-B; Ann. Rep. S. C. I. 1925, **10**, 149; 1926, **11**, 618; Chem. Zentr. 1926, I, 274. Aust. P. 102307. U. S. P. 1674405.

2. L. Lilienfeld, D. R. P. 455589. 3. *Ibid.* D. R. P. 438918.

1000 parts ethyl sulfate. After standing for up to 8 hrs., a white precipitate forms which is washed until neutral, treated with 1-10% sulfuric acid, washed until neutral and air dried. The product is soluble in 90% alcohol, alcohol-ether 2:1, acetone, ligroin-alcohol 1:1 to 2:1, hexane-alcohol, chloroform, alcohol-chloroform, tetrachlormethane, methyl acetate, benzene-alcohol, glacial acetic acid, diethylaniline-alcohol, quinoline, α-dichlorhydrin, tetrachlorethane, ethylene dichloride, pyridine, amyl acetate-alcohol, ethylenechlorhydrin, benzyl alcohol, amyl acetate, ethyl benzoate, chlorbenzene, ethyl citrate, ethylnaphthol, ethylene bromide-amyl alcohol, chlornaphthalene, dibenzyl ether, allyl alcohol, acetyleneacetone, eugenol, ethyl lactate, α-picoline, epichlorhydrin, and o-chlorphenol.

As a size, cement and thickening agent[1], xanthamides have been advocated, prepared by treating a cellulose xanthoacetic acid with monoethylamine.

A difficultly classifiable nitrogenous cellulose derivative has been described by W. Harrison[2], and obtained by the oxidation of viscose by means of a current of air in the presence of ammonia or amines, especially hydroxylamine. Agents which oxidize hydrogen sulfide are used, as ferricyanides, bichromates and peroxides. Oxygen may be used in the nascent stage electrically generated. The carbohydrate compound and ammonia derivative may be either mixed before or after the addition of the oxidizing agent, the oxidation being carried out in neutral, acid or alkaline solution —preferably the latter. These compounds dissolve in alkali hydroxides, zinc chloride and cuprammonium solutions.

1. L. Lilienfeld, E. P. 247223; abst. C. A. 1927, **21**, 648.
2. E. P. 285331; abst. C. A. 1929, **23**, 155; Chem. Zentr. 1928, II, 305. See also E. P. 264261, 286331, 286332. S. Trotman, Silk J. 1930, **6**, #73, 46.