CELLULOSE ACETATE

ITS MANUFACTURE AND APPLICATIONS

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By

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PREFACE

THE literature relating to cellulose acetate is at present very scattered, and consists in the main of patent specifications, isolated papers in scientific and technical journals, and brief descriptions of manufacturing processes in books dealing with rayon in general. The patent specifications are widely distributed throughout the various classes, so that it is no easy matter to segregate them, and they are frequently misleading, while the accounts given in books dealing with rayon are inadequate, and are marred in many cases by inaccuracies such as the inclusion of references to worthless patent specifications.

While the present work does not claim to be exhaustive, it is intended to give a clear exposition of manufacturing processes, and to describe the lay-out of plant for the manufacture of cellulose acetate and of acetate rayon. In addition, there are chapters dealing with the chemistry and physics of cellulose and cellulose acetate in the light of recent researches. The work of the chemist in the acetate industry is described in connection with the testing of raw materials, process control and research, and his relationship to the other departments of the factory is discussed. The manufacture of fabrics including dyeing, printing and finishing is dealt with ; and other uses of cellulose acetate, as in the manufacture of films and plastics, have received attention.

It is scarcely necessary to apologize for the use of the term rayon instead of artificial silk, since the newer name has so much to recommend it. The application of the epithet "artificial" conveys the idea of an inferior substitute ; this may have been justifiable in the early days of the rayon industry, but is certainly not so to-day. Modern rayon is a textile material in a class by itself, and should be judged entirely on its own merits.

The frequent references to British patents were unavoidable, owing to the enormous volume of specifications which has appeared in connection with cellulose acetate during the past thirty years. The situation in regard to these patents is extremely complicated, and it is difficult to define what may or may not be done by the manufacturer who does not wish to run the risk of actions for infringement. The question of chemical patents in general was very ably discussed by Dr. Levinstein in an address to the Bristol Section of the Society of Chemical Industry in 1929, and some of his words are particularly applicable in the case of the acetate industry. He pointed out that nobody would start a new manufacture requiring capital if the consequences were to be a patent action costing anything from £600 to £1,000 per day, and that if a patent be granted to a wealthy corporation for something which has no real subject matter, the effect may be that the State is helping this corporation to oppress a smaller independent manufacturer, who is entitled to make and trade in the product claimed, but is afraid of fighting an action. The remedies suggested by Dr. Levinstein, viz. rigid examination for subject matter before the grant of a patent and a curtailment of existing monopolies, would give a new impetus to the chemical industry in general and to the cellulose acetate industry in particular.

In common with all other industries, the one with which we are concerned is suffering from the effects of a trade depression of such magnitude that it is scarcely possible to make any definite predictions concerning its future. But, as Mr. Courtauld indicated to his shareholders last year, if no immediate improvement is to be expected, considerable confidence may be placed in the more distant future. While he referred to the rayon industry in general, his remarks may also be applied to acetate rayon in particular. The hoped-for revival seems to have been brought appreciably nearer by the events of the last few months.

I am very much indebted to Dr. Kurt Hess for the loan of microphotographs of crystalline preparations of cellulose acetate, and of the diagram, Fig. 46; to Dr. H. Mark for photographs and diagrams to illustrate the section dealing with cellulose as revealed by the X-rays; to Dr. H. Suida for similar help in connection with the section concerned with the recovery of acetic acid; and to my wife for her assistance with references, and proof reading.

I have further to thank the Comptroller of H.M. Stationery Office for permission to quote from patent specifications and abridgments, and to reproduce diagrams from the same; and also the following firms who have lent blocks or photographs for the purposes of illustration: Messrs. Blairs, Ltd., Glasgow; British Carbo Union, Ltd., London; Thomas Broadbent & Sons, Ltd., Huddersfield; A. Gallenkamp & Co., Ltd., London; General Electric Co., Ltd., Birmingham; Goodbrands, Ltd., Stalybridge; The Northrop Loom Co., Ltd., Blackburn; Petrie & McNaught, Ltd., Rochdale; Prince-Smith & Stells, Ltd., Keighley; Francis Shaw & Co., Ltd., Bradford, Manchester; Shawinigan, Ltd., London; and William Whiteley & Sons, Ltd., Lockwood.

Finally my thanks are due to the Editor of the *Rayon Record*, for permission to reproduce portions of articles which have already appeared in that journal.

A. G. L.

HALIFAX.

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ABBREVIATIONS

The abbreviations used in the references follow the same system as that adopted by British Chemical Abstracts, except for the following :—

B.P.	British Patent.
D.R.P.	German Patent.
F.P.	French Patent.
U.S.P.	United States Patent.

In the case of British Patents, the addition of an asterisk to the number indicates that the patent is no longer in force, and the addition of a dagger after the number indicates that Renewal Fees are due on the patents concerned. In certain cases of expired patents, applications for extension of the term may be pending.

Abbreviations in the names of firms :—

A.-G.	Aktien-Gesellschaft.
Anon.	Anonyme.
Chem.	Chemische.
Cie.	Compagnie.
Elektrochem. Ind.	Elektrochemische Industrie.
Fabr.	Fabrication ; Fabrik.
Ges.	Gesellschaft.
I.G. Farbenind. A.-G.	Interessen Gemeinschaft für Farbenindustrie Aktien-Gesellschaft.
N.V.	Naamlooze Vennootschap.
Soc.	Société.
S.C.I. in Basle	Society of Chemical Industry in Basle.

CHAPTER I

INTRODUCTION

Although an acetate of cellulose was prepared as long ago as 1865 by Schutzenberger,[1] its industrial development has occurred during the past forty years, and it is a tribute to the patience, skill, and ingenuity of the chemists and technicians who have brought about that development that a great variety of fabrics dyed in fast and beautiful shades and made wholly or in part from cellulose acetate, as well as a range of moulded articles such as fountain-pen parts, motor-car fittings, lampshades, cigarette cases, etc., and also films and lacquers are available to-day at reasonable prices.

Rayon or artificial silk has been on the market for less than fifty years. In spite of its comparatively recent origin, however, it is no easy matter to decide how and when the idea of producing artificial textile fibres resembling natural silk originated. It is, of course, obvious that the earliest workers in this field were inspired by the activities of the silkworm, and they sought to produce a fibre resembling natural silk as closely as possible.

Natural silk is the coagulated secretion of various species of silkworm (*Bombyx mori*, *Bombyx mylitta*, etc.), and it forms the protective covering, or cocoon, within which the caterpillar develops into a moth. The silkworm has been cultivated in China from the earliest times, its origin being lost in the legendary history of that ancient country. According to these legends the first man, P'an ku, was followed by a number of celestial kings called Tien Wang, who were succeeded by eleven terrestrial kings or Ti Wang, and nine human kings known as Jen Wang. Following these came the Five Sovereigns: Fu-Hi, inventor of writing; Shin-nung, the patron of agriculture; Hwang-Ti, who introduced the fine arts; Shao-hao, who established the various classes of civil and military officials; and Chuen-hiu, inventor of the calendar. It was to the wife of Hwang-Ti that the art of raising silkworms and weaving silk was attributed, which therefore indicates the year 2500 B.C. for the birth of the silk industry. Of course, little

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[1] P. Schutzenberger. *Compt. rend.*, 1865, **61**, 485–6.

reliance can be placed on a date so derived, but the existence of such legends certainly indicates the great antiquity of the arts of spinning and weaving silken materials.

The secrets of silk production were very jealously guarded down the ages, and it is said that the cultivation of the silkworm was introduced into Europe from China by monks. The throwing of silk remained an Italian monopoly until in 1718 one John Lumbe, assuming the disguise of a workman, obtained entry into a Piedmont factory and made drawings of the machinery in use there. On his return to England he established a silk mill at Derby and for many years manufactured organzine of good quality. Factories sprang up in many places, and by the year 1770 there was a thriving silk industry in this country with a considerable export trade. During the next fifty years, however, although the industry continued to thrive under a policy of protection, the lack of foreign competition led to neglect of improvements and modernization of machinery, with a consequent falling-off in the quality of the goods produced. The abolition of the duties on raw silk in 1824, and the 50 per cent reduction in those on thrown silk led to an increased production of all kinds of silk goods, which continued until the invention of the power loom in 1861. Intoxicated by the possibilities of this machine, the manufacturers were led to over-production which, together with decline in quality, increasing wage rates, and further reductions in the duties in 1846, brought the industry to a sorry pass. In 1860 Great Britain and France signed a commercial treaty which, among other things, completely abolished the silk duties; from that time the industry steadily declined until the end of the nineteenth century, since when it has remained in a stationary condition.

The method of spinning employed by the silkworm is particularly interesting since upon it are based the processes used in the spinning of rayon. A large portion of the body of the worm is occupied by two large glands which secrete a viscous liquid which solidifies on exposure to the air. The spinning organ is a minute opening situated beneath the mouth of the silkworm and having a diameter of about 0·01 mm. By a muscular contraction the insect causes a drop of the liquid to exude from the opening or "spinneret" and attaches it to some neighbouring object; the spinning process proper then commences—by a series of backward jerks of the head and with the assistance of the forefeet, the liquid is drawn out into a thread, which solidifies almost immediately forming fibroin. Before the liquid reaches the spinneret it passes the opening of another gland which secretes a second liquid also possessed of the property of solidifying in the air to form sericin or silk gum. This gum serves to unite the two threads from the separate glands into a single fibre.

The raw silk as it comes from the cocoon is a brownish coloured fibre with a harsh handle owing to the coating of sericin upon the surface. Before the silk is thrown this gummy layer is removed by scouring with a hot soap solution, when the fibres become soft and lustrous, and when washed and dried are found to have the characteristic " scroop " of silk.

Silk threads are of uniform, almost circular cross-section, and have the following physical properties, when degummed :—

Fineness in deniers.	Breaking load in gms.		Loss per cent.
	Dry.	Wet.	
1·27	7·8	7·3	6·4

(P. Krais. *Textilindustrie,* 1924, p. 43.)

The fibre is very hygroscopic, being capable of absorbing more than 30 per cent of its weight of water from the atmosphere.

The idea of producing an artificial filament resembling natural silk can be traced back to the middle of the seventeenth century, for Hooke in his *Micrographia,* a work describing the microscopical examination of all kinds of plants, animals, minerals, and various other materials, mentions " a pretty kinde of artificial stuff . . . looking like transparent Parchment, Horn, or Ising-glass ". He found that this stuff could be dyed " with a great variety of very vivid colours, and to the naked eye it look'd very like the substance of the Silk ". He goes on to suggest that a way might be found of making " an artificial, glutinous composition much resembling, if not full as good, nay better, than that Excrement, or whatever other substance it be out of which the Silk-worm wiredraws his clew ". This was in 1664. Seventy years later de Reaumur[1] made a similar suggestion and proposed gum lac as a suitable substance for the preparation of an artificial silk. In 1840, Schwalbe, a silk manufacturer of Manchester, read a paper to the British Association describing a machine he had invented for the production of artificial filaments based on the process used by the

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[1] de Reaumur. *Mémoire pour servir a l'histoire des insectes,* vol. i, p. 154.

silkworm ; the paper attracted little attention, however, and was soon forgotten. The discovery of gun-cotton by Schonbein of Basle in 1846 was followed by the granting of a patent to Audemars of Lausanne [1] in 1855 for the manufacture of artificial threads from nitrocellulose derived from mulberry twigs ; the compound obtained was dissolved in an alcohol-ether mixture, together with some caoutchouc, and threads were drawn out from the solution with a needle and wound on reels. It is not stated whether the use of mulberry twigs as a raw material was suggested by the staple diet of the silkworm. During the next thirty years various attempts were made to utilize such substances as starch, glue, resins, tannins, fats, etc.,[2] or silk fibroin in conjunction with a spinneret [3] without success.

As is frequently the case it was the need of another industry which provided an incentive to further development, viz. the progress of the incandescent electric lamp trade. The earliest lamps had a carbon filament made by carbonizing cotton threads with sulphuric acid ; the search for a better filament culminated in the patent of J. W. Swann [4] in 1883, which described the spinning of a solution of cellulose nitrate in glacial acetic acid. Not only was the process used for making lamp filaments, but Swann also produced a certain amount of artificial silk which he denitrated with the aid of ammonium sulphide, and he later exhibited samples of cloth woven from this fibre at a meeting of the Society of Chemical Industry in London.[5] In the year following Swann's invention, Count Hilaire de Chardonnet [6] described an improved process of producing filaments from cellulose nitrate by extrusion into heated air, which at once evaporated the solvent ; this, incidentally, is the first example of a dry-spinning process. Although the costs of Chardonnet's method of manufacture were very high, and despite the absence of a satisfactory method of denitration, he was evidently satisfied with the possibilities of the industry for he at once founded the Société Anonyme pour la Fabrication de la Soie de Chardonnet at Besançon with a capital of six million francs. A factory was also acquired at Spreitenbach

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[1] Audemars. B.P. 283/1855.*
[2] Hughes. B.P. 67/1857.*
[3] Ozanam. *Compt. rend.*, 1862, **55**, 833.
[4] J. W. Swann. B.P. 5973/1883.*
[5] *J.S.C.I.*, 1885, 39.
[6] de Chardonnet. F.P. 165,349/1885.

in Switzerland, but so many difficulties were experienced that in 1890 reconstruction was necessary and a further six million francs were provided; it was not until 1895 that success was achieved and the first dividend paid.

During the same period a German named Lehner, who had been employed by Chardonnet at Spreitenbach, succeeded in simplifying the process by using a less viscous solution containing a mixture of cellulose nitrate and silk fibroin[1] or vulcanized drying oil.[2] He also greatly improved the denitration process by using ammonium sulphide together with a soluble magnesium salt to neutralize the alkalinity, and returned to the wet-spinning process of Swann using water or aqueous alcohol as the coagulating bath. He was producing on a commercial scale by 1898, and two years later his factory at Glattbrug and the Chardonnet factory at Spreitenbach were united under one control as the Vereinigten Kunstseide Fabriken A.G. Frankfurt-am-Main.

In the meantime research had been proceeding along other lines. The difficulty of successfully denitrating nitro silk led to the development of the cuprammonium process which had first been used by Weston for the production of lamp filaments in 1884.

The method was not used commercially for the production of artificial silk until 1897, when Frémery and Urbain obtained the rights of a patent due to Pauly[3] which describes a process substantially the same as that in use to-day in the cuprammonium industry. In 1891 Cross and Bevan had observed the formation of sodium cellulose xanthate from alkali cellulose and carbon bisulphide and obtained patents for the product,[4] which they termed " viscose ". Here again it was to the incandescent electric lamp that encouragement was due—C. H. Stern and C. F. Topham being commissioned by the Zurich Lamp Company to investigate the use of spinning baths consisting of aqueous solutions of ammonium salts.[5] Their efforts were so successful that the Viscose Syndicate, a firm established in 1893 to exploit Cross and Bevan's discoveries, decided to co-operate with Stern in forming the Viscose Spinning Syndicate, with a capital of £4000. To Topham we owe the invention of the centrifugal spinning-box, one of the

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[1] Lehner. D.R.P. 58,508/1890.

[2] Ibid. D.R.P. 82,555/1894.

[3] Pauly. D.R.P. 98,642/1897.

[4] Cross and Bevan. B.P. 8700/1892,* 4713/1896.*

[5] Stern and Topham. B.P. 1020/1898.*

most remarkable developments on the mechanical side of the artificial silk industry. From the commencement of the present century the viscose process steadily supplanted the older processes, and its manufacture was taken up by various firms, notably by Samuel Courtauld & Co. in this country; by the Société Française de la Viscose in France; and by the Fürst Guido von Donnersmarcksche Kunstseide und Acetatwerke at Sydowsaue in Germany, the latter firm being absorbed in 1911 by the Elberfelder Glanzstoffabriken. The viscose process still retains the first place both for cheapness and volume of production, forming about 85-90 per cent of the total world production of rayon to-day.

Cellulose acetate remained in the sphere of academic interest for nearly thirty years after its original preparation in 1865 by Schutzenberger, who heated cellulose and acetic anhydride in a sealed tube at 140° C.[1] It is very doubtful whether this original preparation can be truly described as cellulose acetate; the experimental conditions would no doubt produce considerable degradation, and it is to Franchimont and Girard that we must credit the first acetylation process using a catalyst, which was published some ten years later. During that period a large number of papers relating to the acetylation of cellulose and hydro cellulose were published by Hoermann, Girard, Liebermann, Guignet, Ewingst, Königs, Cross and Bevan, and others. A complete bibliography of these publications is given by E. C. Worden in his *Technology of Cellulose Esters*. With the appearance of the first of Cross's patents relating to cellulose acetate in 1894 [2] the industrial history of the subject may be said to have begun, although, as in the case of the other forms of rayon, many years were to elapse and innumerable difficulties had to be overcome before the industry could be said to be established on a profitable basis. The method described by Cross and Bevan was as follows: Hydrated cellulose was intimately mixed with a concentrated solution of two equivalents of zinc acetate and the mixture was dried and dehydrated at 110° C. After finely powdering, the product was mixed gradually with two equivalents of acetyl chloride to one of zinc acetate, the mixture being well stirred and maintained at a temperature below 30° C. The zinc salts were then removed by washing with water, and after pressing and drying, the cellulose

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[1] P. Schutzenberger. *Compt. rend.*, 1865, **61**, 485-6.
[2] Cross and Bevan. B.P. 9676/1894.*

acetate was extracted by such solvents as chloroform. The product was claimed to be of use for the manufacture of films, and in place of collodion varnish. In 1898 C. O. Weber, C. F. Cross, and I. Frankenberg[1] described the manufacture of so-called cellulose tetra-acetate by the action of a mixture of two molecules of acetyl chloride and one molecule of acetic anhydride upon regenerated cellulose (obtained from viscose) mixed with an equimolecular proportion of magnesium acetate. The reaction was controlled by the addition of a cellulose acetate solvent such as nitrobenzene or epichlorhydrin, and by the use of a jacketed mixer, the temperature being kept below 70° C. At the end of three hours the mixture was poured into alcohol, and the precipitated product was freed from traces of magnesium salts and dried below 80° C. Later in the same year they patented a similar process[2] in which zinc or magnesium acetate in concentrated solution was mixed with a molecular proportion of structureless cellulose, and after drying on the water bath the product was mixed with two molecular proportions of acetyl chloride and a small quantity of anhydride. The resulting mixture was heated on the water bath until thickening began, when addition of nitrobenzene was commenced in gradually increasing quantities, the amount added at each stage being just sufficient to keep the temperature below 70° C. The ester was then precipitated by pouring into alcohol. The patent was described in terms of cellulose esters generally. The value of these basic inventions was realized by Fürst Henckel von Donnersmarck, who secured the patent rights and developed a process at Stettin, marketing the product under the name of " Cellestron ". The rayon produced can have had little practical value, since the harsh treatment to which the cellulose was subjected must have resulted in considerable degradation, with consequent loss of strength. Indeed, all the earlier patents for the manufacture of cellulose acetate are remarkable for the high temperatures employed. The products were characterized by their solubility in chloroform and insolubility in acetone.

During the same period pioneer work was carried out in Germany by Eichengrün for the Bayer Co., and by Knoevenagel for Knoll and Co. The use of sulphuric acid as an acetylation catalyst is first mentioned in British patent literature by Lederer[3] and

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[1] C. O. Weber, C. F. Cross, and I. Frankenberg. B.P. 18,283/1898.*

[2] Ibid. B.P. 22,029/1898.*

[3] Lederer. B.P. 11,749/1900.*

a year later, in 1901, by Eichengrün.[1] The latter states that by using hydrocellulose a product soluble in water is obtained, although it is difficult to see what use such a cellulose acetate could have. Many other catalysts have been suggested from time to time, for use alone or in conjunction with sulphuric acid, but there is little doubt that with proper control the latter is the most successful compound for this purpose, and it may be safely conjectured that a very large proportion of the cellulose acetate of to-day is made by methods involving the use of that catalyst. In this connection, besides the zinc and magnesium salts of the early patents, mention may also be made of the use of copper and iron salts as catalysts.[2] There are also a large number of patents covering the use of sulphuric acid derivatives as aids to esterification, for example: ammonium bisulphate,[3] phenol sulphonic acid,[4] dimethyl sulphate,[5] ethylsulphuric acid,[6] aniline bisulphate,[7] etc. For a full index of the earlier patents and literature of this subject reference should be made to Worden's *Technology of Cellulose Esters*. The action of these catalysts is no doubt due to the more or less "free" sulphuric acid which they contain; the presence of basic radicals possibly exercises a modifying influence, preventing to some extent the degradation of the cellulose. In addition, such substances as nitric acid,[8] ammonium nitrate,[9] anhydrous copper salts,[10] trichloracetic acid,[11] monochloracetic acid,[12] chlorides of phosphorus,[13] and chlorides of sulphur[14] have been suggested as catalysts. These patents are interesting as indicating the trend of research, but none of the British ones are now in force; some of them, no doubt, were only applied for as "hedge" patents.

A notable landmark in the history of cellulose acetate was the

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[1] Eichengrün. B.P. 21,628/1901.*

[2] Knoevenagel. *Z. angew. Chem.*, 1914, **27**, 505. Cf. Knoll & Co., D.R.P. 203,178/1906 and 206,950/1907.

[3] Soc. l'Oyonnithe. F.P. 427,265/1911.

[4] Mork, Little, and Walker. U.S.P. 709,922/1902.

[5] A. Borti and *Fabr. de Produits Chimiques Flora Soc. Anon.* U.S.P. 826,229/1906.

[6] C. Dreyfus. F.P. 430,606/1911, abs. *J.S.C.I.*, 1911, **30**, 1375.

[7] F. Bayer & Co., U.S.P. 987,692/1911; B.P. 14,721/1910.*

[8] Knoll & Co. B.P. 8369/1907.*

[9] Lederer. B.P. 26,502/1906.*

[10] Safety Celluloid Co. B.P. 15,868/1912.*

[11] Knoll & Co. D.R.P. 20,364/1906.

[12] A.G. für Anilin Fabr. B.P. 14,255/1906.*

[13] M. Baltsch and J. F. Briggs. B.P. 10,243/1903.*

[14] Chem. Fabr. von Heyden. B.P. 24,382/1910.*

work of Miles, described in American and British patents in 1903-1905,[1] which was directed towards obtaining an acetate of improved solubility characteristics. The early types of cellulose acetate on account of their insolubility in common solvents of a non-poisonous nature, although they had been made the subject of numerous patent applications and great expectations had been based on them, were for all practical purposes valueless. Miles' process consisted in a partial hydrolysis with dilute sulphuric acid, and this is probably the basis of most of the methods of producing acetone soluble cellulose acetate now in use, since it possesses the virtue of simplicity. Efforts towards improving solubility were also made by Eichengrün, Becker, and Guntrum in 1905, by treating the primary acetate with weak acids, which converted it into a product readily soluble in acetone. Production on these lines was undertaken on the large scale by the Bayer Co., the product being known as Cellit, and until the commencement of the European war, they were the only company producing cellulose acetate on the commercial scale. The product was used for cinematograph films, non-inflammable celluloid (Zellon), lacquers, etc., but not for the manufacture of rayon. Cellit, while it resembled Miles' product in its acetyl content and solubility, differed from it in being insoluble in acetylene tetrachloride.

The development of the acetate industry as far as rayon was concerned was arrested by the outbreak of war in 1914. Research was at once concentrated in this country on the production of " dopes " for aeroplane fabrics, most of which had hitherto been produced in Germany. With the assistance of the British Government a company was floated in 1916 for the purpose of manufacturing cellulose acetate for war purposes, under the direction of Drs. C. and H. Dreyfus—the British Cellulose and Chemical Manufacturing Co., Ltd. The company successfully supplied the allied countries with " dope ", which entailed a very large production, and owing to the shortage of acetic acid and anhydride, considerable quantities of calcium carbide were made from which these essential materials were synthesised. With the close of hostilities it was necessary to find another outlet for the large production of cellulose acetate, and the earliest efforts were directed to the manufacture of non-inflammable films and celluloid, but with little success. Encouraged by the growing demand for

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[1] Miles. U.S.P. 733,729/1903; 828,350/1904; B.P. 19,330/1905.*

rayon, the company then turned its attention to spinning; here its efforts were successful, so that "Celanese", the company's trade-mark for rayon, has become a household word not only in Great Britain but in Canada, the United States, and many other countries. Of recent years the difficulties experienced in the production of films and celluloid substitutes have been largely overcome, and British Celanese, Ltd. (the new title of the company), now manufactures large quantities of so-called "plastics". It is gratifying to note that the major portion of the world's production of cellulose acetate is manufactured by British Celanese, Ltd., and its associated companies, and that the many improvements and new processes which have been evolved during the past ten years are in large part due to the researches of British chemists and technicians.

Two methods are available for the conversion of raw cellulose acetate into rayon, viz. wet spinning and dry spinning. Although the former is the more logical method of producing artificial filaments, since it possesses obvious advantages such as the reduction in the number of stages in the process of manufacture, the elimination of costly solvents and of the expense of their recovery, it has not yet proved satisfactory in practice for reasons which will be dealt with in the chapter relating to spinning. The dry or evaporative process for making filaments from cellulose acetate dissolved in volatile solvents was first described by Eichengrün in 1904,[1] and from acetone soluble cellulose acetate in 1906,[2] but the high price of the solvents used and the absence of a satisfactory method for their recovery rendered the rayon produced too expensive to compete with Chardonnet rayon. Thirteen years elapsed before acetate rayon was produced commercially by the British Cellulose and Chemical Manufacturing Co., Ltd., and since that date numerous improvements both in the spinning process and in methods of solvent recovery have been made. These will be described later in the appropriate chapters.

The final difficulty which prevented the general use of acetate rayon in the textile industry was the difficulty of dyeing. Since, unlike other rayons, acetate threads consist of cellulose acetate and not regenerated cellulose, they have no affinity for direct dyestuffs, and for the same reason, viz. absence of free hydroxyl

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[1] Farbenfabr. vorm. Fr. Bayer. F.P. 350,552; B.P. 28,733/1904.*

[2] Ibid. B.P. 24,067/1906.*

groups in the molecule, they have a low wetting power, which considerably increases the difficulty of the dyeing process. The earliest attempts to solve the problem were naturally directed to making coloured threads *ab initio* by the addition of dyes to the spinning solution,[1] or even by the acetylation of previously coloured hydrocellulose.[2] A logical deduction from the known composition of cellulose acetate led to saponification processes which sought to remove the acetyl groups from the surface of the fibre, thus leaving a layer which could be dyed with direct dyestuffs.[3] Methods depending on the action of swelling agents or solvents on the rayon previous to dyeing have also been used successfully [4] but, except in the case of certain dyeing "assistants", this process is now obsolete. It is only during the last ten years that the problem has been studied systematically, and to-day, as a result of the labours of the research staffs of British Celanese, Ltd., the British dyestuffs concerns, and of numerous continental companies, special dyestuffs for acetate rayon are obtainable in a wide variety of shades of great fastness to light and washing.

The story of artificial silk in general and of acetate rayon in particular forms one of the most romantic chapters in the history of industrial research. The story is one which also possesses its philosophical side, but with that we are scarcely concerned in this present volume. We should have taken leave of Professor Teufelsdröckh with even greater astonishment had he survived to interpret it for us.

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[1] L. A. Levy. B.P. 227,146.*

[2] Bayer. D.R.P. 237,210.

[3] H. S. Mork. B.P. 20,672/1910.* Cross and C. Dreyfus. B.P. 125,153*, etc.

[4] Briggs, Palmer, and the British Cellulose and Chemical Manufacturing Co., Ltd. B.P. 158,340. Knoevenagel. U.S.P. 981,574/1911, etc.

CHAPTER II

CELLULOSE AND ITS STRUCTURE: CELLULOSE ACETATE AND ITS PROPERTIES

> "Our raw material, cellulose, the principal constituent of all plant walls, is a typical colloid gel; in this lie all its merits and most of its problems."—DR. H. LEVINSTEIN, *Lecture before the Institution of Chemical Engineers, 24th January,* 1930.[1]

It is now close on a century since Payen described the action of various reagents upon the constituents of the cell walls of woody and other vegetable tissues, and was in consequence enabled to differentiate between cellulosic and non-cellulosic constituents.[2] He was the first to postulate that cellulose is the principal component of the membranes of all vegetable cells, and in 1859 he came to the conclusion that cellulose, from whatever source it is obtained, has the empirical composition $C_6H_{10}O_5$. The various theories which have been propounded to explain the formation of cellulosic tissues do not concern us here—they are adequately dealt with by Dr. K. Hess in his treatise on cellulose[3]—but it is interesting to note that the X-ray diagrams of the various tissues seem to indicate that the cellulose is identical in every case, being merely mixed with the other constituents of the cell wall, and not chemically combined with them.[4]

The chemical constitution of cellulose has been the object of an enormous amount of research work during the past seventy years, but owing to its colloidal nature and peculiar properties this complex carbohydrate has provided the organic chemist with an exceedingly difficult problem. The various formulæ suggested from time to time by workers in this interesting field need scarcely be reproduced since their merits and demerits have been dealt with in considerable detail in the standard works on cellulose;

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[1] *J.S.C.I.*, 1930, **49**, 55 T.

[2] A. Payen. Compt. rend., 1838, **7**, 1052; 1839, **8**, 51, 169; 1839, **9**, 149; 1840, **10**, 941. See also his *Mémoires sur les développements des végétaux*, Paris, 1842, p. 271.

[3] K. Hess. *Die Chemie der Zellulose*, Leipzig, 1928, p. 32.

[4] P. Scherrer. *Zsigmondy's Kolloidchemie*, 3 Aufl., 1920, p. 408. R. O. Herzog and W. Jancke. Ber., 1920, **53**, 2163; 1925, **58**, 1258.

we shall confine ourselves, therefore, to the important results obtained by Sir James Irvine, Professor W. N. Haworth, and their co-workers, as far as the purely organic side of the question is concerned, and pass to the physical side of the question.

It has been known for many years that cellulose yields d-glucose on hydrolysis; thus Braconnot in 1819 treated hemp and flax with sulphuric acid and claimed to have obtained a theoretical yield of a sugar which he stated was identical with starch sugar. More exact work carried out by Flechsig[1] in 1882 resulted in yields of d-glucose varying from 25 to 98 per cent according to the concentration of the sulphuric acid used for hydrolysis, and the conditions under which the experiment was carried out. This was confirmed by Ost and Wilkening[2] in 1910; on hydrolysis of cellulose with 2 per cent sulphuric acid for 1½ hours at 120° C., they obtained d-glucose in 95 per cent yield. Small quantities of by-products were obtained, consisting of organic acids and ω oxymethylfurfural, thus accounting for the difference between the theoretical figure (assuming cellulose to be $(C_6H_{10}O_5)_n$) and the actual yield of glucose.

In none of the above experiments was the glucose isolated, but reliance was placed on measurements of the optical rotation or reducing power of the solutions obtained. Irvine and Soutar and also Irvine and Hirst[3] have more recently shown that the transformation of cellulose into pure crystalline methylglucoside by acetylation followed by simultaneous hydrolysis and methylation gives a 95·1 per cent yield of glucose in the form of pure crystalline methyglucoside. Further confirmation was obtained by Monier-Williams[4] in 1921 by a modification of Ost and Wilkening's method, which enabled him to isolate the d-glucose in its pure, crystalline state in about 91 per cent of the theoretical requirement of the equation:

$$(C_6H_{10}O_5)_n + H_2O \rightarrow nC_6H_{12}O_6.$$

In addition to d-glucose, it is possible by submitting cellulose to graded hydrolysis by a process of acetolysis to obtain a disaccharide—cellobiose—in the form of its octa-acetate. The

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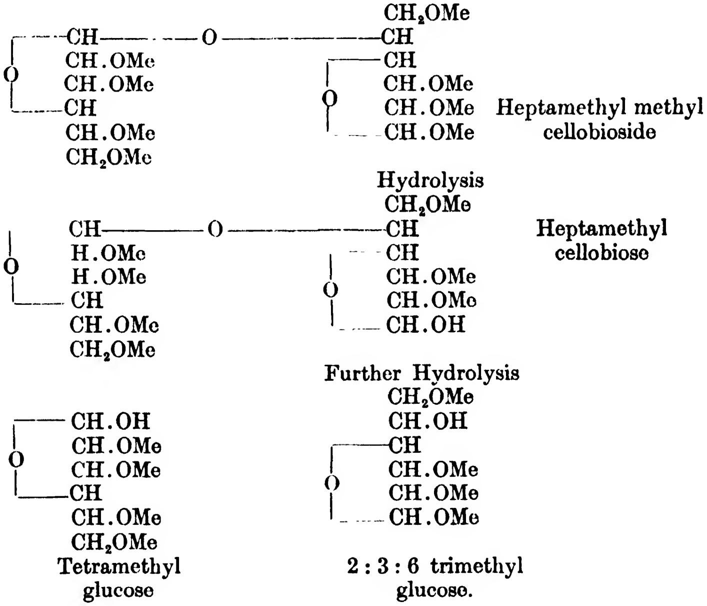
[1] E. Flechsig. *Z. physiol. Chem.*, 1883, **7**, 523.

[2] H. Ost and L. Wilkening. *Chem. Ztg.*, 1910, **34**, 460.

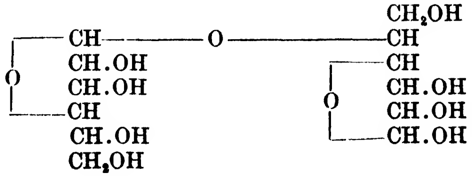
[3] Irvine and Soutar. *J.C.S.*, 1920, **117**, 1489. Irvine and Hirst. *J.C.S.*, 1922, **121**, 1585.

[4] G. W. Monier-Williams. *J.C.S.*, 1921, **119**, 803.

constitution of cellobiose was established by Haworth and Hirst,[1] who methylated its potassium compound by means of methyl sulphate and aqueous caustic soda with the production of hexamethyl-cellobioside; on treatment with silver oxide and methyl iodide this compound gave heptamethyl methylcellobioside. When the last-named compound was hydrolysed it gave a mixture of about equal amounts of tetramethylglucose and a trimethylglucose, which was found to be 2 : 3 : 6 trimethylglucose, i.e. identical with the product obtained by Denham [2] by the hydrolysis of methylated cellulose. These facts may be represented as follows —



whence it is concluded that the constitution of cellobiose is represented by :—



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[1] Haworth and Hirst. *J.C.S.*, 1921, **119**, 193.
[2] Denham. *J.C.S.*, 1921, **119**, 77.

The linkage of the two glucose residues in the above formula is characteristic only of natural carbohydrates, and the conclusion is drawn that cellobiose exists preformed in the cellulose molecule.

More recently Willstätter and Zechmeister[1] have obtained from cellulose, crystalline cellotriose and cellotetrose, all of which evidence clearly points to a long chain structure for cellulose, in which the units are glucose residues. This conclusion is also in accordance with the results of X-ray methods of investigation, which are dealt with in the following section. If this long chain hypothesis is correct, and if the glucose residues are united by principal valencies, it follows that the residues at the ends of the chain will have four hydroxyl groups, while the remainder will only have three. It would be possible to determine the length of the chain if the following series of reactions could be realized: (*a*) complete methylation of cellulose; (*b*) complete hydrolysis of the methylated cellulose obtained; (*c*) quantitative separation of the tetramethyl and trimethyl glucoses formed, when the proportion of the former to the latter will determine the length of the chain. Professor Haworth[2] has recently announced that he has succeeded in completely methylating cellulose, and that he has found only 0·55 per cent of tetramethylglucose in the products of hydrolysis; he therefore concludes that the cellulose molecule is a straight chain containing not more than 100 cellobiose or 200 glucose units, corresponding to a molecular weight of about 30,000, the lowest limit being 25,000.

Micellar Theory of the Structure of Cellulose.—When cellulose fibres are examined with the aid of the polarizing microscope they display various characteristic colours; this property is known as double refraction, and substances which possess it are said to be anisotropic. From a study of such substances C. von Nägeli,[3] the botanist, formulated the theory that cellulose and other organized bodies are not built up directly from molecules, but from groups of molecules, which he termed micellæ. These submicroscopic particles, he concluded, possess a crystalline structure, since they exhibit the phenomenon of double refraction. That the anisotropic property is inherent in the micellæ is demonstrated

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[1] Willstätter and Zechmeister. *Ber.*, 1929, **62**, 722.

[2] W. N. Haworth. *Nature*, 1932, **129**, 365.

[3] C. von Nägeli. Stärkekörner, 1858. Beobachtungen über das Verhalten des polarisierter Lichtes gegen pflanzliche Organismen; Theorie d. Gahrung. München, 1879.

by the fact that no amount of bending will alter the colours obtained when a thread of cellulosic material is observed with the polarizing microscope, but if a fine thread of glass be similarly examined, and then be bent, there is an immediate development of colour due to the strain set up, and the colours produced change as the direction of the strain is altered.

von Nägeli also explained in terms of his theory the difficulty which is experienced in dispersing cellulose, starch, and other complex substances in solvents, and the colloidal nature of the dispersions when they are obtained. In the case of a substance like sugar, dispersion to the stage of chemical molecules readily takes place in a solvent such as water; with cellulose, however, solvents such as dilute alkali have no power to rupture the intermolecular linkages within the micelle; in favourable circumstances, however, they may penetrate the intra-micellar spaces and give rise to swelling phenomena. Other solvents, for example cuprammonium solution, can not only penetrate between the micellæ in this fashion, but eventually succeed in separating them completely, giving rise to a micellar or colloidal dispersion. von Nägeli was of the opinion that the micelle is made up of a number of chemical molecules, but more recently it has been suggested that the micelle and the molecule are one and the same, the peculiar properties of such monomolecular micellæ being attributed to their large size. While this may be true in the case of many large molecules, e.g. those of certain dyestuffs, chemists and physicists are now returning to the views of von Nägeli in the case of such bodies as cellulose.

The micellar theory has received remarkable support of recent years, as a result of the study of cellulose, rubber, silk fibroin, and other natural products by the methods of X-ray spectrography. These methods as applied to cellulose have been developed by a number of distinguished workers including Debye and Scherrer, R. O. Herzog and his co-workers, K. Hess and I. R. Katz, Sponsler and Dore, Hengstenberg, H. Mark, Trillat, and others.

The Röntgen or X-rays are of a similar nature to light, but are characterized by their extremely short wave length (1·54 Å in the case of the *K* radiation from a copper anticathode, where Å- the Ångstrom unit is equal to 10^{-8} cm.); they are emitted by solid bodies interposed in the path of the cathode rays. The X-rays emitted by an element are made up of rays of different wave lengths; the number of such wave lengths is, however, comparatively small in the case of any given element. The decomposition of X-rays into their constituent wave lengths was first achieved by von Laue in 1912, who made use of the symmetrical lattice structure of a crystal as a diffraction grating, and in this way obtained an X-ray spectrum analogous to that which is formed when white light is analysed by passing it through a diffraction grating. It was found that the X-ray spectrum of every element consists of a number of lines which can be divided into series, the lines in each series lying very close to each other.

It was further found that if X-rays of a single series, for example the *K* series, from a copper anticathode, be passed through a single crystal and then received on a photographic plate, a diffraction pattern, called a Laue pattern, consisting of a symmetrically arranged series of spots, is produced. It is possible to determine by means of these patterns the arrangement of the atoms in the crystal; the remarkable results achieved in this field by Sir William Bragg and his son are too well known to call for further mention. If X-rays are passed through a crystalline powder in a similar manner, instead of the Laue pattern, a number of uniform rings is obtained when a photographic plate is exposed to the emergent rays; these are known as Debye-Scherrer rings. Yet a third type of pattern is obtained when cellulose, stretched rubber, silk fibroin, and other natural colloidal materials are examined by the methods of X-ray spectrography. In this case the pattern exhibits local intensity maxima corresponding to portions of the Debye-Scherrer

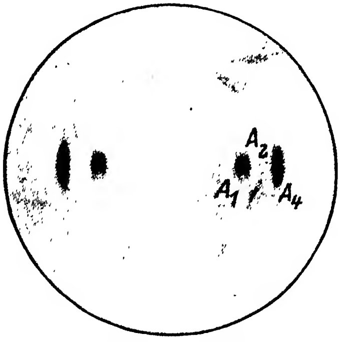

FIG. 1. X-ray diagram of ramie.

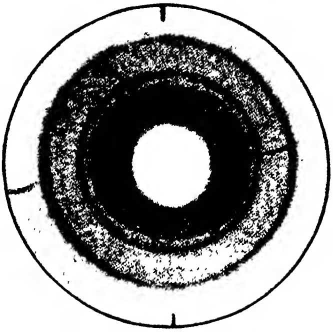

FIG. 2. X-ray diagram of raw cotton.

rings obtained with crystalline powders. Typical patterns of this nature obtained by Dr. H. Mark in the case of ramie and raw cotton are shown in Figs. 1 and 2. The X-ray tube used for these investigations is illustrated in Fig. 3, and consists of a Selmayr

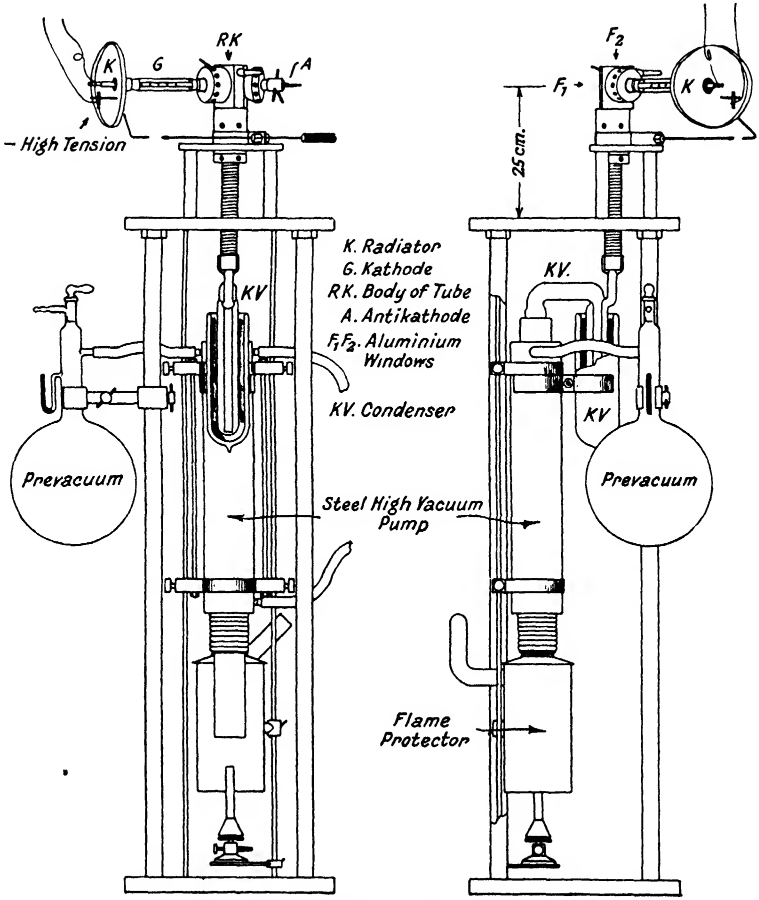

FIG. 3. Selmayr X-ray tube.

X-ray tube with a high vacuum pump attached. The X-rays are derived from a copper anticathode, *A*, and leave the tube through the aluminium windows, F_1, F_2.[1]

Since cellulose does not produce a Laue pattern it is evident that the fibre does not consist of a single crystal, and equally,

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[1] See also "Methods and results of the X-Ray investigation of sub-crystalline materials." F. D. Miles. *J.S.C.I.*, 1932, **51**, 247 T.

since it does not produce a series of Debye-Scherrer rings, it is not a haphazard collection of crystal grains. From the pattern actually obtained it is concluded that the fibre is built up of a large number of crystallites or micellæ having a crystalline structure, and so oriented that a common crystallographic direction of each micelle lies more or less parallel to the fibre axis. The diffraction pattern is the same, whether the cellulose be in the native condition or if it has been subjected to purification to remove hemicelluloses and other impurities, and it is therefore concluded that cellulose has a true and persistent crystalline structure.

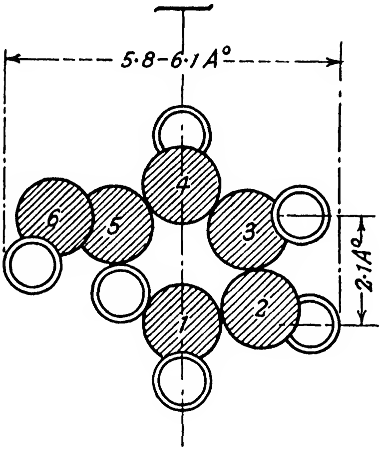

FIG. 4. Glucose Residue.

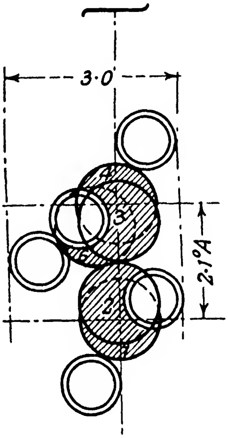

FIG. 5. Glucose Residue (side view).

From the analysis of measurements made on X-ray diffraction patterns of cellulose, Mark and Meyer[1] have deduced the facts that the unit crystal cell of cellulose belongs to the monoclinic system, and that it has the dimensions 8·5 × 10·3 × 7·9 Å. This unit cell contains four $C_6H_{10}O_5$ groups.

Mark[2] has constructed a model for cellulose based upon its properties and upon the results obtained by X-ray examination, and has compared the calculated intensity data with those actually observed. Starting with the usually accepted structural model of a dehydrated glucose residue (Figs. 4 and 5), in which the shaded circles represent the carbon atoms (diam., 1·4–1·5 Å) and the

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[1] Mark and Meyer. *Ber.*, 1928, **61**, 593; *Z. phys. Chem.*, 1929, 2 B, 115.
[2] Mark. *Melliand's Textilber,* 1929, Sonderdruck No. 9.

double circles the oxygen atoms (diam., 1·2–1·3 Å), he passes to the cellobiose residue (Fig. 6), which is formed by the union of two glucose residues by a 1 : 4 oxygen bridge. Hitherto it had been postulated that a unit crystal cell should contain a whole number of molecules, but in view of the high molecular weight of cellulose, and of its distinctive fibrous structure, it is scarcely likely that the unit cell will contain isolated cellobiose residues. It is therefore concluded that long chains of glucose residues are built up, the individual glucose residues being united by the primary valencies of the 1 : 4 oxygen bridges. These are known as Principal Valency Chains. The molecule of cellulose is as long as the principal valency chain, which may be 500 Å in length. To explain the fact that the periodicity along the fibre axis is only 10·3 Å, it is assumed that the chain has a screw formation, in which each turn of the axis corresponds to the periodicity. A model constructed on these lines accounts for all the experimental data obtained by X-ray methods.

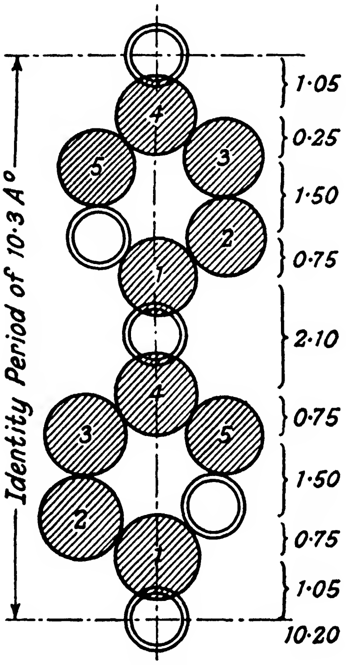

FIG. 6. Cellobiose Residue.

From forty to sixty of these principal valency chains, held together in a bundle by the auxiliary valencies of the hydroxyl groups and oxygen bridges, form the micelle. Finally, the micellæ are built up into macroscopic fibres, being held together by tertiary forces. A summary of the various magnitudes involved in the case of ramie, as given by Mark and Meyer,[1] is set out below :—

Unit.	Weight.	Volume. cc.	Surface. sq. cm.
Glucose residue . .	162	—	—
Cellobiose residue . .	324	—	—
Unit cell . . .	648	$6 \cdot 8 \times 10^{-22}$	—
Micelle . . .	$\sim 10^5 – 10^6$	$1 \cdot 2 \times 10^{-18}$	$8–12 \times 10^{-12}$
1 g. substance . .	—	$\sim 0 \cdot 6$	$1 \cdot 3 \times 10^7$

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[1] Mark and Meyer. *Z. phys. Chem.*, 1929, 2B, 128.

Unit.	Glucoses.	Cellobioses.	Unit Cells.	Micellæ.
Glucose residue	1	—	—	—
Cellobiose residue	2	1	—	—
Unit cell	4	4	1	—
Micelle	6000–12,000	3000–6000	1500–3000	1
1 g. substance	$3 \cdot 7 \times 10^{21}$	$1 \cdot 8 \times 10^{21}$	$\sim 9 \times 10^{20}$	$3 \cdot 7 \times 10^{17}$

These findings are in striking agreement with the conclusions arrived at by purely chemical means, and indicate that the cellulose molecule is not necessarily well-defined, but that its length may vary within certain limits. The micellæ, as well, may also vary somewhat in length and thickness, thus accounting for the variations which occur in natural fibres.

The micellar theory is of great value, since it enables us to explain the properties of cellulose and of its derivatives, and to account for their behaviour with various solvents and reagents. Thus, it has been found that mercerized cellulose has a unit cell shorter than that of the original substance, along the fibre axis, and longer on the other axes. This is referred to a turning of the cellobiose chains through an angle of approximately 45°, half in one direction and half in the other. The increase in the dimension of the unit cell at right angles to the fibre axis is due to an opening of the oxygen bridge linkages between parallel cellobiose chains, and it is this which probably accounts for the greater reactivity of mercerized compared with original cellulose. It has been found that pretreatment of cellulose before acetylation with various reagents increases its reactivity ; this is probably due to an opening up of the micelle by the treating agent with consequent exposure of free hydroxyl groups, which are normally protected by the structure of the micelle. The theory also explains the necessity for employing only cellulose with a high α cellulose content as a raw material for the manufacture of cellulose acetate. The drastic purification which other forms of cellulose, such as wood-pulp, receive, results in micellar degradation with consequent loss of viscosity in their derivatives, and decreased tensile strength in the artificial fibres derived from them.

That the micellar structure persists when cellulose is modified in various ways, as for example by esterification, is indicated by the well-marked X-ray diffraction diagrams which are obtained with treated fibres. Thus, cotton may be fully acetylated without losing its fibrous form, and the acetylated fibre gives a characteristic diagram with a periodicity along the fibre axis of 10·3 Å, the same as in cellulose itself. Such a diagram, due to Dr. Mark, is shown in Fig. 7. In the case of cellulose acetates prepared by a process which involves complete solution and loss of the fibrous form, there is complete loss of orientation of the micellæ, and films produced by dissolving such an acetate in acetone, followed by evaporation, give X-ray diagrams characterized by broad diffused rings. It has been shown by Trillat,[1] however, that the X-ray diagrams for such films are modified by the application of tension, the rings gradually becoming ellipses, and as the tension reaches still higher values, new intensity maxima appear in the same positions as those which are characteristic of the substance in the crystalline state. It is clear that the application of tensile forces tends to improve the orientation of the micellæ, although this never reaches the perfect alignment found in the natural fibrous state.

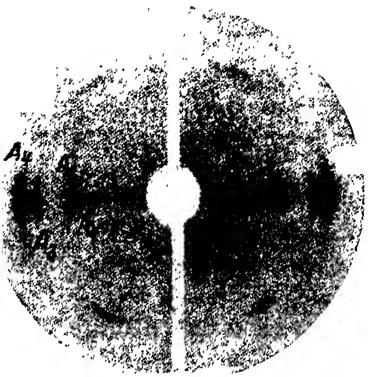

FIG. 7. X-ray diagram of cellulose acetate.

It would appear that the hemicelluloses (β and γ celluloses) which occur to a small extent in cotton and the nobler celluloses, and to a greater extent in celluloses which have received harsher purification treatment, such as wood-pulp, are fragments broken from the cellulose micelle. It is, of course, impossible to subject cellulose even to the mildest chemical treatment without causing some degradation, so that it is difficult to say exactly what is the condition obtaining in the native cellulose. Much work remains to be done in this important connection.

CELLULOSE ACETATE

The properties of a given sample of cellulose acetate will depend upon the method of preparation which has been used. The primary acetate made by the method outlined in Chapter IV has the following properties :—

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[1] Trillat. *J. Phys. Radium*, 1929, **10**, 370.

Appearance	Translucent, horny fragments.
Total sulphate	1–2 per cent.
Fusion point	Below 190° C.
Acetyl content	58–61 per cent.
Acetone	Insoluble or soluble with difficulty.
Chloroform	Readily soluble.
*Alcohol-benzene	More than 15 drops of water required to bring sample into solution.

The secondary acetate made by the ripening and stabilizing process described in Chapter IV has the following characteristics :—

Appearance	White, friable, fibrous masses.
Total sulphate	Less than 0·1 per cent.
Fusion point	240–300° C.
Ash	Not exceeding 0·15 per cent.
Acetyl content	53–55 per cent.
Free acetic acid	Not exceeding 0·01 per cent.
Acetone	Readily soluble to a clear, brilliant solution.
Chloroform (hot)	Very good plastic.
,, (cold)	Granular plastic.
*Alcohol-benzene	1–2 drops of water required to bring sample into solution.

* For explanation of this test see p. 66.

Although cellulose acetate as generally prepared, whether it be primary or secondary acetate, is in an amorphous condition, Dr. Hess has succeeded in preparing both triacetylcellulose and the lower acetates in a crystalline form.[1] In the case of the triacetate, a 1–2 per cent solution of the carefully purified substance is prepared in tetrachlorethane, and submitted to very slow concentration. After two to three months a fine precipitate forms, some of which falls to the bottom of the containing vessel, and the remainder is suspended in the form of a cloud. This is probably non-cellulosic material, and is filtered off. The filtrate after further concentration for two to three months commences to deposit crystals, which continue to increase in number and grow, until in about a year's time most of the cellulose acetate has crystallized out in the form of masses which exhibit double refraction under the polarizing microscope (Figs. 8 and 9). Many single well-defined crystals are also observed. After decanting the yellowish mother-liquor, the crystals are dissolved in fresh tetrachlorethane. It is observed that the cellulose acetate is much more difficult to dissolve

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[1] K. Hess. *Die Chemie der Zellulose*, Leipzig, 1928, pp. 395–8.

than the original preparation. On slow concentration of the resulting solution, further crystals are obtained, as shown in Figs. 10 to 12. Figs. 10 and 11 are in polarized light, while Fig. 12 is the same as Fig. 11, but in ordinary light. Fig. 13 (in polarized light) represents well-formed crystals which it is possible to obtain on the first concentration. The crystals probably belong to the rhombic system. Besides this rhombic form, needle-shaped crystals are also formed, but these are evidently in a metastable condition, as they are observed to change into the rhombic form gradually. That the crystalline form is identical with the amorphous form is demonstrated by dissolving the crystals in chloroform and precipitating them with ether. According to more recent researches to be published shortly in the *Zeitschrift für physikalische Chemie*, Abt. B, by Dr. Hess, it appears probable that these crystals are double compounds of acetylcellulose with the solvent.

The so-called diacetate (Bayer's Cellit) can also be prepared in crystalline form by very slow cooling of a solution in equal volumes of alcohol-benzene. The regularity of the crystals increases on repeated crystallization.

Dispersions of Cellulose Acetate.—It has become customary to refer to solutions of cellulose acetate in various solvents in the same way that one refers to solutions of sugar or salt in water; this is misleading, for cellulose acetates do not dissolve in that sense but they form colloidal dispersions. We may picture the process of dispersion of cellulose acetate in an organic solvent as a gradual penetration of the intermicellar spaces by the solvent followed by a complete separation of the micellæ. The solvent power of a liquid for cellulose acetate will depend upon its power to bring about this separation. In the case of primary acetates (triacetate) chloroform readily penetrates between the micellæ, and effects their separation, with complete dispersion of the substance; acetone, on the other hand, can only partially penetrate the intermicellar spaces and therefore only brings about a swelling of the acetate. With secondary (acetone-soluble) acetates, the converse is true: chloroform merely causing swelling, while acetone disperses the substance completely. The study of the dispersion of cellulose acetates in various solvents is rendered difficult by the complex nature of the acetates themselves, and no satisfactory explanation of the facts is at present available;

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.

Fig. 12.

Fig. 13.

[*To face page* :

most of the work which has been done is of an empirical nature, being directed towards practical ends; and the subject offers a wide field for profitable and interesting research. In the case of the secondary acetates, as indicated in Chapter IV, it seems probable that the presence of reverted cellulose or the presence of accompanying moisture, or acetic acid and moisture, tends to prevent dispersion in chloroform, but is essential to dispersion in acetone.

Hess,[1] as a result of the X-ray investigation of the swelling and dispersion of cellulose acetate in organic solvents, has concluded that the process of dispersion proceeds further than the micellæ, the solvent penetrating the micelle itself, and breaking it down into smaller molecular aggregates. This is in agreement with the work of Sheppard and Keenan,[2] carried out in the Kodak Research Laboratories, on the measurement of thin films of cellulose esters. These films were produced by allowing a solution of the derivative to evaporate on a mercury surface. The thinnest coherent films of cellulose diacetate (acetyl ca. 38 per cent) had a thickness of 4·1 Å and those of a triacetate (acetyl 44·6 per cent) 9·5 Å. They concluded that such a small dimension could hardly be the diameter of a spherical molecule, and that it therefore represents the transverse dimension of long, chain-like or sheet-form molecules, oriented parallel to the surface (instead of end-on, as in the case of fatty acid molecules). Sheppard and Houck [3] conclude that in sufficiently dilute dispersions of cellulose acetate in certain solvents the crystallites (or micellæ as we have hitherto termed them) do not necessarily persist as entities, the ultimate "micellæ" in such dispersions being either chain- or leaf-like structures, produced by intra-crystallite swelling and complete solvation, and which are of molecular dimensions transversely. They further state that in more concentrated dispersions, aggregation of these macromolecules to micellæ of higher order would be expected, and that a study of dispersions produced by careful concentration of these dilute dispersions is under way.

Viscosity.—The viscosity of cellulose acetate dispersions depends upon the nature of the acetate, and of the solvent or solvents

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[1] Ibid. *Z. angew. Chem.*, 1930, **43**, 178.

[2] Sheppard and Keenan. *Nature*, 23rd June, 1928. R. L. Keenan. *J. phys. Chem.*, 1929, **33**, 371.

[3] Sheppard and Houck. *J. Rheology*, 1929, **1**, 20.

used, and upon the temperature of the dispersion. From the point of view of rayon manufacture, dispersions in which acetone is the solvent are of the greatest interest.

The viscosity of dispersions of cellulose acetate in acetone increases rapidly with the concentration. It would appear from the conclusions of Sheppard, outlined above, that this is due to the changing state of aggregation as we pass from the dilute to the more concentrated dispersions. Earlier workers attributed the increase to the formation of molecular complexes between the ester and the solvent, but there is little or no evidence to support this view.

Sheppard and Houck (loc. cit.) have shown that the addition of polar solvents such as methyl alcohol or water to acetone dispersions of cellulose acetate cause a reduction in the viscosity. This is not a simple dilution effect since, if viscosity be plotted against composition of solvent mixture for any given concentration of cellulose acetate, the curve exhibits a minimum viscosity. The cellulose acetate used in these experiments had an acetyl content of 39·7 per cent, and the concentration of acetate was 20 per cent. In the case of acetone-methyl alcohol mixtures the minimum viscosity occurred when there was about 14 per cent of methyl alcohol in the solvent mixture. The acetone-water dispersions examined contained 10 per cent of cellulose acetate, and here the minimum occurred when 4·5 per cent of water was present in the solvent mixture. Similar results have been obtained by the author in the case of acetone-water dispersions of commercial cellulose acetates having acetyl contents of 53–4 per cent. Dispersions containing 0 to 5 per cent of water are quite stable, but those containing more than 5 per cent of water tend to form gels on standing. Similar results were obtained by Barr and Bircumshaw [1] using "Dreyfus" acetate in 5 per cent dispersion in acetone-water mixtures; in this case the minimum viscosity occurred with about 6·5 per cent of water present in the solvent mixture.

The viscosity of cellulose acetate dispersions diminishes with increasing temperature. The curve, Fig. 14, shows the effect of temperature on the viscosity of a dispersion of 15 parts of cellulose acetate in a mixture of 80 parts of acetone and 5 parts of water, the acetate having an acetyl content of 53·2 per cent. It will be

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[1] Barr and Bircumshaw. *Report on the Physics and Chemistry of Colloids*, London, 1921, p. 72.

noted that there is very little decrease in viscosity after the temperature has reached 35–40° C.

It has been customary to regard the viscosity of cellulose acetate as an index of the tensile strength to be expected in films and filaments derived from it. Chaumeton and Yarsley[1] have very properly pointed out that while this may have been true to some extent in the case of the earlier acetates, recent research work indicates that there is little direct connection. Given two samples of cellulose acetate prepared from similar cellulosic material, if one has been prepared by high temperature acetylation and the other by a low temperature process, the former will have a lower viscosity than the latter, and will yield fibres of a lower tensile strength. Both these results are due to the increased degradation undergone by the cellulose at the higher temperature. As will be realized after a perusal of Chapter IV, some degradation is inevitable

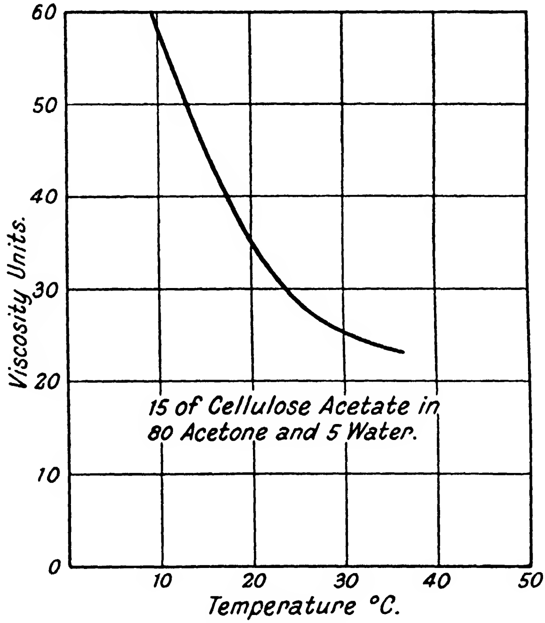

FIG. 14. Variation of Viscosity of Cellulose Acetate Solution with Temperature.

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[1] Chaumeton and Yarsley. *British Plastics*, 1931, **2**, 452.

in the preparation of cellulose acetate on a commercial scale, and it is not yet possible to control completely the amount of such degradation. Two samples of cellulose acetate, for example, prepared from the same raw material under exactly the same conditions, may vary as much as 10 per cent in viscosity. It is evident therefore that viscosity does form a guide when examining the products of a factory which employs a standardized method of manufacture. It is also necessary to determine the viscosities of the various batches of cellulose acetate in order to be able to blend to a constant viscosity, thus facilitating filtration. It is useless, however, to attempt to reduce the viscosity of a blend to the desired figure by including in it batches of acetate which have been deliberately prepared with a low viscosity by allowing the acetylation temperature to rise above the usual limit. The viscosity will certainly be lowered, but the quality of the rayon spun from the blend will also be lower.

CHAPTER III

RAW MATERIALS

Cellulose.—The most important kind of cellulose, as far as the manufacture of cellulose acetate is concerned, is cotton, which is the name given to the seed hairs of plants of the species *Gossypium.* The natural function of these hairs is to enable the plant to propagate by the dissemination of its seeds by the wind, and in this respect they resemble the hairs attached to the familiar dandelion seed. The cotton plant is a native of India, but it is now cultivated in many parts of the world possessing a tropical climate. The most important varieties are *G. hirsutum,* which is widely cultivated in the United States, and *G. barbadense,* grown in the West Indies, and forming the Sea Island Cotton of commerce. The latter variety is also grown in Egypt and Brazil, while other less important kinds include *G. vitifolium* (Pernambuco), *G. conglomeratum, G. acuminatum* (India), *G. arboreum* (India), and *G. herbaceum* (Macedonia and Bengal).

The cotton fibre is a unicellular seed hair, and appears under the microscope as a broad, spirally twisted band, pointed at the end remote from the seed, and having a central lumen. It consists of the cell-wall proper constituting the bulk of the material of which the hair is made up, an outer layer or cuticle, and an inner layer consisting of a small amount of dried protoplasmic residue.

Chemically, cotton is almost pure cellulose, but contains in addition small quantities of fats, proteins, mineral matter, and colouring substances. These " impurities " as we must regard them from the chemical point of view, are contained chiefly in the cuticle, and are removed along with it during the bleaching process, during which the cotton loses about 5 per cent of its original weight.

The specific gravity of cotton is about 1·5, and the fibres vary in length (" staple ") from 10 to 50 mm. according to the variety, *G. barbadense* supplying the longest staple cotton, and *G. herbaceum* the shortest. The thickness of the fibres varies from 0·01 to 0·05 mm. In contrast to other seed hairs, cotton has a very high tensile strength, the breaking load of a single hair varying between

5·3 and 6·4 grm., and the tensile strength varying between 2·2 and 4·5 dynes per sq. cm., according to Clegg and Harland.[1] Occasionally there are to be found unripe and dead fibres ; in these there is no twist, and the lumen is absent. The tensile strength of such fibres is small, they dye very badly, and may be recognized chemically by the slow rate of solution in Schweitzer's reagent, during which process they develop none of the characteristic bulbous swellings produced in ordinary cotton by that reagent. Owing to the more or less complete absence of cuticle they dissolve rapidly in concentrated sulphuric acid.[2]

Staple fibre is, of course, too expensive for use as a raw material for the manufacture of rayon ; fortunately, however, in addition to the longer hairs forming the staple fibre, the cotton seed is also covered with short hairs, which are not removed during the ginning process. These short hairs are known as cotton linters, and they form the principal source of cellulose for the manufacture of cellulose acetate. Spinners' waste may also be used for the manufacture of acetate, but in both cases purification is necessary before the material is suitable for esterification. The rayon manufacturer will generally purchase cotton linters in a condition ready for use, but a knowledge of the methods used in preparing the so-called " chemical cotton " is necessary for a proper understanding of its properties, and a brief description of these methods will therefore be given.

The staple fibre is first removed from the ripe cotton seeds by the action of a machine called a gin ; following this treatment the seeds are freed from foreign matter, sand, vegetable debris, etc., and are then submitted to the action of a linters or saw gin, which contains a number of high-speed circular saws. According to the adjustment of the machine, the percentage of fibre removed from the seed varies ; the adjustment of the machine is known as the setting, and the quantity of fibre removed as the cut.[3] According to Munson (loc. cit.) three types of linters are produced : a low first cut, mill run, and second cut. The first and second cuts, as their names imply, are obtained in two successive operations, while the mill run consists of fibre produced in one operation.

Standards for raw linters were set up by the U.S. Department of

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[1] Clegg and Harland. *J. Text. Inst.*, 1923, **14**, 489. Clegg. *Idem*, 1924, **15**, 1.
[2] J. von Wiesner. *Die Rohstoffe des pflanzenreichs*, 4th ed., vol. i, p. 502.
[3] Munson. *I. and E.C.*, 1930, **22**, 467.

Agriculture in 1924, at the request of the Cottonseed Crushers' Association, and Munson (loc. cit.) states that most of the chemical cotton now produced is from second cut linters corresponding to U.S. Grades 6 and 7. He gives the following figures as a typical analysis of raw linters :—

	Per cent.
Chemical yield of cellulose by caustic soda digestion . .	80–85
Ash	1·0–1·5
Iron	0·06
Ether extract	1
Lignin insoluble in sulphuric acid	3
Moisture	6

In plant practice the yield is about 5 per cent lower than that stated above owing to mechanical losses.

Chemical Purification.—The following account is due to Munson (loc. cit.): 7,000 lb. of linters are opened into the digester, a large cylindrical vessel capable of being rotated, into which is pumped a solution of caustic soda of constant volume and percentage (2·3–3·5). The digester is rotated and steam is introduced through each end below the liquid level, and the pressure is raised to that required for cooking, varying from 40–80 lb. according to the chemical characteristics required in the final product. Throughout the cooking period (3–5 hours) the digester is rotated to ensure agitation and constant mixing of the contents. At the end of the cook the pressure is released, and water is introduced through the ends to dilute the caustic soda solution and to serve as a first wash. This treatment disintegrates and dissolves the non-cellulosic materials. After cooking the batch is dropped through manholes into a steel wash tank, where it is washed with water until free from caustic soda and black liquor. The linters are then pumped to the bleaching tubs, which are of wooden stave construction, fitted with vertical agitators and perforated false bottoms to permit drainage of spent bleach and to allow of washing. When the cotton is at a definite temperature the measured quantity of available chlorine in the form of calcium hypochlorite (0·75–1·25 per cent) is introduced, and the batch is thoroughly agitated. After draining the discoloured solution a measured quantity of dilute sulphuric acid is added to accelerate bleaching and to reduce ash content. The process is modified according to the qualities required in the resulting linters. Sodium bisulphite or other reducing agent is used as an antichlor. An oxalic solution is sometimes used after bleaching to reduce the iron content. The linters are finally washed. In a concentration of less than 0·5 per cent of cotton in water the liquid is pumped through a riffling system, where removal of foreign matter of a higher density than water is effected. It is thus possible to deposit in traps sand, cinders, and even fine silt-like organic matter not removed by the digestion process. The drying process is continuous, each digester charge retaining its identity throughout the process. The cotton cellulose is then conveyed through rubber squeeze rolls for extraction of water to less than 50 per cent bone dry, into a Sargent wet picker, which blows the opened cotton on to the travelling apron of a continuous air drier. The material progresses at comparatively slow speed to the dry end of the dryer, air being continuously circulated over steam coils through the cotton. With the cotton picked and fluffed up by the agitation during the drying it is possible to employ air at the comparatively low drying temperature of 150–160° F. The finished linters are baled in 100–150 lb. bales. The following is a typical analysis of purified and bleached linters :—

	Per cent.
α cellulose	99
Ash	0·10
Ether extract	0·20
Lignin insoluble in sulphuric acid	0·20
Iron	0·002
Moisture	5

Various sources of information regarding the purification and bleaching of raw cotton linters differ in their details from the above process, and it is probable that each manufacturer of linters has his own methods, which are modified according to the purpose for which the cotton is required. Sometimes a purifying solution is used containing not more than 5 per cent by weight of caustic soda, and about 3 per cent of soda ash, and higher concentrations of available chlorine up to 7 or 8 per cent have been used. The bleaching bath may be made up with electrolytic bleach liquor. It is preferable to use a series of light bleaches rather than one heavy one.

In order that the spinning solutions shall filter easily and therefore economically, it is necessary that the cellulose acetate used should have a high clarity, i.e. be free from dirt and unacetylated fibres. The latter factor depends upon thorough acetylation, which in turn is dependent on the nature of the cotton linters used. Cotton linters which have received a severe purification are usually more reactive and therefore acetylate more readily than those which have received a mild treatment. On the other hand severe treatment probably results in breaking down of the micellæ to some extent, and even in a certain degree of degradation of the cellulose, both of which are undesirable. It is therefore necessary to strike a mean between over-purified linters which give high clarity, low viscosity, and uniform acetylation, and under-purification which gives poor clarity, high viscosity, and possible over-acetylation or acetylosis of a part of the batch. This result should be achieved by the chemist acting in conjunction with the suppliers of linters before a contract is signed, and once a satisfactory material has been found, the standard should be rigidly maintained and insisted upon, or costly difficulties will arise in the spinning section of the factory.

It is now generally accepted that the viscosity of a cuprammonium solution of cotton determined by a standard method gives a fair indication of the viscosity which is to be expected in the acetylated product, provided that the methods of acetylation and ripening are standardized. According to Munson (loc. cit.) a reduction in viscosity may be obtained, if necessary, by more drastic chemical treatment. The temperature of digestion is the most important factor, time of treatment and concentration of alkali having correspondingly less effects. He states that to produce lower viscosities economically it is best to adopt high pressure cooks of 80 lb. or more. Bleaching also tends to reduce viscosity, and in practice the relative reduction of viscosity in each stage of the purification process is established for each viscosity type of cellulose produced. Tests made on samples after digestion permit the modification of subsequent processes, with consequent control of viscosity. Technical control of plant operations is difficult, and the results are not infallible (Munson, loc. cit.).

The cotton linters as they are delivered in England will contain from 8–10 per cent of moisture, but more may be present if they have been exposed to damp conditions in transit. The determination of the average moisture content of consignments immediately on delivery, and a moisture clause in the contract with the suppliers are therefore matters of great importance.

When the bales are opened it will be found that the linters can be readily separated into layers about 4–6 inches thick, parallel to the ends of the bale. These layers or slabs are fed into the opening end of an opening and drying machine (Fig. 15), which by means

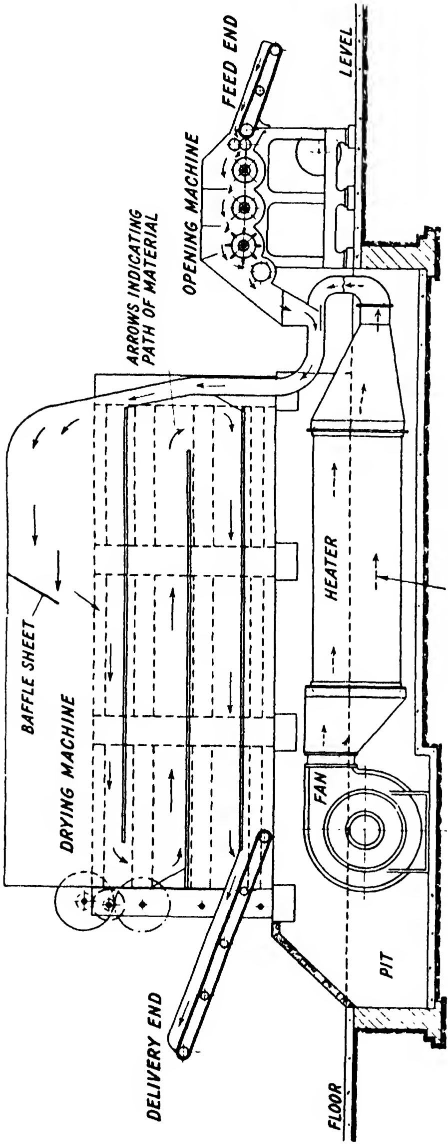

Fig. 15. Linters Opening and Drying Machine (Section). (Petrie and McNaught, Ltd.)

of breaking and teasing rollers opens up and separates the linters into small bundles of fibres. The opened linters are then blown by a heated air current in the direction shown by the arrows on to a travelling belt, of which there are three, one above the other, the middle one moving towards the opening end of the machine, and the others travelling to the delivery end. The effects of the drying process and amount of remaining moisture will vary with the acetylation process used—for the milder methods in use at the present time, the drying temperature should not exceed 60° C. Higher temperatures harden the fibre causing difficulty and lack of uniformity in the acetylation process. In this connection it is probable that age is a determining factor, for it has been found that cotton after being stored for some months develops hard fibres and does not acetylate so well as originally. This may be due in part to surface oxidation, and in part to further slow drying.

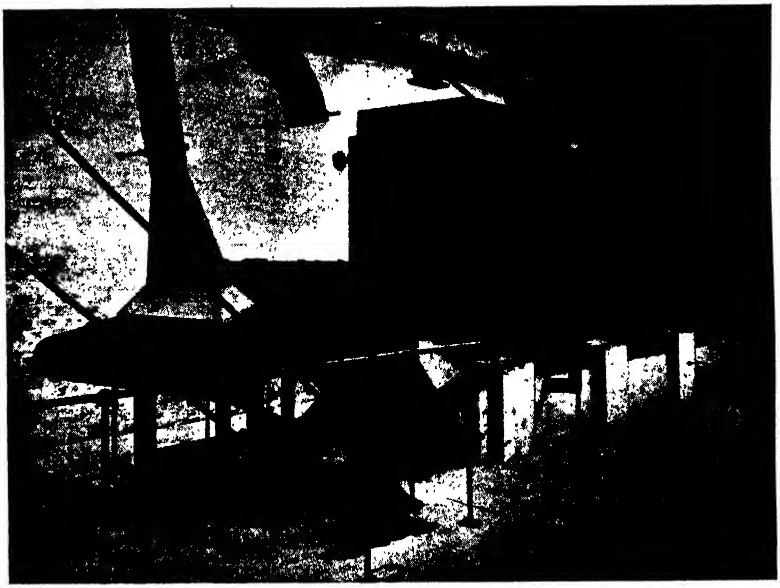

FIG. 16. Linters Opening and Drying Machine. (Petrie and McNaught, Ltd.)

The fibres in cotton linters vary in length from 2–3 mm. down to fine dust. It is very important that this dust shall remain evenly distributed during the drying process, otherwise it tends to produce bunches in the acetylation process which are difficult to wet, thus giving rise to uneven acetylation. For this reason the type of machine illustrated in Figs. 15 and 16 is more satisfactory than a machine in which the linters are blown through a fan. The machine illustrated is made by Messrs. Petrie and McNaught, Ltd., of Rochdale.

The methods of analysis for cotton linters are outlined in Chapter VII.

Other Sources of Cellulose.—Attempts have been made from time to time to substitute other forms of cellulose for the cotton which is generally used in the manufacture of cellulose acetate, mainly with the object of cheapening the process of manufacture. Ramie, flax, and hemp are examples of bast fibres, consisting mainly of cellulose. Of these, ramie and flax can be acetylated quite readily. They are made up of thick-walled vessels which form the groundwork of the stem of the plant. Flax has been used to some extent in the manufacture of viscose, but as previously indicated cotton is the raw material *par excellence* for cellulose acetate.

The most important source of cellulose from the point of view of price is wood. The primary cells in all vegetable organisms consist of a thin wall or envelope enclosing the protoplasm which is the vital constituent. This envelope consists of nearly pure cellulose. Primitive or growing cells are thin walled (parenchyma) and their wall is saturated with water containing traces of mineral matter. The tissue of a plant or tree is entirely composed of these meristematic cells as they are called, modified in various ways: by growth of the surface of the cell wall, by thickening of the cell wall, by chemical alteration and impregnation of the cell wall with various substances, and by changes of the cell contents and by cell fusion. These various changes are fully described in textbooks of botany; for the present purpose it is sufficient to note that wood is made by the continued thickening and lignification of these cellular structures. In wood three principal types of cell are found: e.g. tracheids, which make up the bulk of the tissue; parenchymatous tissue; and sclerenchymatous tissue. Tracheids are thick-walled cells from which the protoplasmic contents have disappeared, and which serve to conduct water and food materials to the various parts of the tree; the parenchymatous tissue contains living protoplasm and also serves to store up reserve food materials such as starch, etc.; and the sclerenchymatous tissue forms the thick-walled ground tissue of the tree—it is absent from conifers.

The cellulose content of wood is comparatively low, being of the order of 50 to 55 per cent; in addition there are present other carbohydrates to the extent of about 10 per cent, lignin about 30 per cent, and resinous bodies to the extent of about 5 per cent. In order to obtain the cellulose in a reasonably pure condition, the wood must be submitted to very drastic treatment with caustic alkali, bisulphites, etc., at elevated temperatures, resulting in considerable degradation. About 80 per cent of the world's production of rayon is made from wood pulp by methods other than the acetate process. It seems unlikely that it will prove a suitable material for the latter process, since it rarely contains more than 85 per cent of *a* cellulose. In addition to *a* cellulose, it contains 15 per cent or more of hemicelluloses, various resinous and fatty substances, pentosans, and traces of lignin, which have escaped the chemical treatment.

It is possible that flax may prove of importance in years to come, especially as it can be produced in the British Isles. Its use would depend on guaranteed supplies. In the preparation of flax fibres for the manufacture of linen, after retting, the fibres are separated from the " shives " or " short tow ". It is the latter which is used for preparing flax cellulose, and it consists of a mixture of woody material and short fibre. The former can be almost entirely eliminated, and the latter, after digestion with various materials to remove pectinous matter and fats, is washed and dried and can be used for acetylation.

Acetic Acid.—In the form of vinegar, acetic acid has been known for centuries. It was first prepared in the pure state by Stahl in 1720, but its constitution remained unknown until 1814, when it was elucidated by Berzelius.

The main source of this acid until recent years was the wood distillation industry. It was isolated in the form of crude calcium acetate by passing the vapours from the distillation through milk of lime, which allows the other substances present such as acetone, methyl alcohol, etc., to pass, but absorbs the acetic acid. The crude, grey calcium acetate obtained by the evaporation of the resulting solution was distilled with sulphuric acid, and the crude acetic acid purified by redistillation with potassium permanganate, followed by fractionation.

Although Lavoisier had prepared acetic acid by the oxidation of alcohol, and patents covering its production appeared as long ago as 1871, the synthetic production of the acid was not attempted on any great scale until the European War rendered the normal sources inadequate to supply the demand. The starting point of modern synthetic processes is calcium carbide; in contact with water this generates acetylene, which, in presence of a mercury salt, readily takes up water to form acetaldehyde, and the latter can then be oxidized to acetic acid. From 1914 to the present time numerous patents have appeared covering various modifications of this process, and also for processes in which ethyl alcohol is the starting material, and is dehydrogenated in presence of a copper catalyst. The production of acetic acid by these synthetic processes calls for the expenditure of a very large amount of power, and they cannot be exploited economically in this country except in conditions of emergency such as existed during the war. In Canada, however, especially in the provinces of Ontario and

FIG. 17. Aeroplane View of Shawinigan Falls.

Quebec, an enormous supply of hydro-electric power is available at small cost, and this fact, together with the existence of plentiful supplies of raw materials in the form of coal and limestone, has resulted in the foundation of a flourishing electrochemical industry. producing calcium carbide, acetic acid and many other products. Shawinigan Chemicals, Ltd., whose plant is situated at Shawinigan Falls, Ont., produce large quantities of glacial acetic acid of a high degree of purity, which is extremely suitable for use in the manufacture of cellulose acetate. Figs. 17 and 18 give some idea of the extensive nature of the hydro-electric undertaking at Shawinigan Falls, and of the plant of the firm in question.

FIG. 18. Works of Shawinigan Chemicals, Ltd., Shawinigan.

Acetic Anhydride.—The methods used for the production of acetic anhydride are dealt with at length in Chapter V.

Acetic anhydride for use in the manufacture of cellulose acetate should contain at least 95 per cent of anhydride, the remainder being acetic acid. It should be free from more than the merest traces of metallic impurities.

Sulphuric Acid.—Adequate supplies of pure and cheap sulphuric acid are available, so that the manufacturer of cellulose acetate will scarcely consider manufacturing it for himself. The methods of manufacture need not be described here.

Acetone.—The liquid obtained on condensation of the vapours from which acetic acid has been removed by absorption in lime, as described above, contains in addition to water considerable amounts of methyl alcohol and acetone. These are separated from the water by fractional distillation, and the methyl alcohol is removed from the distillate by the action of anhydrous calcium chloride, with which it combines. The crude acetone is then purified by distillation followed by separation in the form of the bisulphite compound, which is distilled with sodium carbonate to regenerate the acetone, and the final product is dehydrated over calcium chloride. It is also made to some extent by the dry distillation of grey calcium acetate, and purified as above.

During the War, a number of fermentation processes for producing acetone from starches or sugars were developed, particularly in the United States. The flax retting organism possesses the property of being able to convert starch mashes, with the production of comparatively large amounts of acetone and butanol, with traces of organic acids. The mash is prepared from maize starch, and is cooked for two hours under pressure, after which it is cooled to 37° C. and inoculated with a pure culture of the organism. The process is carried out in closed vessels, and the gaseous by-products, chiefly carbon dioxide and hydrogen, are collected. According to Vargas Eyre,[1] in the normal course of fermentation the acidity rises from practically zero to approximately half-normal, but falls rapidly after the eighteenth or twentieth hour with the production of acetone, butanol, and ethyl alcohol in the proportions 30, 60, and 10 parts respectively. The process was carried out in a small way at King's Lynn during the War, but difficulties arose on account of the high and varying prices of maize in this country; on account of the production of ethyl alcohol, which brought in the difficulties of excise control, and particularly on account of the fact that the products are obtained in a more or less fixed proportion, whereas the demand is not in the same ratio. At present the process can only be operated at a profit in maize-producing countries such as the United States. Organisms mentioned in patents which are

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[1] J. Vargas Eyre. Streatfield Memorial Lecture, 1931.

still valid include *B. granulobacter pectinovorum* and[1] *B. butylicus* B.F., found in animal refuse.[2]

Large quantities of acetone are now produced by synthetic methods, especially in localities having plentiful supplies of cheap power.

The analysis of acetone is conveniently carried out by the well-known Messenger process. In the preparation of spinning solutions allowance must be made for any water present in the acetone.

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[1] C. Weizmann. B.P. 149,355.

[2] Soc. Ricard, Allenet et Cie. B.P. 176,284.

CHAPTER IV

MANUFACTURE OF CELLULOSE ACETATE

Owing to the colloidal nature of cellulose and its derivatives, and to the fact that the esterification process is reversible and accompanied by many little-understood side reactions, a considerable variation in the properties of the final product can be expected according to the nature of the cellulosic raw material, the composition of the acetylation mixture, the catalyst used, the temperature at which the reaction takes place, and the time for which it is allowed to continue. It is difficult, if not impossible, to obtain two exactly similar batches of cellulose acetate, although the cotton linters be thoroughly blended and the same conditions be adhered to throughout. Hence, in making acetate, especially for the manufacture of rayon, a large stock of linters should be held from which uniform blends may be prepared, and a considerable number of batches of cellulose acetate should be made before large scale spinning is attempted, the batches being blended to uniform viscosity and acetyl value.

Pretreatment.—The acetylation of cellulose is facilitated to some extent by subjecting it to a preliminary treatment with suitable reagents, e.g. formic or acetic acid, acetic acid containing a small amount of sulphuric acid, lactic acid, phenol, halogens or halogen halides, etc. Such pretreatment probably serves to weaken the cohesion between the micellæ, and in some cases the reagent may even penetrate within the micelle, forming indefinite compounds with the cellulose molecule ; sulphuric acid, for example, may act in this manner, forming an intermediate compound analogous to ethyl hydrogen sulphate in the ordinary esterification process.

Among patents granted for processes of pretreatment with acetic acid may be mentioned the following :—

The Société Chimique des Usines du Rhône have covered pretreatment of cellulose with a small amount of acetic acid such that there is formed with the moisture present in the cellulose an acid of 70–85 per cent strength.[1] H. Dreyfus treats cellulose (which has

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[1] Soc. Chim. des Usines du Rhône. B.P. 237,567.

preferably received alkaline treatment) with the vapour of a lower fatty acid, e.g. acetic or formic acid at ordinary or elevated temperatures.[1] The vapours are removed by means of a current of air or other indifferent gas, following which the material is esterified in the usual manner.

H. Mallabar has described the production of cellulose acetate soluble in acetone and having a high charring point by the acetylation of cellulose which has received a preliminary treatment with a mixture of sulphuric and acetic acids (e.g. about 1 per cent sulphuric acid), the sulphuric acid being neutralized before acetylation, and zinc chloride being used as acetylation catalyst.[2]

Pretreatment with 80 to 90 per cent formic acid containing sulphuric acid of density 1·83, or anhydrous zinc chloride in the proportion of less than 20 per cent by weight of the mixture at ordinary or reduced temperatures for a period of two hours, has been covered by the Soc. Lyonnaise de Soie Artificielle.[3] The I.G. Farbenind, A.-G.[4] also have a patent covering pretreatment of cellulose with a small quantity (less than 2 per cent) of sulphuric acid diluted with an aliphatic acid.

The Cellulose Acetate Silk Co., Ltd.,[5] and others claim that products of high viscosity are obtained by acetylating cellulosic materials which have been previously treated with a lower fatty acid and a small quantity of sulphur dioxide (less than 5 per cent of the total amount of the acetylating bath), with the addition of concentrated sulphuric and acetic acids if desired. The process is carried out below 20° C.

The use of hydrofluoric acid as a pretreating agent for the purpose of removing siliceous matter has been described by British Celanese Limited.[6]

There are a number of patents covering the use of various halogen compounds as pretreating agents for cellulose. Thus, Dreyfus [7] treats the cellulose with from 2 to 50 per cent, preferably 5–10 per cent of a hydrogen halide, alone or in conjunction with a lower fatty acid, and/or halides of iron (ferric), tin (stannic),

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[1] H. Dreyfus. B.P. 263,938.
[2] H. J. Mallabar. B.P. 258,020.
[3] Soc. Lyonnaise de Soie Artificielle. B.P. 264,181.
[4] O. Y. Imray (I.G. Farbenind. A.-G.). B.P. 281,927.
[5] Cellulose Acetate Silk Co., Ltd., Chaumeton and Wakefield. B.P. 348,292.
[6] British Celanese, Ltd. B.P. 308,348.
[7] H. Dreyfus. B.P. 312,098.

manganese, cobalt, nickel, or copper. The reagent may be applied in vapour form or in aqueous solution, and the reaction is allowed to proceed for from 1 to 24 hours at ordinary temperatures, depending on the nature of the cellulosic material, the concentration of the treating agent, the temperature and the degree of reactivity required. In an addition to this patent, British Celanese, Ltd.,[1] extend the process to include pretreatment with a quantity of hydrogen halide less than 2 per cent calculated on the weight of the cellulose. Ruzicka [2] treats glacial acetic acid with dry chlorine below 30° C. in presence of a lower fatty acid anhydride and/or one or more halogen compounds of acetic or other lower fatty acid. The solution so obtained is used for the treatment of dry cellulose, the temperature being less than 50° C., and when the chlorination and acetylation of the cellulose has proceeded far enough, the product is acetylated at a temperature below 30° C. by means of acetic anhydride and a catalyst such as sulphuryl chloride or zinc chloride.

Nitric acid and oxides of nitrogen have also been claimed as pretreatment agents for cellulose. British Celanese, Ltd.,[3] for example, use 0·5–4 per cent of nitric acid, preferably mixed with a considerable amount of a lower aliphatic acid. The pretreating process is continued for about an hour at 35–60° C., after which anhydride is added, and the process continued for a further hour in the absence of catalysts. It is claimed that the acetate obtained on acetylation of this product has a high clarity and good colour. Kodak, Ltd.,[4] hydrate the cellulose before acetylation with 68 per cent nitric acid for one hour, followed by esterification with the appropriate aliphatic acid in absence of a catalyst. The same firm [5] have also covered pretreatment with a solution of nitrogen peroxide in a lower aliphatic acid at 0° C.

Acetylation.—It has been established that cellulose cannot be esterified beyond the stage of triacetate or trinitrate, the so-called cellulose tetra-acetates of the earlier workers being really esters of degradation products of cellulose. According to Heuser,[6] the acetylation reaction may be represented by the equation—

$$C_6H_{10}O_5 + 3(CH_3CO)_2O = C_6H_7O_5(CH_3CO)_3 + 3CH_3COOH.$$

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[1] British Celanese, Ltd. B.P. 342,739.

[2] C. Ruzicka. B.P. 303,432.

[3] British Celanese, Ltd. B.P. 342,745.

[4] Kodak, Ltd. B.P. 344,151.

[5] Ibid. B.P. 345,235.

[6] E. Heuser. *Textbook of Cellulose Chemistry*, translated by West and Esselen, 1924, p. 45.

This indicates that 162 parts of dry cellulose require 306 parts of acetic anhydride yielding 288 parts of cellulose triacetate containing 62·5 per cent of combined acetic acid. In actual practice a considerable excess of anhydride is used, and the product rarely contains more than 60 per cent of combined acetic acid ; the yield is also less than theoretical (rather less than 90 per cent of the cellulose used is recovered) owing to unavoidable degradation and losses due to the solubility of the ripened acetate in weak acetic acid.

Deschiens[1] in 1925 divided the acetylation processes into two groups, viz. those in which the cellulose acetate is obtained in the form of a solution, and those in which it retains the fibrous form. From the point of view of rayon spinning the former group is by far the more important, although the second group has a particular interest in connection with the so-called immunized cotton. The patents relating to the second group as far as they concern the manufacture of cellulose acetate were probably applied for to cover processes which might at some future time assume commercial importance.

There is little doubt that the most satisfactory process of acetylation in use at the present time is one which involves the use of acetic anhydride as acetylating agent, and in which sulphuric acid, or one of its acid derivatives, e.g. an aromatic sulphonic acid is the catalyst, a considerable amount of acetic acid being present during the reaction, acting no doubt as a swelling agent for the cellulose in the early stages, and dissolving the cellulose acetate as it is formed. As previously mentioned (p. 6), Cross and Bevan made use of acetyl chloride as acetylating agent. Wohl[2] apparently realized the destructive effect upon the cellulose of the free hydrochloric acid produced during the reaction, and therefore proposed to acetylate in presence of pyridine. The earliest mention of the use of acetic anhydride as acetylating agent is due to Lederer[3] in 1901.

Although, as stated in Chapter I, Lederer was also the first to describe the use of sulphuric acid as catalyst, his process, in common with all the earlier ones, made use of hydrocellulose as starting material, and it is to Eichengrün and Becker[4] that credit must

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[1] M. Deschiens. *Chimie et Industrie*, **44**, 902–7, 1925.
[2] Wohl. D.R.P. 139,669/1899.
[3] Lederer. B.P. 11,749/1900.*
[4] Eichengrün and Becker. D.R.P. 159,524/1901.

be given as originators of the process in which unmodified cellulose in the form of cotton is acetylated directly with acetic anhydride in presence of sulphuric acid. They argued that a less degraded product should thus be obtained, since hydrocellulose is itself a breakdown product of cellulose. In the following year appeared the patents of Little, Mork, and Walker[1]; these differ from the above in recommending the use of phenol sulphonic acid in place of sulphuric acid as catalyst, and in the addition of sodium phenol sulphonate. The study of other catalysts of milder action than sulphuric acid, which so enriched the patent literature of cellulose acetate during the first ten or twelve years of the present century, was to some extent the outcome of the high temperatures employed in the acetylation process; with the introduction of lower temperatures and controlled reaction, the need for these milder agents was less insistent, and sulphuric acid became generally recognized as a suitable catalyst.

The action of sulphuric acid in promoting the acetylation of cellulose has not been completely explained. It is not a true catalyst since the product invariably contains more or less combined sulphuric acid—the so-called sulphoacetates described in 1919 by Ost.[2] Some interesting work has been carried out recently by two Japanese chemists, K. Atsuki and N. Ishii,[3] on the acetylation process, which throws some light on the function of the sulphuric acid. From a study of the conductivity, viscosity, surface tension, and freezing point depression of mixtures of two or more components of the acetylation bath, they conclude that sulphuric acid forms a compound with acetic anhydride, which can dehydrate and combine with organic compounds such as cellulose. Whatever the exact mechanism of the process, it is fairly certain that there is actual combination between the sulphuric acid and the cellulose, with or without the intervention of acetic anhydride, and this intermediate compound reacts with acetic anhydride, the sulphuric acid content of the cellulose acetate decreasing as the acetyl content increases, as shown by Schwalbe.[4]

The use of halogens, halogen acids and metallic halides as catalytic

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[1] Little, Mork, and Walker. U.S.P. 709,922/1902; B.P. 20,660/1902*; and F.P. 324,862/1902.

[2] *Ost. Z. angew. Chem.*, 1919, **32**, 66.

[3] K. Atsuki and N. Ishii. *J. Soc. Chem. Ind. Japan*, 1931, **34**, 331–335B and 335–339B.

[4] Schwalbe. *Z. angew. Chem.*, 1911, **24**, 1256.

agents in the acetylation process has received a considerable amount of attention during the past twelve years, and there are a number of British patents in force covering the application of these compounds, but it is difficult to say what value these processes have, without examining cellulose acetates prepared according to the directions given in the specifications. The destructive action of hydrochloric acid as exemplified in the " tendering " of cotton, and in the production of hydrocellulose according to Girard,[1] would, of course, be greatly modified in the cases where water is substantially excluded from the sphere of action.

Zdanowich [2] describes the manufacture of cellulose acetate by treating a mixture of cellulose, acetic acid, and acetic anhydride with a halogen or a compound which yields a halogen such as chloride of bromine. In this way a halogen-acetic acid is formed, and in the nascent condition it acts as a condensing agent. The reaction is completed in about two hours at 70° C., after which further esterification is brought about by the addition of strong acids such as sulphuric or chlorsulphonic acid. The specification also draws attention to the hydrolytic action of the halogen upon the cellulose and states that this action may be varied by varying the temperature, the amount of halogen, or the length of time for which the action is allowed to continue. Three years later [3] he described the production of solutions of cellulose acetate which could be extruded directly into coagulating baths for the manufacture of rayon. This process is carried out in two stages, as in the foregoing example, the quantity of acetic acid present being nine times the weight of cellulose taken, the whole being added at the commencement or at a later stage (even at the end of the process), or it may be replaced in part by another solvent such as formic acid, ethylidene-diacetyl, or acetylene tetrachloride. For example, cellulose is treated with three parts of acetic anhydride and nine parts of glacial acetic acid at 49–50° C., and the mixture is treated with chlorine until the cellulose disintegrates, when it is cooled to 15–18° C., and 0·005–0·015 parts of sulphuric acid are added and the reaction is allowed to proceed until the mixture becomes clear. Alternatively only 3–3·5 parts of acetic acid are added at the beginning of the process, the remaining 6–5·5 parts

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[1] Girard. *Memoir sur l'hydrocellulose et ses dérivatives,* 1881.
[2] Zdanowich. B.P. 139,232.
[3] Ibid., B.P. 196,641.

being added after acetylation is complete. A year later [1] the process was further modified by treating the reaction mixture with sulphur dioxide or an oxide of phosphorus at the end of the first stage. The compound added reacts with the excess of chlorine intentionally added in the first stage, to form a substitute for the strong condensing agent, such as sulphuric acid, used in the second stage. The acetylation may be completed in this manner or by the addition of a very small amount of a strong condensing agent, e.g. 0·01–0·1 per cent of sulphuric acid.

The use of hydrofluoric acid as a condensing agent was described in 1928 by H. Barthélémy (assigned to Ruth Aldo Co. Inc.),[2] who mentioned that a very small amount of an oxidizing agent and of a non-solvent such as benzene or carbon tetrachloride could also be added. Such a process could have little to recommend it, and the objectionable nature of hydrofluoric acid, both from the physiological and material point of view, would render it commercially of little value.

In 1929 a series of patents by H. Dreyfus covered various phases of the use of halogen acids and metallic halides in the acetylation process.[3] Cellulose pretreated with organic acids is esterified by means of a fatty acid anhydride in presence of at least 2 per cent each of a hydrogen halide and zinc halide, e.g. 5–10 per cent of hydrochloric acid and a similar amount of zinc chloride. The process was later extended to untreated cellulose, and to the use of halogen salts of other metals such as manganese, iron (ferric), nickel, cobalt, or copper. In the third patent of this series halides of arsenic, antimony, or phosphorus were put forward as condensing agents, either alone or in presence of a hydrohalide acid, suitable quantities being from 10 to 15 per cent, e.g. 10–15 per cent each of antimony or phosphorus pentachloride and hydrochloric acid on the weight of cellulose used. Here again the esterifying agent is acetic anhydride. In this connection it is interesting to note that chlorides of phosphorus were mentioned by Balston and Briggs in a patent specification in 1903.[4] The later patents of this series describe the esterification of cellulose, previously treated with organic acids, by a fatty acid anhydride

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[1] Ibid. B.P. 244,148.
[2] Ruth-Aldo Co. Inc. (Assignees of H. Barthélémy). B.P. 303,136.†
[3] H. Dreyfus. B.P. 308,322–3, 309,201, 311,790, 312,095–6.
[4] R. M. Balston and J. F. Briggs. B.P. 10,243/1903.*

using a ferric halide as condensing agent, e.g. 10–30 per cent of ferric chloride on the weight of cellulose taken, the temperature being kept at or below the ordinary temperature ; and finally the use of a stannic halide in presence or absence of a hydrohalide acid. The specification states that halides of iron, manganese, copper, nickel, or cobalt may also be present. Suitable quantities are 7–25 per cent of stannic chloride and of hydrochloric acid on the weight of cellulose, which may or may not have received previous treatment with fatty acids.

The I.G. Farbenindustrie A.-G. covered the use of halogen derivatives of sulphur dioxide, e.g. thionyl chloride, together with a heavy metal salt which in itself is capable of acting as a condensing agent in the esterification of cellulose. For example, 25 gm. of cotton can be completely acetylated in six hours by using a mixture of 75 parts of acetic anhydride, 100 parts of acetic acid, 0·25 parts of zinc or cuprous chloride, and 1·4 parts of thionyl chloride at a temperature of 65° C.[1]

In addition to the two-stage acetylation processes of Zdanowich, described above, in which a halogen acetic acid forms the condensing agent in the first stage, he secured a further patent in 1921 for a two-stage process in which no condensing agent is used in the first stage, and a strong condensing agent is added in the second stage in a quantity not exceeding 4 per cent on the weight of cellulose taken.[2] The first stage is preferably prolonged and is carried out under reflux or in a closed vessel under normal or increased pressure, and at temperatures of 40–100° C. ; half the necessary quantity of esterifying agent, acetic anhydride or acetyl chloride, may be added in the first stage and the remainder before the commencement of the second stage. A diluent such as formic or acetic acid or ethylidene-diacetyl, may be added at any stage of the process. The first stage is concluded when the cellulose is thoroughly disintegrated ; the mixture is cooled to normal or lower temperature, and the necessary quantity of sulphuric, phosphoric, chlorsulphonic acid or other strong condensing agent is added after which the reaction is continued till the solution becomes clear and colourless.

The use of zinc chloride as acetylation catalyst was protected as recently as 1928 by Dr. A. Wacker Ges. für Elektrochem. Ind. G.m.b.H., definite conditions being laid down, viz. a reaction time

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[1] W. Carpmael (I.G. Farbenind A.-G.). B.P. 289,973.
[2] Zdanowich. B.P. 190,732.

of 3–6 hours, the esterification being conducted at 55° C. in the early stages and later at 40° C.[1]

A method of esterification using pyridine sulphuric anhydride as catalyst was described by Wylam, Thomas, and Scottish Dyes, Ltd., also in 1928.[2] In an example, 15 parts of cellulose in paper form are treated with a mixture of 20 parts of glacial acetic acid, 10 parts of acetic anhydride and 15 parts of pyridine sulphuric anhydride at 100° C. The reaction is allowed to proceed at that temperature for about 15 minutes, and after cooling the cellulose acetate is precipitated with water. The resulting product is said to give viscous solutions with acetone; and by varying the conditions, acetate containing different proportions of acetic acid can be obtained. The claim is rather surprising as one would have expected such severe treatment to have resulted in loss of viscosity. Pyridine has been frequently mentioned in the patent literature of the acetylation process, since it undoubtedly exercises a moderating influence when strong catalysts are used. Thus pyridine sulphate was suggested as catalyst by Claessen in 1908[3]; pyridine in conjunction with acetyl chloride as esterification agent, was put forward in 1928 by the I.G. Farbenind. A.-G.,[4] who stated that an organic medium such as chlorbenzene, which will dissolve (at least in part) the reaction product of the acetyl chloride and pyridine, but which is not a solvent for cellulose acetate, should also be present; and the Society of Chemical Industry in Basle described a two-stage acetylation, in the first stage of which the cellulose is partly esterified by the action of acetic anhydride in presence of pyridine or other basic agent.[5]

There are a number of other patents dealing with modifications of the ordinary acetylation process, of which the following may be cited: Ruzicka[6] treats the cellulose with an esterifying mixture containing the whole of the anhydride required, with or without a catalyst, such as sulphuric acid, and some or all of the diluent; the subsequent esterification is controlled by adding acetic, butyric, or propionic acids or a mixture thereof in sufficient quantity to reduce local over-heating, thus preventing discoloration and

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[1] Dr. A. Wacker Ges. für Elektrochem. Ind. G.m.b.H. B.P. 291,001.
[2] Wylam, Thomas and Scottish Dyes, Ltd. B.P. 310,556.
[3] C. Claessen. D.R.P. 222,450/1908.
[4] I.G. Farbenind. A.-G. B.P. 291,360.*
[5] W. W. Groves (S.C.I. in Basle). B.P. 343,889.
[6] Ruzicka. B.P. 316,593.

irregular esterification. The reaction is carried out at 20° C. British Celanese, Ltd., have protected the production of low viscosity acetates which possess all the desirable properties of high viscosity esters, and are also compatible with natural or synthetic resins by esterifying at a temperature greater than 50–55° C., depending on the amount of sulphuric acid used, and ripening as described in B.P. 300,140 (q.v.) to a stage between solubility in hot chloroform, and very slight plasticity therein, while at the same time the cellulose acetate is soluble in a mixture of hot alcohol and benzene without the addition of water. The acetates so obtained are said to be suitable for lacquers and coating compositions.[1]

An interesting and suggestive specification is due to the British Enka Artificial Silk Co., Ltd.,[2] which states that the viscosity of cellulose acetate may be controlled to a great extent by allowing the acetylation bath to stand for 2–10 hours before adding the catalyst and cellulose. In this way the water content is reduced to a minimum (practically to zero in 10 hours), and by adding cellulose of the appropriate water content an acetate of any desired viscosity may be obtained, since the viscosity of the product increases with decreasing moisture content in the acetylation reaction mixture. One would imagine that this patent would be hard to enforce, as infringements would be very difficult to detect.

From 1905 onwards various methods have been suggested for the acetylation of cellulose without altering the fibrous form by diluting the acetylation mixture with a non-solvent for cellulose acetate such as benzene, in place of acetic acid. Numerous patents were applied for by Lederer, Mork, Dreyfus, Knoll & Co., Société Chimique des Usines du Rhône, and others, none of which are now in force. References to these are given in Worden, *Technology of Cellulose Esters.* At first sight the production of cellulose acetate by some such method is very attractive, since it eliminates the precipitation process and the necessity for recovering large quantities of acetic acid. Unfortunately, however, it is extremely difficult entirely to eliminate the non-solvent diluents from the cellulose acetate, and the fact that there are so few patents now in force which cover such methods is a clear indication that they have not yet reached a commercial stage. An example of a more recent process is due to H. Dreyfus,[3] in which cellulose pretreated with

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[1] British Celanese, Ltd. B.P. 326,515.
[2] British Enka Artificial Silk Co., Ltd. B.P. 263,771.
[3] H. Dreyfus. B.P. 264,937.

the vapours of organic acids is esterified in the absence, or substantially in the absence, of benzol or other diluents by treatment with the vapours of the acetylating agent, alone or mixed with air or other indifferent gases or with acetic acid vapours, in presence of a condensing agent such as sulphuric acid. A very similar process was patented by Kodak, Ltd., last year,[1] cellulose mixed with a catalyst being heated with the saturated vapour of acetic anhydride in a closed vessel substantially free from air, the acetic acid formed during the reaction being retained in contact with the material till acetylation is complete.

It has long been known that liquid sulphur dioxide will dissolve cellulose acetate, but the use of this substance as a substitute for acetic acid in the acetylation process is of recent origin, the earliest patents in this connection having appeared during the last two or three years. The use of such a solvent is attended with many difficulties: its low boiling-point (−8° C.) necessitates the use of very low temperatures in the acetylation process, or alternatively the employment of increased pressures[2]; and its unpleasant physiological properties call for special care and attention in the factory. On the other hand, it presents many advantages which would seem to make further investigation worth while. There is firstly the elimination of the acetic acid recovery plant, since the sulphur dioxide can be allowed to evaporate and can be readily reliquefied by pressure or by merely cooling to −15° C. to −20° C., the cost of plant, labour, and energy required to effect this recovery being much less than for a corresponding amount of acetic acid; secondly the use of sulphur dioxide enables the reaction temperature to be more easily controlled, cooling being brought about by allowing some of the liquid to evaporate[3]; thirdly degradation of the cellulose is to some extent prevented, especially that due to oxidation; finally if the reaction has been conducted under pressure, by suddenly releasing this pressure at the end of acetylation the cellulose acetate is obtained in a light fluffy form, specially suitable for further treatment,[4] or by adding water to the mixture until the ester is on the verge of precipitation, and then discharging it in the form of a jet in contact with streams of

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[1] Kodak, Ltd. B.P. 345,800.
[2] I.G. Farbenind. A.-G. B.P. 348,960.
[3] U.S. Industrial Alcohol Co. B.P. 355,382.*
[4] Ibid. B.P. 329,718.

hot water and steam, the sulphur dioxide is rapidly liberated and the acetate precipitated in a loose, fibrous form.[1] The chief patentees of processes involving the use of liquid sulphur dioxide are the I.G. Farbenind. A.-G. in Germany, and the United States Industrial Alcohol Company in America.

The proportions of acetic acid, acetic anhydride and sulphuric acid used for the acetylation of a given amount of cellulose can probably vary considerably if the accounts given in the patent literature and elsewhere are accurate. In the Table below various processes are compared, the amounts of the acids and of anhydride used being calculated, for convenience in comparison, on a basis of 100 parts of dry cellulose in each case.

Reference.	Parts used per 100 Parts Dry Cellulose		
	Acetic Acid.	Acetic Anhydride.	Sulphuric Acid.
Miles (D.R.P. 252,706)	390 to 410	270 to 310	5 to 16
Dreyfus (F.P. 478,023)	300 „ 400	250	10 „ 15
Zdanowich (B.P. 139,232)	333	280	1·3*
Dreyfus (B.P. 207,562) †	600 to 2000	180 to 250	10 to 15
Eichengrün ‡	350	350	10
Hottenroth §	360 to 400	360 to 400	4 to 6
Method outlined below	415 „ 420	248 „ 250	12·7 „ 12·9

* Two-stage acetylation sulphuric acid added at beginning of second stage.
† Production of high-viscosity acetates.
‡ Reference : *Enzyklopädie der Technischen Chemie*, Berlin, 1928, p. 123.
§ *Artificial Silk*, by Hottenroth.

The temperature conditions and period of acetylation also vary considerably in the processes mentioned above as shown.

Ref. :	Miles.	Dreyfus.	Zdanowich.	Eichengrün.	Hottenroth.
Maximum Temp.	50° C.	20° C.	70–80° C.	30° C.	20–25° C.
Period (hours)	36–40	—	—	2–6	5–6

In adopting a method of acetylation, regard must be paid to the purpose for which the acetate is required, and certain modifications may also be necessary according to the reactivity of the cellulose used, and to whether it receives any pretreatment. The following

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[1] Ibid. B.P. 346,824.

is a method suitable for use with normal, untreated cotton linters, when making acetate for spinning rayon :—

A mixture of 1,200 Kg. of acetic anhydride and 2,000 Kg. of acetic acid is prepared in a suitable mixing vessel ; when thoroughly blended it is analysed by a suitable method, and its composition is adjusted, if necessary, by the addition of acetic acid or anhydride. Further analysis is necessary after remixing, and the process is repeated until the composition of the mixture is within 0·5 per cent of the calculated. This mixture forms the stock from which the requirements for the individual acetylations are drawn.

520 Kg. of the above mixture are run into a cooling vessel and brought to a temperature of 5° C. by circulating brine in the jacket. 10 Kg. of sulphuric acid (at 100 per cent) are then added slowly, with stirring, the temperature rising to about 10° C. in the process. (N.B.—The sulphuric acid used usually has a strength of 97–8 per cent, and the amount must be adjusted accordingly. Similar corrections will be necessary in the case of the acid-anhydride mixture.).

The esterification mixture is then blown over into the acetylizer and cooled to 5° C. with the stirrers running. At this temperature crystallization commences. The acetylation process proper now commences, and it can be divided into six well marked stages, viz. :

(1) First stage : Addition of cotton linters to the acetylizing mixture.

(2) Second stage : From the end of stage (1) until the contents of the acetylizer assume a fluid consistency.

(3) Third stage, marked by a gradual stiffening of the mixture, which eventually reaches a doughy consistency.

(4) Fourth stage : From the end of stage (3) until the maximum temperature is attained.

(5) Fifth stage during which acetylation is completed, marked by a gradually decreasing temperature.

(6) Final stage consisting in the addition of sufficient water to convert excess anhydride into acetic acid, and to enable the ripening reaction to proceed.

The addition of cotton linters occupies from 30 to 45 minutes, 80 Kg. being used at 2–3 per cent moisture content. The moisture content is important ; too dry a cotton is not very reactive, while excessive moisture not only results in waste of anhydride, but makes the temperature more difficult to control, and produces a lower viscosity acetate. The reaction mixture is kept thoroughly stirred from beginning to end of the process. When all the cotton has been added the temperature will have risen about 2° C., from 5 to 7°. The temperature should thenceforth be taken every 15 minutes, the stirrers being momentarily stopped for that purpose, unless indicating thermometers are fixed in the acetylizers. In either case the temperature must be carefully watched throughout the process, as it is one of the prime factors in successful acetylation.

During the second stage, which occupies from one to two hours, according to the reactivity of the cotton, the temperature should rise at the rate of about one degree Centigrade each quarter of an hour, so that at the end of this period, it will have attained 10–13° C., and the contents of the acetylizer will have assumed a fluid state.

The third stage occupies about half an hour during which time the temperature rises 2·5–3·5° C., the mixture becoming doughy in consistency.

From this point onwards the reaction becomes more vigorous, and the temperature must be controlled so that it rises at a rate not exceeding 2–2·5 degrees per quarter of an hour. The method of controlling the temperature is only acquired by experience and consists in the skilful use of the minimum quantity of brine, combined with thorough agitation of the mixture by reversing the stirrers from time to time, if the temperature shows signs of getting out of hand. Over cooling must be avoided, since (*a*) it is uneconomical; (*b*) if the temperature is checked back too much, the reaction is "deadened" and the period thereby lengthened; (*c*) there is risk of freezing the mass in contact with the surface of the acetylizer, which may result in the jamming of the stirrers. If this occurs, the brine should be immediately drained from the acetylizer jacket, and water at 20–30° C. substituted and every effort made to free the stirrers as soon as possible, the temperature of the reaction mixture being observed at frequent intervals.

The maximum temperature to which the mixture is allowed to attain depends on the type of cotton employed, and on the properties required in the finished acetate. It is not advisable, however, to employ temperatures exceeding 35° C.

During the fifth stage the temperature should fall at the rate of half a degree every fifteen minutes, and in one to one and a half hours after reaching the maximum temperature, a small sample of the acetylation mixture should be pressed out into a thin film between two microscope slides, and examined under the low power of the microscope for unacetylated and incompletely acetylated fibres, of which there will probably be large numbers at this stage. A test should also be applied to give a rough indication of the amount of free acetic anhydride still present. This may be carried out as follows: About 20 gm. of the mixture is put into a stout glass or stoneware jar, which has been previously brought to the temperature of the batch, and which is insulated from loss or gain of heat by being placed in a box packed loosely with sawdust. 10 c.c. of water are then added and thoroughly mixed in with a glass or hard wood rod as rapidly as possible. The maximum temperature attained is noted. The normal increase for the first test is from 7 to 8° C.; if it is less, there is insufficient free anhydride in the mixture to complete the acetylation, and an addition of 1·5 Kg. should be made to the batch for each degree below normal. On the other hand, a high increase indicates excess of anhydride, and this must be reduced to the required amount by the addition of water at the rate of 0·5 Kg. per degree above normal.

Thereafter a microscopical examination and an anhydride test should be made every hour, until with a normal or slightly subnormal increase of temperature in the anhydride test, a clear solution, free from all but the slightest trace of unacetylated fibre, results.

The normal period from the attainment of maximum temperature to the completion of acetylation is three to four hours, depending on the nature of the cotton linters, the maximum temperature attained, and the deviation from the correct amount of anhydride.

A final test should be made for excess anhydride; normally it will be found that the increase in temperature will be from 5 to 7° C. If this is the case, and the temperature of the batch has fallen about the same amount below the maximum, i.e. batch temperature should be 23° C., an addition of water is made to convert excess anhydride to acetic acid. This will usually be about 4·5 Kg., and it will be found that the temperature of the batch will rise almost to the maximum attained in the fourth stage. About 15 minutes later a further quantity of water, amounting to 20–25 per cent of the weight of cellulose used, i.e. 16–20 Kg. is added and thoroughly incorporated. The batch is then allowed to cool to the ripening temperature (20–22° C.), poured into the ripening vessel, and removed to the constant temperature room.

It must be clearly remembered that the patent situation in regard to the manufacture of cellulose acetate is extremely complicated, and the publication of the above method does not necessarily mean that at some point or other it may not infringe a patent which is still in force. At the same time, it is very doubtful whether a process such as that described is still covered by valid patents.

Records.—Complete and careful records of weights, times, temperatures, and results of tests should be made in respect of every batch of cotton acetylated, and these records should be filed in the laboratory, as it is only by the accumulation of data that successful operation can be attained. In addition, the careful analysis and consideration of such data by the technical staff frequently leads to improvements in the process, although, of course, no alteration in the routine should be permitted until its effect has been ascertained in the research and experimental departments. A third and no less important reason for keeping detailed records is the production of a psychological effect upon the workers, which conduces to greater efficiency. In this connection it is interesting to note that in any industry where a chemist is employed, as soon as the workers realize his ability to discover errors in the processes, there is an immediate increase in efficiency, which is maintained only so long as he is seen about the factory at frequent intervals, or so long as regular sampling to the laboratory is practised. Each record sheet should be signed by the person responsible for the acetylation, and also by the shift foreman; and, naturally, the production manager and chemist will exercise sufficient supervision to ensure that the records are being accurately entered at the time the observations are made, otherwise they are useless.

Two curves indicating the courses of typical acetylations are shown in Figs. 19 and 20.

Ripening.—If the primary solution of cellulose acetate obtained by the process described above is immediately precipitated with water, and the product is washed and dried, it will be found to have the following properties: Hard, horny fragments, soluble in chloroform and similar solvents, insoluble or only slightly soluble in acetone, and soluble in a mixture of equal volumes of absolute alcohol and benzene only on the addition of a comparatively large amount of water, and on heating to boiling. The dry product will be found to char if heated to 180° C. or thereabouts, and the combined acetic acid varies from 58–60 per cent. In view of these properties, and considering the difficulty of dyeing, it is not surprising that cellulose acetate achieved little commercial importance until the discovery by Miles of the process of rendering it soluble in acetone. The precise significance of the term solubility in relation to cellulose acetate has already been discussed (p. 24); in this section which deals mainly with the practical side of the ripening process, the terms solubility, solvent, solution, and so forth will be understood in the light of that discussion.

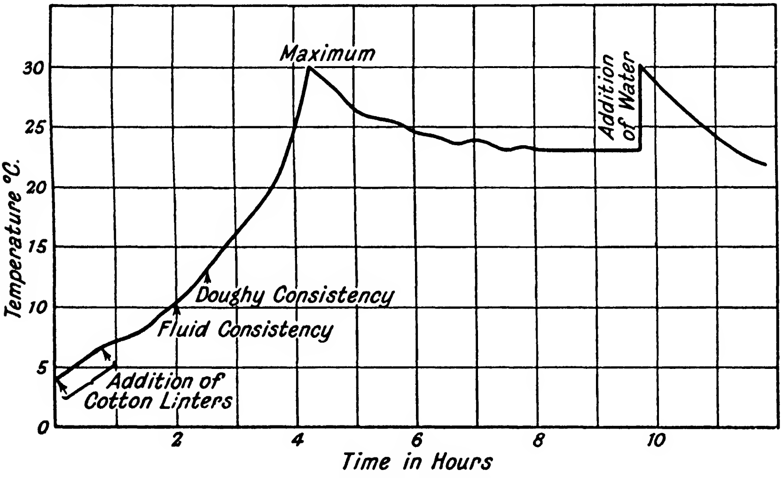

FIG. 19. Course of Acetylation.

The patent of Miles (B.P. 19,330/1905) is so important in this connection that it will now be dealt with more fully. The method of acetylation was as follows: 100 gm. of dry cellulose, 400 gm. of glacial acetic acid, 240 gm. of acetic anhydride, and 10–20 gm. of sulphuric acid of 95 per cent or greater strength were mixed thoroughly and maintained at a temperature of 60–70° C. for about eight hours. Miles states that this treatment produces cellulose tetra-acetate, or possibly cellulose triacetate in part. This uncertainty of composition was due to the partial acetolysis suffered by the cellulose on account of the high temperature used in acetylation, but we can take it that the product approximated closely to the so-called cellulose triacetate. At the end of the acetylation process he added a mixture of 90 parts of water, 10 parts of sulphuric acid, 99 per cent strength, and 100 parts of glacial acetic acid, and after thorough stirring the whole was allowed to stand for twelve hours at 50° C. On precipitation by excess of water he obtained a fine powdery solid, which was soluble in pure acetone, plastic in chloroform, and insoluble in alcohol or water. The high temperatures employed in the acetylation and ripening processes described by Miles must have resulted in considerable degradation of the cellulose; modern processes employ lower temperatures, and the acetates so obtained are not soluble in acetylene tetrachloride as was the product of Miles.

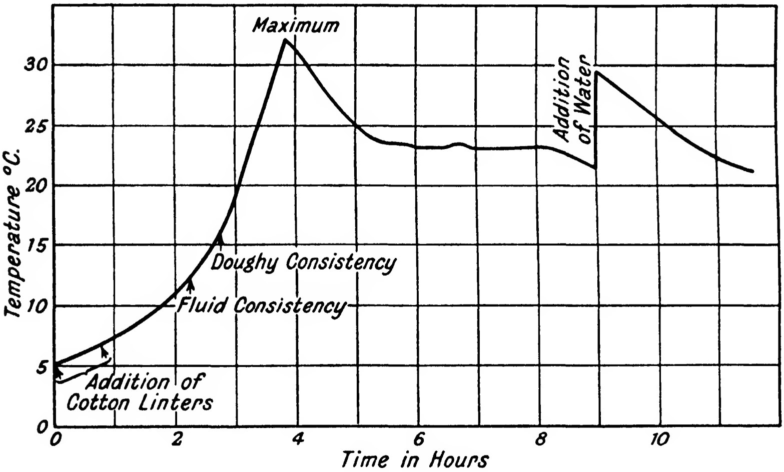

FIG. 20. Course of Acetylation.

The precise nature of the ripening process has not yet been satisfactorily explained. Earlier theories naturally attributed the solubility in acetone of these secondary acetates to the formation of a diacetate as the result of hydrolysis. That acetic acid is split off is evident from the analysis of cellulose acetate before, during, and after ripening, and is clearly shown by the figures given below. The total sulphate figures indicate that sulpho-acetates are also gradually decomposed during the ripening process. The calculated acetic acid contents for mono-, di-, and triacetates are also given :—

Hours ripening	0	18	26	40	48	64	70
Acetyl content	59·2	59·1	57·7	57·2	56·7	55·8	52·7
Total sulphate	1·51	0·52	0·38	—	0·22	0·16	0·17

Hours ripening	0	15	24	38	48	63¼	71
Acetyl content	58·3	58·2	57·9	56·5	55·3	54·1	53·5
Total sulphate	1·53	0·49	0·28	0·22	0·21	0·19	0·17

	Monoacetate.	Diacetate.	Triacetate.
Acetyl content calculated	29·4%	48·8%	62·5%

While in each of the examples given above the sample taken at the beginning of ripening was soluble in chloroform and insoluble in acetone, and the final sample in each case was soluble in acetone and became plastic in chloroform, it cannot be logically deduced that this change in solubility characteristics is due to the conversion of some of the higher into lower acetates. The existence of these lower acetates has recently been called into question by Fox,[1] who bases his conclusions on X-ray evidence. He agrees that this conclusion has been contested especially by specialists of the explosives industry, but favours the theory that the alleged mono- and di-esters are really mixtures of the tri-ester with cellulose. He instances the following facts : " (*a*) the approximately 100 per cent triacetate disperses moderately well in chloroform, but not in acetone ; (*b*) the partially hydrolysed acetate containing some cellulose, moisture, and acetic acid disperses in acetone, but only swells in chloroform ; (*c*) the addition of water drop by drop to a dispersion of the standard B.E.S.A. D 50 type causes a considerable increase of viscosity until eventually the emulsion breaks with separation of phases, with coagulation of dispersoid, and with rapid diminution of viscosity, in the manner reminiscent of the salting out of soap dispersions when the active mass of sodium ions is increased sufficiently. This fact does not appear to be recorded in the literature of the subject, and is being further investigated. These facts taken together appear to indicate that the presence of reverted cellulose, or the presence of accompanying moisture or acetic acid and moisture, tends to prevent dispersion in chloroform, but is essential to dispersion in acetone, and that water increases the viscosity perhaps by increasing the envelope content. That is to say the triacetate adsorbs acetone no more sufficiently than to cause swelling ; when 8–12 per cent of reverted cellulose and some corresponding moisture are present the adsorption increases and

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[1] C. J. J. Fox. *J.S.C.I.*, 1930, 49, 83T.

becomes sufficient to cause dispersion. The addition of water and the consequent hydrolysis leads to the production of free acetic acid, which may play a large part, because it is common knowledge that small changes of concentration and composition have enormous effects on viscosity when organic dispersion media are concerned." The theory here advanced is supported by the fact that it is not possible to arrest the acetylation process previously described at the appropriate acetyl content and obtain an acetone soluble acetate; the product in such a case is a mixture of unchanged cellulose and chloroform soluble cellulose acetate. It is possible that a certain amount of degradation is necessary in the ripening process, and that the products so formed penetrate the micelle and facilitate dispersion in acetone by their attraction for the solvent.

A different view was taken by Knoevenagel,[1] who, as long ago as 1914, advanced the theory that the production of acetone solubility is a result of the depolymerization of the ester, and described the production of an acetone soluble acetate by heating the primary acetate under pressure with acetic acid or benzene without any change in the acetyl content of the product. Pringsheim, Kusenack, and Weinreb [2] agree with Knoevenagel, having converted primary acetate into the acetone soluble variety by heating it at about 280° C. in an inert medium, such as molten naphthalene or tetralin, without loss of acetic acid. Knoevenagel's results were challenged by Schultze and Hess,[3] who cast doubts upon the accuracy of his analyses; they regard both depolymerization and reduction of acetyl content as essential to the production of secondary acetates.

While it is not yet possible to reconcile these conflicting views, it may safely be conjectured that a complete and satisfactory explanation of the mechanism of the dispersion of cellulose acetates should not be long delayed.

Methods of producing acetone soluble cellulose acetates directly have been suggested from time to time. Thus Bayer & Co. [4] describe a method in which 200 parts of cellulose are treated with 800 parts of acetic anhydride and 20 parts of sulphuric acid, yielding an acetone soluble acetate. It has not, however, been found possible

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[1] Knoevenagel. *Z. angew. Chem.*, 1914, **27**, 508.
[2] Pringsheim, Kusenack, and Weinreb. *Papier-Fabr.*, 1927, **25**, 758.
[3] Schultze and Hess. *Annalen*, 1926, **450**, 65.
[4] Bayer & Co. F.P. 317,007.

to reproduce the reaction claimed, all attempts resulting in an acetate soluble in chloroform and insoluble in acetone. More recently the I.G. Farbenindustrie A.-G.[1] have stated that an ester soluble in acetone is produced when in addition to a catalyst such as zinc chloride or sulphuric acid, hydrochloric acid, or a substance yielding hydrochloric acid such as acetyl chloride or tetrachlorethane is also present. The patents of Zdanowich, previously mentioned (p. 47) are also examples of the direct production of secondary products, the halogen employed acting as a mild hydrolytic agent.

Other agents which have been used for modifying the solubility characteristics of cellulose acetate include hydrochloric acid in quantity at least equivalent to the sulphuric acid used as catalyst, in presence of an amount of water 5–15 per cent of the total acids in the mixture[2]; a mixture of hydrochloric and hydrofluoric acids under the same conditions as the foregoing[3]; alkaline phenoxides, the cellulose acetate being dissolved in anhydrous or aqueous phenols, the amount of saponifying agent being that which is theoretically necessary to fix the quantity of acetic acid which it is desired to remove from the cellulose acetate[4]; and comparatively concentrated inorganic acids (about 60 per cent) in presence of salts or esters which are soluble in the acid, but have no solvent action on the cellulose acetate, the function of the latter compounds being to retard the solvent and degrading action of the acid, e.g. a saturated solution of potassium nitrate in 80 per cent nitric acid.[5]

In the methods of ripening based upon the original process of Miles there are three variables which affect the character of the final product, viz.:—

(*a*) The amount of water added to the primary solution.
(*b*) The temperature of ripening.
(*c*) The period of ripening.

Excessive amounts of water increase the destructive action of the sulphuric acid, while too little water renders the process unduly lengthy, thereby again increasing risk of degradation. High temperatures also result in destruction and degradation, and unduly low temperatures mean long ripening periods, which are uneconomical. The period of correct ripening is determined by

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[1] I.G. Farbenind. A.-G. B.P. 301,755.
[2] Ruth-Aldo Co. Inc. B.P. 282,789.
[3] Ibid. B.P. 303,098.†
[4] G. B. Ellis (Soc. des Usines Chimiques Rhône-Poulenc.). B.P. 321,648.
[5] C. F. Boehringer & Sohne G. m. b. H. B.P. 355,419.

the first two factors, and there is an optimum time when these are fixed.

In a typical method of ripening the amount of water added is 22·5 per cent calculated on the weight of the cellulose used, i.e. for the quantities used in the acetylation process described above, 18 litres of water should be added. This water should be free from any considerable amount of temporary hardness, as an excess would tend to delay the reaction. A suitable figure is 3–6 parts per 100,000 expressed as calcium carbonate, the exact amount being immaterial, but it should not vary outside the above limits. After the batch has been cooled to 21° C. and has been transferred from the acetylizer to the ripening vessel, it is taken to the ripening room, which is maintained at a temperature of 21° C. The best method of controlling the temperature and at the same time ventilating the room so as to remove the acetic acid vapours which would otherwise make the atmosphere intolerable, is to blow air over a series of heating or cooling pipes according as the outside temperature is less or greater than 21° C., and to admit this conditioned air into the room at a number of points near to the ground. Provision should be made for the escape of air by a ventilating duct in the roof. The humidity of the air admitted to the room is of little importance, provided it does not exceed 60–70 per cent. The valves controlling the admission of steam or brine to the conditioning apparatus can be operated automatically by a thermostatic control fitted in the ripening room itself.

The ripening period varies usually from about 65–75 hours, and is determined by the results of a series of tests carried out periodically. The first sample is taken about 54 hours after the commencement of ripening. About 200 gm. of the batch is taken and precipitated with water. The best method of precipitation, producing a moderately coarse fibre which can be readily washed, is to add water to the sample a few c.c. at a time, beating in each addition until a homogeneous state results before adding more. When the sample shows signs of turbidity, water should be added rapidly to the extent of about 500 c.c. with continuous beating. If the operation has been performed successfully the acetate will be in the form of moderately coarse fibres 2–3 cm. long. This observation applies only to the later stages of ripening, i.e. after about 24 hours, as previous to that time the acetate has a horny consistency however precipitated. The precipitated sample is then washed in running water; at the end of 30 minutes it is squeezed dry and tested for acidity by spotting with litmus solution. If the litmus remains blue, the acetate is again washed till free from litmus. Generally it will be found that a few hard fragments resist washing for a considerable time. These can be rejected. When the fibre is free from acid, it is dried as rapidly as possible in an electric oven (Fig. 21) (about 10 minutes), ground in a mortar to a uniform coarse powder and tested as follows :—

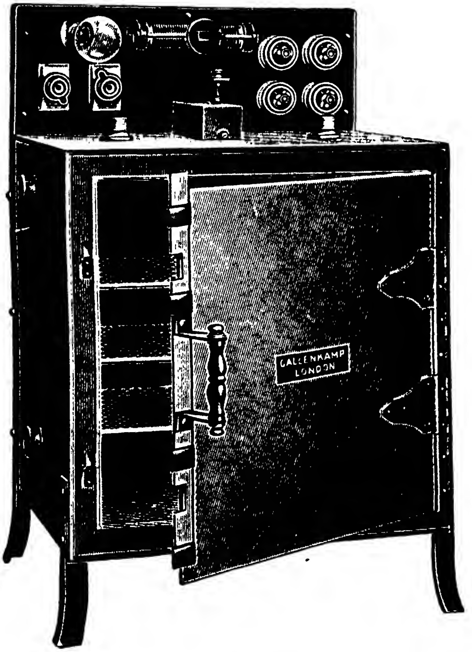

Fig. 21. Drying Oven.

Chloroform Test.—One inch depth of the dry ground acetate is put into a test tube (6 × $\frac{5}{8}$ in.) and 5 c.c. of specially dried chloroform, free from alcohol, is added. The tube is heated in a boiling water bath, and the contents are stirred until the fibre dissolves or there is no further change in the appearance of the plastic. It is very important that all observations made in this test should be at the same temperature, otherwise the results obtained are not comparable. It is convenient to note the results " hot " and " cold ". Before noting the hot result the tube should be kept in boiling water for 2–3 minutes; and for the cold result it should be cooled to 15° C. and maintained at that temperature for about 5 minutes before making the observation.

The results obtained in this test will vary from solubility to a very hard plastic, which emits a " scrunching " sound when rubbed up and down the tube with a glass rod. At least nine gradations are distinguishable between these two points, and a definite system of nomenclature should be adopted for describing the results of the test. A useful system is as follows :—

Soluble.
Incipient Plastic.
Incipient Plastic. +
Very soft plastic
Very soft plastic +
Soft plastic
Soft plastic +
Fair plastic
Fair plastic +
Good plastic
Good plastic +

Actual experience of the test is necessary to appreciate the possibility of making such fine distinctions with the ease called for in routine testing; but it is quite easy to train a youth of normal intelligence to record his observations satisfactorily. There is, of course, variation to some extent as from one worker to another, but individuals should make consistent observations at all times.

In general there is a definite correspondence between the " hot " and " cold " plastic for the same sample of acetate, but exceptions do occur as would be expected from the complex nature of the partly hydrolysed material. These corresponding conditions are enumerated below :—

Hot.	*Cold.*
Soluble	Soluble
Soluble	Incipient plastic
Soluble	Incipient plastic +
Soluble or incipient plastic	Very soft plastic
Incipient plastic or incipient plastic +	Very soft plastic +
Incipient plastic + or very soft plastic	Soft plastic
Very soft plastic or very soft plastic +	Soft plastic +
Very soft plastic + or soft plastic	Fair plastic
Soft or soft + plastic	Fair plastic +
Soft + or fair plastic	Good plastic
Fair or fair plastic +	Good plastic +
Good plastic	Firm plastic
Good plastic +	Very firm to granular plastic
Good plastic + to Firm	Granular (no coherence)

Only in very exceptional circumstances is the last condition met with in ripening, and it indicates over-ripening.

Alcohol-Benzene Test.—This is carried out in the same way as the chloroform test, 5 c.c. of a mixture of equal volumes of absolute alcohol and dry benzene being substituted for the chloroform. The tube and contents are heated in the water bath with stirring until the liquid boils. When the fibre is saturated water is added drop by drop from a burette (the drops must be of equal size), heating and stirring after the addition of each drop of water. The number of drops of water required to bring the fibre into clear solution is noted. It will be found that this number decreases from about twelve to two as ripening proceeds. When the chloroform test indicates a good plastic in the cold (hot-soft) and the alcohol-benzene test two to three drops, the ripening process is complete and the batch must be precipitated. It is only necessary to carry out this test on the first and last samples unless it is desired to accumulate data.

Acetone Test.—The procedure is again similar to that for the chloroform test, 5 c.c. of dry acetone being used instead of chloroform. It is only necessary to carry out this test on the last sample to make sure that the ripened product gives a clear, bright solution in acetone.

A suitable form for recording ripening tests is shown in Fig. 22. When ripening is complete the form should be signed by the person who made the tests and handed to the laboratory supervisor, who will order the charge to be precipitated. This is best done by means of a second form, which is handed to the foreman of the precipitation department, who will retain it until the batch passes from his hands to the foreman of the stabilizing department. He will then return it to the precipitation laboratory for filing. The test recording form should be retained for a considerable length of time, as the information thus accumulated may prove exceedingly valuable, but the second form need only be kept until the batch is dried and analysed, so that should questions arise as to the correctness or otherwise of the batch, any fault may be traced to the person responsible.

Precipitation.—Numerous patents have been granted covering the use of various non-solvents of cellulose acetate for its precipitation, and also for mechanical methods of achieving that end. Among more recent examples may be mentioned the use of higher fatty acid esters of monohydric alcohols, e.g. ethyl stearate, as precipitating agent.[1] K. Werner describes a method of precipitation in which separate streams of the cellulose acetate solution and precipitating liquid flow into each other through a centrifugal pump, thus ensuring intimate admixture.[2] Kodak, Ltd., obtain cellulose acetate in a fluffy form by including in the acetylation bath an inert water immiscible, volatile solvent, and subsequently precipitating in water at or above the boiling point of the solvent. The amount of acetic acid is, of course, less

PRECIPITATION CONTROL

Batch No.............
Ripening commenced at..............
Date..............

Sample No.	Time and Date.	Hours ripened.	Character of fibre.	Results of Tests.				Tested by.
				Chloroform.		Acetone.	A/B	
				Hot.	Cold.			

FIG. 22. RIPENING CONTROL FORM.

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[1] Ruth-Aldo Co. Inc. (Assignees of H. Barthélémy.) B.P. 308,272.
[2] K. Werner. B.P. 338,214.

than in the normal acetylation process, since the presence of the volatile solvent ensures solution of the cellulose acetate as it is formed. Solvents mentioned as suitable are trichlorethylene, chloroform, and dichlorethane.[1] In some cases the precipitating bath consists of a non-solvent so chosen as to facilitate the subsequent recovery of acetic acid, as, for example, by the formation of azeotropic mixtures. The use of such liquids is attended by various complications, e.g. possible fractionation of the cellulose acetate with undesirable results, and there is no doubt that the most satisfactory precipitant is water, with an addition of sodium acetate or carbonate in quantity equivalent to the sulphuric acid present. While it is not absolutely necessary to make this addition, it simplifies the acetic acid recovery process, and probably helps to produce a fibre of satisfactory character. The quantity of sodium acetate required to neutralize the sulphuric acid present in a batch of the size described above will be 28 Kg. of crystalline salt ($CH_3COONa.3H_2O$) or 17 Kg. of the anhydrous acetate, assuming 100 per cent purity. Since excess acetic acid is a by-product of the manufacture of cellulose acetate, it is cheapest to use a solution of sodium acetate made up from the distilled, dilute acid recovered from the precipitation process, neutralized with soda ash. The most convenient concentration for this purpose is 18 per cent, CH_3COONa. The table below gives the quantities of dilute acetic and of soda ash of various strengths which, diluted to 6,000 litres with water, will give such a solution.

Dilute acetic acid required.			*Soda ash required.*	
Per cent strength.	*Kg.*	*Litres.*	*Per cent strength.*	*Kg.*
34	2,547	2,435	96	797
32	2,706	2,593	92	831
30	2,887	2,773	88	869
28	3,093	2,977	84	911
26	3,331	3,124		

The amount of such solution required per batch is 94·4 kg. or 86·1 litres. Preparation in the manner described will result in the production of considerable quantities of carbon dioxide; it is therefore advisable to make up the solution in a large vat capable of holding 10,000 litres, fitted with stirrers, and having a close fitting lid with trap for the admission of chemicals and water, and

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[1] Kodak, Ltd. B.P. 351,118.*

a wide trunking, 2–3 feet in diameter, should be provided to conduct the carbon dioxide outside the building. Since the gas is heavier than air, there should be a fall in the trunking; and the outlet should be clear of doors, windows, roads, or footpaths, since in still weather the gas is liable to stagnate, and might cause serious inconvenience and even death if inhaled. The volume of gas produced per batch of 6,000 litres of 18 per cent solution is rather more than 140,000 litres so that on a large production of cellulose acetate it might be worth while considering the compression of the gas into cylinders for sale. In making the solution the soda should be dissolved in a large volume of water and the dilute acetic acid added gradually with stirring. When the reaction is complete, water should be added to produce the required volume.

The plant used for precipitation is described later (p. 110), and consists essentially of a large vessel in which beaters or stirrers can be rotated at two different speeds. The method is really a modification of the laboratory procedure for precipitation described above. The ripening vessel containing the batch to be precipitated is taken into the precipitation department, which should be kept at a reasonably high temperature in winter (18° C., say), in order to prevent the freezing of the acetic acid. The precipitation vessel is well wetted internally before pouring in the batch, following which, an inch or two of water is run on to the surface of the acetate and the sides of the precipitating vessel are scraped clear of skins. The stirrers are then set in motion at low speed (150-200 r.p.m.), and the required amount of sodium acetate solution is added and thoroughly beaten in. Water at a reasonably constant temperature (18° C.) is then admitted in a slow stream, beating being continued. The exact point at which the water should be turned on full, and the speed of the beaters increased, is determined by the appearance of the mixture, and this is somewhat difficult to describe. Incipient precipitation is indicated by a turbid appearance, readily recognized by an experienced worker, and as soon as this point is reached, the water is turned on full and the speed of the beaters is increased to 250–300 r.p.m. When about 400 litres of water have been added in all, the stirrers are stopped, and a sample of the fibre is washed under the tap and examined. It should consist of white fibres averaging 3–4 inches in length, and should be free from "gels". If such are present, they indicate bad precipitation, and are liable to cause considerable trouble during later processes, in fact, they have been known to persist through the washing process, and to make their appearance in the dried cellulose acetate, where, of course, they give rise to high acidity. At this point of the precipitation process a little more water is added and the batch is allowed to stand until the fibres have hardened (about half an hour). The dilute acetic acid is then allowed to drain off via the hydro-extractor to the storage vats. When almost all the acid has drained away, the stirrers are rotated gently, causing the acetate to fall into the hydro-extractor below. It is there centrifuged free from liquor, and with the basket still in motion, it is washed with a spray until a test portion of the effluent liquid has an acetic acid content of 10 per cent or less. At this point the effluent is turned over to waste, and washing is continued until the acidity of the washings is 1 per cent or less, expressed as acetic acid. The acetate is then hydro-extracted until no more liquid flows out, after which it is transferred to the stabilizing department.

A simple test for the acidity of the effluent which can be carried out in the department itself is as follows: 42 c.c. of 2N caustic soda solution is placed in an 8 oz. jar of clear glass. 1 c.c. of phenol phthalein solution is added, followed by 50 c.c. of the liquor to be tested. If the colour is at once discharged, washing must be continued until a 50 c.c. sample just fails to decolorize the phenol phthalein. At this point the acidity is 10 per cent as acetic. For the final washing, 4·2 c.c. of the soda solution is treated in the same way. It would also be possible to control the washing process automatically by a conductivity method, i.e. two platinized platinum electrodes immersed in the effluent liquid would be connected to a suitable relay arranged to ring a bell when the conductivity of the solution reaches the figure corresponding to 10 or 1 per cent of acetic acid respectively. The former method, however, has the merit of simplicity.

Washing and Stabilizing.—A stabilizing process is necessary to remove the small amount of combined sulphuric acid which the cellulose acetate still contains. Although this is very small, amounting only to 0·1–0·2 per cent on the dry weight of the acetate, it is sufficient to lower the charring temperature of the material by 30–40° C., and if it were not removed it would cause gradual decomposition of the rayon or other products made from the unstabilized acetate. In addition to the removal of sulphuric acid there is also a slight diminution in the acetyl content during this process ; there is also a further change in the chloroform plastic, which becomes firmer ; this change is greater than that produced in ripening by an equal diminution in the combined acetic acid. It seems probable that the stabilizing process brings about a reduction in particle size or depolymerization.

The usual method of stabilizing consists in boiling the fibre with very dilute sulphuric acid (about 0·02 per cent), and is a process which demands careful laboratory control. Orders to the foreman should be issued on distinctive coloured forms as indicated in the description below, and duplicates should be kept in the control laboratory until the batch is dried and analysed.

The precipitated fibre, having been transferred to the stabilizing department, is put into a large wooden vat fitted with stirrers. It is first given three preliminary washes with hot water (at 60–80° C.) with stirring. A fourth quantity of cold water is then added, and after stirring, a sample containing both fibre and liquid is passed to the laboratory. The fibre is removed, washed rapidly, and dried as quickly as possible, and a chloroform test is carried out on it in the same manner as described under precipitation. The resulting plastic will probably be a little firmer than the final precipitation plastic, owing to the time which must elapse between final sampling and precipitation. It is for this reason that batches should be ordered out of the ripening room a little before the plastic is satisfactory. The liquor is titrated, using phenol phthalein as indicator, and if the acidity does not exceed 0·01 per cent expressed as acetic acid, stabilizing may be commenced. Otherwise it is necessary to continue washing until the desired figure is reached. Before stabilizing, a sample of the water used should be titrated as follows : 250 c.c. of the water is placed in a 400 c.c. beaker, and six drops of litmus solution are added ; the liquid is then brought to the boil and titrated with 0·1N sulphuric acid, the end-point being attained when the liquid remains just red on prolonged boiling. The titration should be recorded directly, together with the factor of the standard acid used, if this is not exactly 0·1N, on the stabilizing form.

When the acidity is satisfactory, the order to boil may be given (white form). This is done by turning live steam into the vat contents and occupies about one hour.

The second sample is brought to the laboratory as soon as boiling commences. It is tested in exactly the same way as the first sample, the chloroform plastic and titration being recorded. At this stage the acidity should be about 0·012 per cent (as acetic); if that figure is greatly exceeded, e.g. over 0·02 per cent, the batch must receive a further wash. If the result is satisfactory an addition of sulphuric acid is made (red form). The amount of acid required depends on the alkalinity of the water used as determined above. For each c.c. of 0·1N acid required in that test sulphuric acid must be added to the bath as follows:—

Strength of acid per cent.	*Add c.c. acid per c.c. of 0·1N sulphuric acid required in the alkalinity determination.*
96	21·5
97	21·3
98	21·1
99	20·9
100	20·7

This quantity of acid is required to neutralize the alkalinity of the water. A further quantity is necessary to give 0·015 per cent strength in the stabilizing bath. This may be found from the following table:—

Strength of acid per cent.	*Add c.c. of acid.*
96	164
97	163
98	161
99	159
100	158

The addition is made by measuring the required amount of sulphuric acid in a graduated cylinder and pouring slowly with stirring into a copper vessel containing about 5 litres of water. This is passed to the process worker together with the red form, and vat number and batch number should appear on both vessel and form to avoid confusion.

The third sample is brought to the laboratory three minutes after the addition of sulphuric acid. The acidity should have risen to 0·027 per cent, i.e. by 0·015 per cent. If the rise is not sufficiently great, more acid must be added, and conversely, if it is too great, more water must be added to the bath. A chloroform test is not necessary at this stage.

Half an hour later a fourth sample is passed to the laboratory, when the acidity will have increased to about 0·05 per cent, but there will be little change in the plastic.

Further samples are tested at quarter-hour intervals. The acidity should rise at a fairly regular rate, about 0·01 per cent per quarter of an hour; this is due to (*a*) sulphuric and acetic acids split off from the cellulose acetate, (*b*) acetic acid which boils out of the fibre, having been held there mechanically. If there is a very large increase at any stage of the process, exceeding 0·03 per cent, boiling water should be added to the bath to bring the acidity down to normal.

The end of the process is determined by the nature of the chloroform plastic and to a small extent by the approach of the acidity of the bath to a constant figure (0·1 to 0·15 per cent as acetic acid). As soon as a chloroform plastic is obtained having the character: Hot – Good +, Cold – Very Firm, and tending to disintegrate (granular plastic), the order may be given to flood the batch with cold water (blue form), which arrests the reaction. The normal time required is from 1¼ to 2¼ hours from the boil. Flooding consists in adding cold water as rapidly as possible until the vat is full. The water is at once drained off, and the acetate is washed until the acidity is reduced to a satisfactory figure. For rapid production the third and succeeding washes should be given with water, of about three times the alkalinity of that used for stabilizing. After the third wash a sample of the fibre is tested as follows:—

20 c.c. of distilled water is boiled for five minutes in a boiling tube to expel carbon dioxide. A few grammes of fibre are then added and the mixture is again boiled for five minutes. The tube and contents are then cooled and the pH of the liquid is determined colorimetrically. This should be from 6·0 to 7·5; if it is less than 6·0, further washing is required. When this test gives a satisfactory result, the order to discharge is given (green form), and the acetate is removed from the vat, and as much water as possible is then hydro-extracted. It is afterwards removed to the drying department.

Drying.—The plant used for the drying process is described later (p. 115). Drying should be carried out at a temperature not greatly in excess of 100° C., otherwise injurious effects may result, and it should be the aim of this department to finish the acetate with a fairly constant moisture content of about 1·5 per cent.

Blending.—This is a most important process, since upon its success depends the uniformity of the rayon or other product manufactured from the blended acetate. Although it does not follow that two samples of acetate having the same viscosity and acetyl contents will have similar properties and yield rayons having equal tensile strengths, these two properties are the most convenient on which to base the blending process, since, if the cotton used is of fairly constant composition, and the manufacture is rigorously controlled, this argument no longer holds good, and viscosity and acetyl content will give a good indication of the behaviour of the rayon produced.

The acetyl content of a blend of a number of batches of cellulose acetate is, of course, the mean of the acetyl values of the individual batches, but it does not necessarily follow that this will be the case with viscosity, the former being a chemical constant while the latter is a physical quantity, which is a function of the degree of ripening and of the state of polymerization of the cellulose acetate. Hence, owing to fundamental differences in the state of aggregation of the constituents of two samples of cellulose acetate made by different processes it is quite possible that, although their separate viscosities are identical, a mixture of equal weights of the two samples will not have a viscosity which is the mean of these single values. Here again, however, in the case of batches of acetate prepared by the same process from similar cellulosic materials, the viscosity of a blend is approximately the mean of the viscosities of the constituent batches. This is clearly illustrated by the following viscosity figures for blends composed of twenty batches each of 100 Kg., the individual batch viscosities varying from 35 to 45 units :—

Blend		1	2	3	4	5	6	7
Viscosity	calculated	42	47	43	46	43	45	45
	found	44	43	43	46	41	41	45

The greatest difference, four units in the case of blends 2 and 6, is only twice the experimental error of the method used for determining these viscosities and might easily have been due to incomplete blending, especially as small blends prepared in the laboratory gave results agreeing within two units with the calculated values.

The acetate, having been suitably dried and blended, it is ready for transference to the spinning or other section for further manufacture. The store should be so constructed that the moisture content of the blends remains fairly constant.

Yield.—Of the cellulose used in the above series of processes about 90 per cent is recovered in the form of cellulose acetate. The losses are made up of (*a*) traces of hemicelluloses in the original cotton, (*b*) losses due to degradation, (*c*) losses due to the solubility of cellulose acetate in dilute acetic acid, (*d*) mechanical losses during the washing and drying processes. Of the total equivalent acetic acid used (includes anhydride) 12 per cent is fixed in combination in the cellulose acetate, and about 76 per cent is recovered in the form of dilute acetic acid (about 30 per cent strength), making a total recovery of 88 per cent.

The following table shows the changes which take place during the ripening and stabilizing processes with a typical batch of cellulose acetate :—

Process.	Hours.	Chloroform.	Acetone.	A/B	Heat Test.	Viscosity.	Acetyl.	Total SO_4.
RIPENING.	0	Sol.	Partly sol.	> 20	185° C.	—	58·4	1·53
	15	do.	do.	20	201° C.	—	58·2	0·49
	24	do.	do.	14	213° C.	—	57·8	0·29
	38	do.	Sol.	11	220° C.	40	56·4	0·23
	48	Incip. plastic.	do.	4	230° C.	36	55·5	0·20
	64	Soft plastic.	do.	2–3	236° C.	24	54·1	0·19
After pptn.		Fair plastic.	do.	1–2	220° C.	33	53·7	0·18
STABILIZING.	At boil.	do.	do.	1–2	237° C.	35	53·6	0·14
	¼	Good plastic.	do.	1–2	238° C.	35	53·1	0·12
	½	do.	do.	1–2	240° C.	34	53·1	0·10
	¾	do.	do.	1	> 240° C.	35	53·1	0·08
	1	V. Good plastic.	do.	1	> 240° C.	34	53·0	0·06

It will be noted that the acetate retains its solubility in chloroform for 38 hours, at which time it is also soluble in acetone. Thereafter up to 70 hours (when the batch was precipitated) there is a continuous increase in the firmness of the chloroform plastic, while the acetone solution becomes brighter. At the commencement of ripening more than 20 drops of water are required to bring the acetate into solution in alcohol-benzene, and this gradually decreases to one drop at the end of the stabilizing process. The resistance to heat increases as the total sulphate content decreases, but the effect is much more marked in the stabilizing process than during ripening. The acetyl content falls from 58·4 to 53·7 during the ripening (a difference of 4·7 per cent), while during stabilizing the decrease is only 0·3 per cent. The viscosity falls to a minimum during the ripening process and then again increases; but during stabilizing in this case there is little or no change. This is not always the case, it more frequently happens that there is an increase in the viscosity during stabilizing of from four to five units.

CHAPTER V

RECOVERY OF ACETIC ACID AND MANUFACTURE OF ACETIC ANHYDRIDE

A consideration of the flow-sheet (p. 78) will show that about 3·75 tons of acetic acid (at 100 per cent) are obtained in the form of a 30 per cent dilution for every ton of cellulose acetate produced. This acetic acid has about half the value of the cellulose acetate produced, so that it is essential that it shall be recovered as cheaply and efficiently as possible. It may be recovered either as glacial acetic acid, in which case there is a surplus of 64 Kg. for each batch acetylated, assuming an efficiency for the recovery process of 95 per cent; this surplus may be converted into acetic anhydride, with a yield of about 49 Kg. at a 90 per cent efficiency, leaving a deficit of 146 Kg. of anhydride per batch to be made up from an outside source; or all the dilute acid may be converted into anhydride, in which case about 330 Kg. of anhydride will be obtained per batch acetylated, leaving a surplus of 135 Kg. per batch, while the whole of the 325 Kg. of acetic acid will have to be supplied from an outside source. It is evident, therefore, taking into consideration the difficulty of disposing of the excess anhydride, that it is preferable to recover the acetic acid in the glacial form, converting only the surplus into anhydride.

The concentration of acetic acid by fractionation is not satisfactory commercially since it is very expensive from the point of view of heat requirements. For example, Mariller[1] states that 40 to 45 Kg. of steam are necessary for each Kg. of concentrated acid obtained when the initial concentration is 10 per cent, and this only results in an acid of 80 per cent concentration. This large consumption of steam is due to the considerable amount of reflux necessary to prevent acetic acid from distilling over with the water. Numerous methods have been devised for the concentration of acetic acid, and these methods fall into three classes.

(*a*) Earlier methods in which the acid is converted into a salt, which is distilled with strong sulphuric or other acid.

(*b*) Those in which the acid is extracted by means of a solvent immiscible with water.

(*c*) Those involving distillation with organic liquids which form binary azeotropic mixtures, generally with the water

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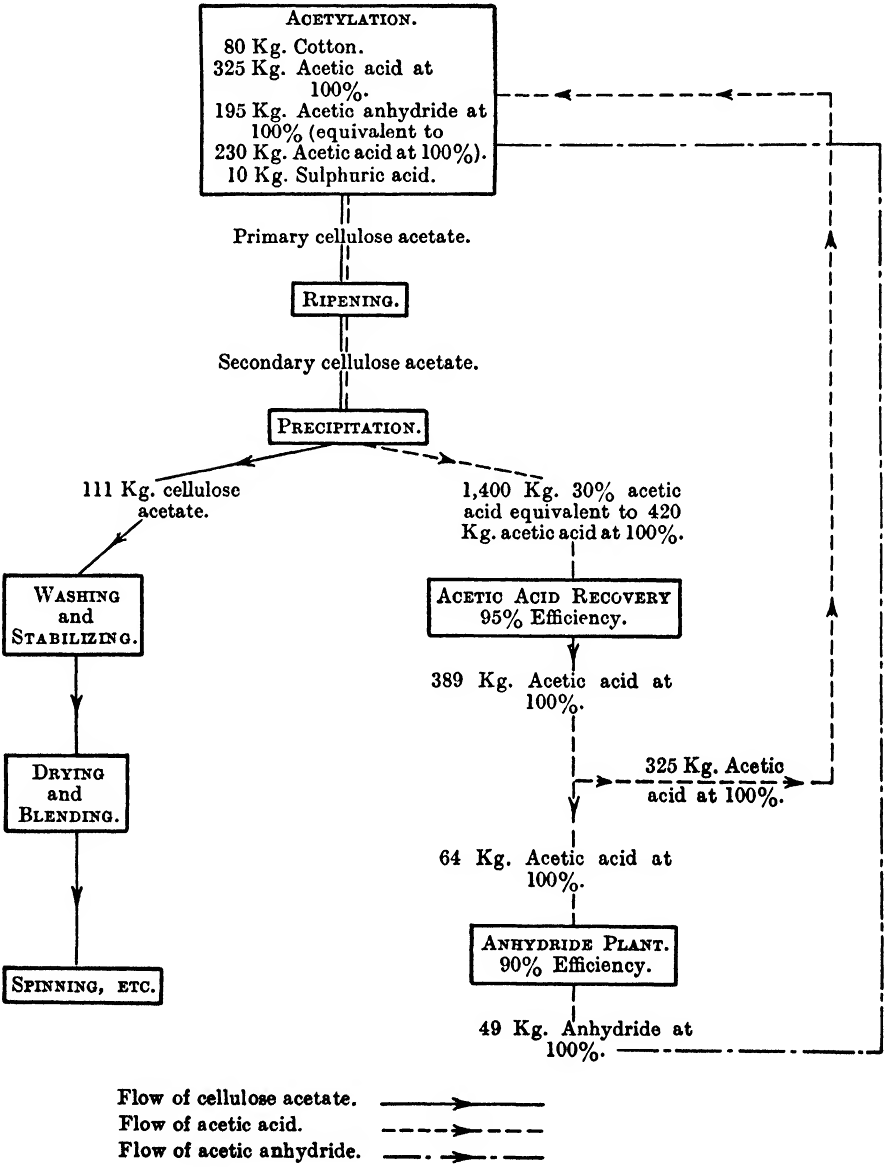
[1] Mariller. *La Carbonisation du bois*, p. 204.

FLOW-SHEET FOR THE MANUFACTURE OF CELLULOSE ACETATE BY THE METHOD OUTLINED IN CHAPTER IV



present, but sometimes with the acetic acid or with both depending on the conditions under which the process is conducted.

(*a*) These methods are very expensive in heat requirements, time, and materials, and cannot be operated continuously. The acid from the precipitators must first be distilled in order to separate the organic matter held in solution or suspension; the distillate is then neutralized with the calculated amount of soda ash, caustic soda, or lime, etc., evaporated to dryness, and after grinding, the salt is distilled with a strong acid. The sulphate obtained as a by-product has little or no commercial value.

Various processes for obtaining concentrated acetic acid from its salts have been made the subject matter of patents, almost all of which have expired. For example, the calcium salt may be treated with excess of dry calcium chloride resulting in the formation of a readily crystallizable double salt, which is recrystallized and then distilled with strong sulphuric or hydrochloric acid.[1]

In another method, cold solutions of alkaline acetates are electrolysed using an iron anode in a cell fitted with a porous partition. The solution in the anode compartment is acidified with acetic acid to initiate the decomposition, and ferrous acetate and alkali are thus produced. The former is oxidized to the ferric condition by agitation with air, and the product is treated with potassium acetate until all the iron is precipitated as ferric hydroxide. Finally, the resulting biacetate of potassium is heated to convert it into free acetic acid and potassium acetate.[2]

According to Behrens[3] glacial acetic acid may be produced directly by dissolving calcium acetate in 60 per cent acetic acid and decomposing the solution with Nordhausen sulphuric acid, without the aid of heat. The calcium sulphate formed does not become stiff by hydration and the acetic acid is removed by distillation, pressing, or decantation.

The Chemische Fabrik Grünau Landshoff und Meyer A.-G. have described a method for recovering acetic acid from its salts by heating them with sulphuric acid in the form of a thin film on a rotary film evaporator, from which the residues are continuously removed. Distillation is effected at atmospheric pressure, and the acid vapours are removed by a fan to a condenser.[4]

Most of these early patents were for processes devised for the

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[1] Condy. B.P. 480/1868.*

[2] Count Plater-Syberg. B.P. 233/1898.*

[3] E. A. and J. Behrens. B.P. 73,013/1900.*

[4] Chem. Fabr. Grünau Landshoff & Meyer A.-G. B.P. 16,215/1915.*

concentration of pyroligneous acid, and it is improbable that there are any plants now working which are based on the above principles. More recently the Holzverkohlungs-Industrie A.-G. have been granted patents for the concentration of acetic acid by the addition of a salt such as sodium acetate followed by distillation under reduced pressure ; dilute acid first distils followed by concentrated acid at a temperature of 170–220° C.[1] The method was later improved by the use of mixed salts so that the mass remains molten. wholly or partially in the heating stage.[2] In an example 50 per cent acetic acid is treated with a mixture of sodium and potassium acetates and distilled. At 170° C. most of the water has been removed as 12 per cent acid, and on raising the temperature to 300° C. with reduced pressure if desired, the remaining acid is distilled off at 95 per cent strength.

(*b*) **Solvent Extraction.**—The extraction of acetic acid from its aqueous solutions was suggested as long ago as 1884 by Goering (D.R.P. 28,064), who proposed to use such solvents as ether, ethyl acetate, etc. The earliest British patent was due to G. B. von Belatini and appeared in 1907. It described the extraction of the acid with a solvent having a boiling point far removed from that of the acid, so that it could be removed by distillation.[3] Preliminary treatment with dehydrating agents such as calcium chloride, ferrous sulphate, copper sulphate, sodium sulphate, aluminium sulphate, borax, etc.,[4] or monohydrated magnesium sulphate (Kierserite),[5] followed by solvent extraction has also been covered.

Interesting modifications based on freezing out the water previous to solvent extraction have been described by the Consortium für Elektrochem. Ind. A.-G.[6] and by the I.G. Farbenind. A.-G.[7] In the former the dilute acid is cooled to a low temperature in presence of a solvent, which is preferably a chlorinated hydrocarbon such as trichlorethylene, until no more ice separates. The ice is separated in a centrifuge and washed with the solvent, the ice and cold extract being used to precool the next portion of weak acid, and the acetic acid is recovered by distillation. In the second patent the acid

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[1] Holzverkohlungs-Industrie A.-G. B.P. 302,268.
[2] Ibid. B.P. 306,105.
[3] G. B. von Belatini. B.P. 20,125/1907.*
[4] Lichtenthaler. B.P. 228,301. †
[5] A.-G. für Anilin Fabr. D.R.P. 302,673.
[6] Consortium für Elektrochem. Ind. G.m.b.H. B.P. 308,210.
[7] I.G. Farbenind. A.-G. B.P. 315,397.*

is concentrated to about 60 per cent strength by freezing out the water, and is then converted into glacial acid by some process other than one involving the formation of an addition compound. Thus it may be treated with solvents in the cold, or distilled with substances forming azeotropic mixtures with water. Alternatively, the 60 per cent acid may be treated with extracting agents of high boiling point, or substances which bind water chemically or physically may be added so that concentrated acid may be distilled off.

An important patent was granted in 1921 to T. J. Brewster,[1] the rights in which have been allowed to lapse, at least as far as this country is concerned, but according to E. P. Partridge,[2] who contributed an article on acetic acid and cellulose acetate in the United States to Industrial and Engineering Chemistry recently, it is still widely used in America for the concentration of pyroligneous acid. The dilute acid is introduced at the top of an extraction column through a distributor while the solvent (ether, and latterly isopropyl ether) is introduced at the bottom so that the acid is systematically extracted. In the case of heavy extractants such as chloroform the process is reversed. According to Partridge, extraction with isopropyl ether yields pure anhydrous acetic acid.

The Carbide and Carbon Chemicals Corporation in the United States have applied for a patent for a method of extracting acetic acid in the cold with isopropyl ether.

Between 1923 and 1929 an interesting and important series of patents were granted to Professor Dr. Hermann Suida, Director of the Institute of Chemical Technology of Organic Materials in the Technical High School of Vienna, for the recovery of concentrated acetic acid from aqueous solutions such as occur in the cellulose acetate industry, and in the dry distillation of wood. There are analogous patents existing in all states.[3]

The process as used in the acetate industry consists in extracting the acetic acid in the form of superheated vapour with high boiling solvents (B.P. greater than 150° C.) and the concentrated acid is then separated from the solvent by distillation, preferably in vacuo. In this way the solubility of the aqueous phase in the

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[1] T. J. Brewster, B.P. 187,603.*

[2] E. P. Partridge, *I. & E.C.*, 1931, **23**, 482–97.

[3] H. Suida. B.P. 218,271, 218,272, 230,447, 255,047, 275,158.

extraction agent is rendered negligible, while that of the acetic acid still remains considerable, so that perfect extraction of the practically anhydrous acid is made possible.

A diagrammatic scheme of the process is illustrated in Fig. 23. The dilute acetic acid from the precipitation department having been distilled to free it from dissolved solids and suspended matter, passes to the weak acid tank on the extreme left of the diagram, from which it is pumped to the preheater, where it is heated by the waste water vapour which escapes from the top of the extraction column. (Alternatively the acid direct from precipitation may be fed to the separating stills, and there separated from solid matter.) The acid leaves the preheater at the boiling point and passes to the evaporator, where it is evaporated, and the superheated vapour is led to the extraction column, which contains suitable packing material, and down which flows the extraction medium. The acetic acid is absorbed by the solvent, and the water vapour passes out at the top of the extraction column, proceeding to the preheater, after which it is condensed, and separated from traces of entrained extraction medium. The solution of acetic acid in the extraction medium is then evaporated, and the vapour passes to the vacuum column, where it is separated into its constituents. The oil flows out from the bottom of the vacuum column, and after cooling, is returned to the extracting oil tank to be used again. The acetic acid vapour passes out at the top of the vacuum column to a dephlegmator, where traces of extraction medium are removed and returned to the vacuum column. The acetic acid vapour is then condensed and flows via a seal pot to the glacial acetic acid storage tank. Any gases which leave the acetic acid condenser are scrubbed twice with weak acetic acid, and finally with water. By this process, dilute acetic acid of a strength of 15 per cent or over can be converted directly into a glacial acid of 99·5 per cent or even greater purity, which can be used directly in the acetylation process, or for the production of acetic anhydride by a contact process, for example.

The problem of concentrating acetic acid, the various processes available, and the theory underlying the method outlined above, have been clearly discussed by Dr. Suida in the Oesterreichischen Chemiker-Zeitung,[1] and later by Mariller in

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[1] Suida. *Oesterr. Chem. Ztg.*, 1927, No. 1.

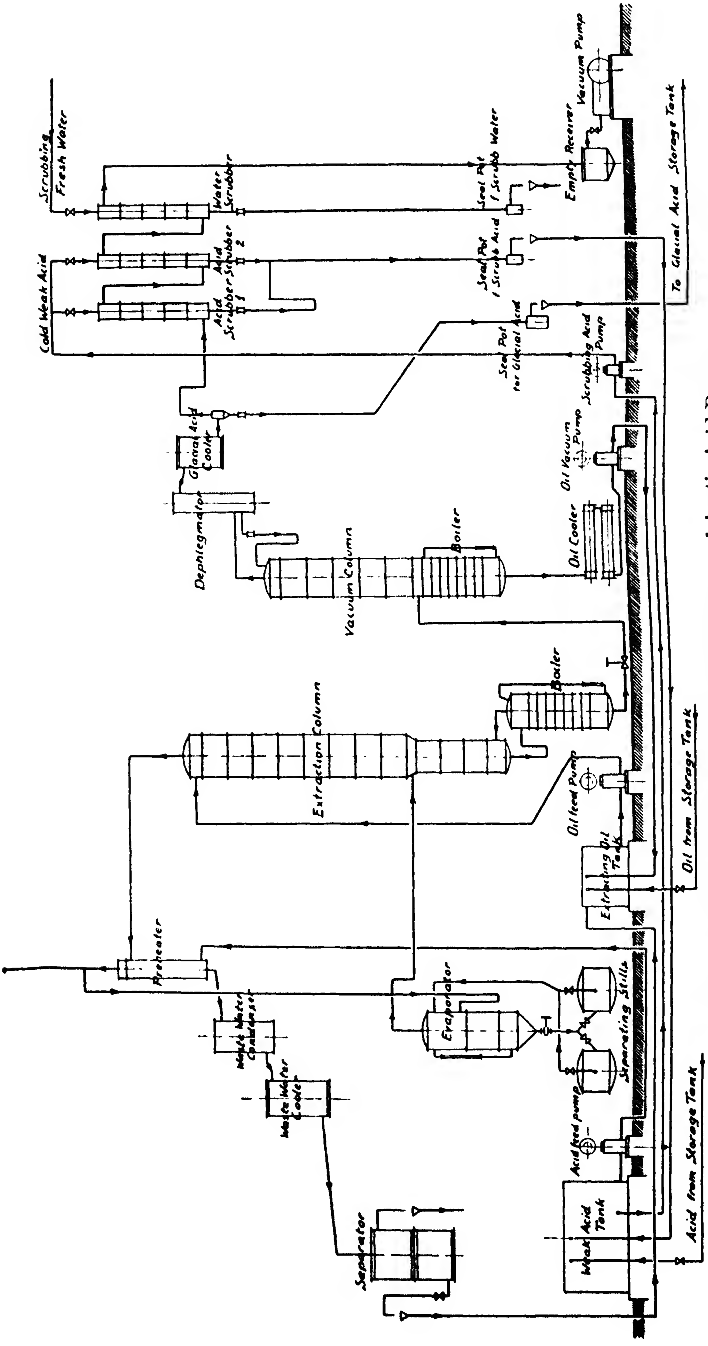

FIG. 23. Diagrammatic Scheme of Suida Process of Acetic Acid Recovery.

Chimie et Industrie,[1] and by Krase in Chemical and Metallurgical Engineering.[2]

The accompanying illustrations give some idea of the compact nature of the plant required to carry out the Suida process, and the ease with which its operation can be controlled. Fig. 24 is a ground-floor view of a Suida plant of one unit, with a capacity

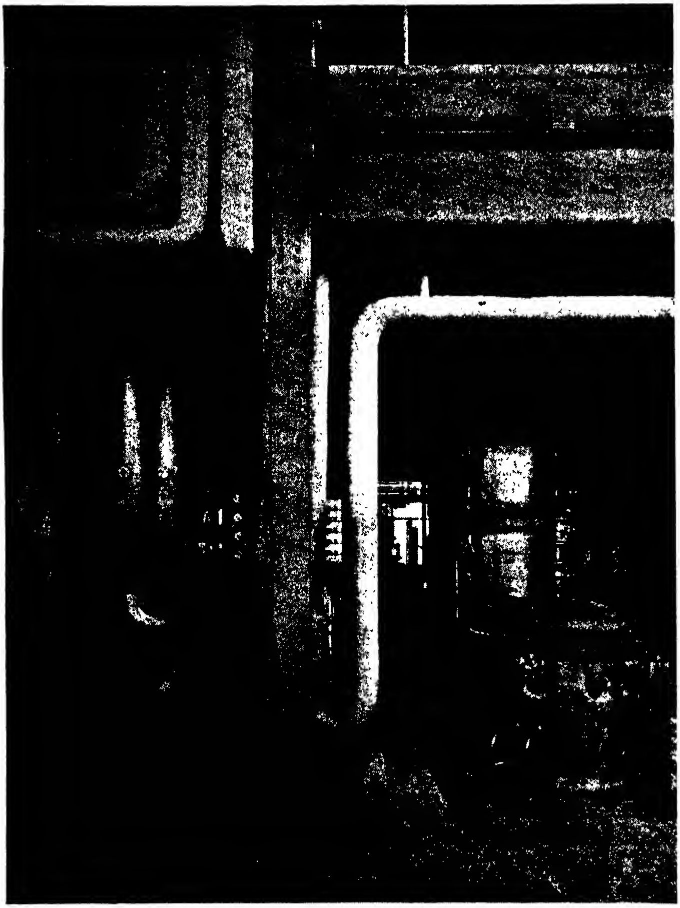

Fig. 24. Suida Plant for Acetic Acid Recovery—Ground Floor.

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[1] C. Mariller. *Chim. et Ind.*, 1929, **22**, No. 5.

[2] N. W. Krase. *Chem. and Met. Eng.*, Nov., 1929, 657–9.

of 6,000 kilos of glacial acetic acid per day. At the right of the picture is the boiler of the extraction column, and immediately behind it the lower part of the extraction column, the middle section of this column being just visible at the top of the picture. Fig. 25 indicates how all the controls, thermometers, and gauges are concentrated at one point, thus facilitating the operation of the plant, and making it possible for a single man to control the whole

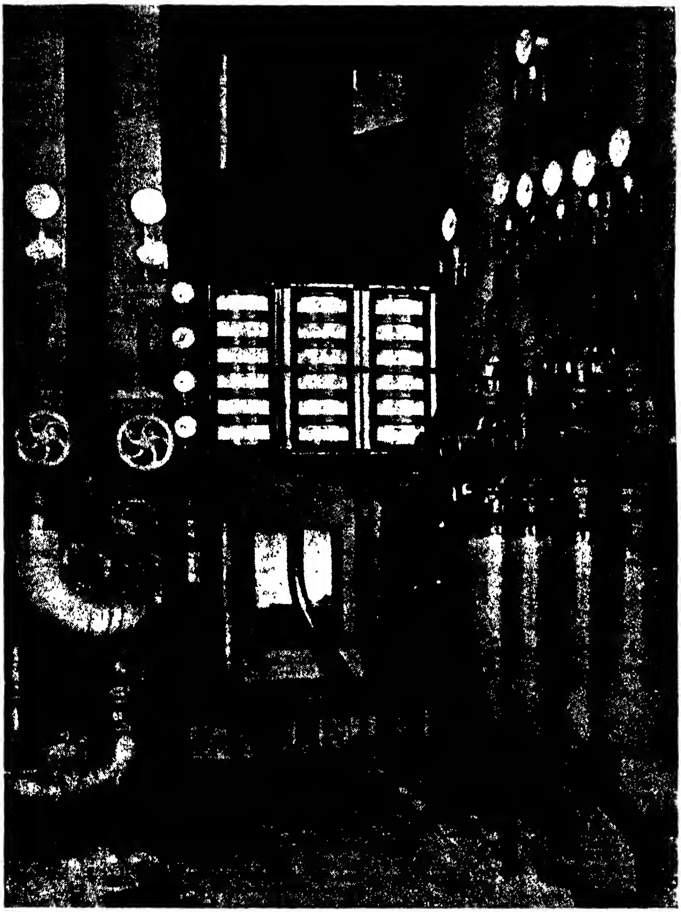

FIG. 25. Suida Plant for Acetic Acid Recovery—Controls.

process. Fig. 26 is a view of the first floor of the same plant. In the foreground can be seen the vacuum column, and to the right and behind the vacuum column is the extraction column. Finally, in Fig. 27 is seen the top floor of a concentration plant for the production of acetic acid at 99·5 per cent strength, consisting of two units, each of 6,000 kilos daily capacity. In the centre of the floor is the head of the extraction column, and immediately behind

Fig. 26. Suida Plant for Acetic Acid Recovery—First Floor.

it, the head of the vacuum column. Against the window at the left are the scrubbers.

Among other specifications covering solvent extraction may be mentioned those of British Celanese, Ltd., they extract, for example with a mixture of an acetic acid solvent and a hydrocarbon, both having boiling points higher than that of the acid,[1] or with methylene chloride.[2] The same firm have also described a two or more stage extraction process, with solvents so chosen that the ratio, acid : water in the extract at any stage is greater than in the preceding stage. For example, aqueous acetic acid is treated with ether, ethyl acetate, ether containing 20–30 per cent petroleum ether, etc.; the extract obtained is distilled, and the distillate is extracted with another solvent such as petroleum ether, benzene, etc., and in the last stage the solvent is preferably one which will form an azeotropic mixture with water.[3]

FIG. 27. Suida Plant for Acetic Acid Recovery—Top Floor.

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[1] British Celanese, Ltd., Dreyfus and Haney. B.P. 283,702.

[2] British Celanese, Ltd. B.P. 301,734.*

[3] Ibid. and Billing. B.P. 320,606.

(*c*) **Azeotropic Mixtures.**—If a mixture of dilute acetic acid and ethyl acetate be distilled, it will be noticed that the fraction up to 70° C. is a mixture of ethyl acetate and water, which, on standing separates into two layers of ester and water respectively; on further distillation up to a boiling point of 77° C., practically pure ethyl acetate distils, leaving a residue of concentrated acetic acid. The binary mixture of ethyl acetate and water is called an azeotropic mixture. The principle is not, of course, confined to these two liquids, and it has formed the basis of a large number of patents covering the separation of liquid mixtures into their components.

The earliest British patent relating to such a process for concentrating acetic acid appeared in 1923,[1] acetone oil being added to form a binary mixture with the aqueous phase.

The Société Anonyme des Distilleries des Deux-Sèvres has devoted much attention to azeotropic methods in connection with acetic acid concentration. In 1923 they described the continuous dehydration of organic liquids in general by such methods.[2] Four years later they covered the concentration of lower fatty acids by distilling with an acetic acid ester, or mixture of fatty acid esters[3]; and in 1928 they described a three-stage process, in which the acetic acid was first extracted with a solvent, the mixture of acetic acid and solvent was then dehydrated azeotropically, and finally the acetic acid was separated by distillation.[4] In a later patent, the same firm describe a method in which the acetic acid is extracted in the cold with a solvent having a boiling point not very far removed from that of acetic acid, the acid being recovered from the solution obtained by adding certain hydrocarbons which form azeotropic mixtures with acetic acid and distilling, addition of a small quantity of water to the distillate causing separation into two layers.[5] This method has also been made the subject of a paper in Chimie et Industrie by Guinot.[6]

Besides the three classes of methods of recovering the acetic acid used in the acetylation process, already described, it was a fairly common practice, before the elaboration of solvent and other

[1] Fabr. de Soie Art. de Tubize Soc. Anon. B.P. 213,914.

[2] Soc. Anon. des Distilleries des Deux-Sèvres. B.P. 226,822.

[3] Ibid. B.P. 273,744.

[4] Ibid. B.P. 296,974. See also B.P. 300,246.

[5] Ibid. B.P. 312,046.

[6] H. Guinot. *Chim. et Ind.*, 1929, **31**, 243–51.

recovery processes, to convert the dilute acetic acid into acetic anhydride by way of the sodium or other salt. Such methods are dealt with below, under the manufacture of acetic anhydride.

Of the methods available for the recovery of acetic acid in the glacial condition, it would appear that there is not much difference as far as capital outlay and working costs (steam, energy, wages) are concerned; but from the point of view of easy manipulation, low solvent consumption, freedom from trouble, and steady running over prolonged periods the Suida process cannot be equalled.

Manufacture of Acetic Anhydride.—The earlier methods of preparing acetic anhydride consisted in treating the sodium or other salt of acetic acid with phosgene, sulphur dichloride, sulphuryl chloride, etc. Typical reactions are as follows:—

$$2CH_3COONa + COCl_2 = (CH_3CO)_2O + CO_2 + NaCl$$
$$4CH_3COONa + SO_2Cl_2 = 2(CH_3CO)_2O + 2NaCl + Na_2SO_4$$
$$8CH_3COONa + 3SCl_2 = 3(CH_3CO)_2O + NaCl + Na_2SO_4 + 2S.$$

Many of these reactions have formed the subject matter of patents, but these have all expired as far as the basic inventions are concerned. Thus, in 1900, the Farbenfabriken vorm F. Bayer and Co. covered the action of sulphur dioxide and chlorine on the dry salts of acetic acid, at a temperature below 20° C.[1] Treatment of the sodium or other salt of the acid with the sodium, potassium, calcium, barium, or other salt of chlorsulphonic acid with gentle heating was suggested by the Badische Anilin und Soda Fabrik in 1902,[2] while in 1910, the A.-G. für Anilin Fabrikation patented the reaction with sulphuryl chloride.[3] Two years later Beatty described the production of acetic anhydride by the action of a mixture of carbonyl chloride and sulphuryl or polysulphuryl chloride or both upon a salt or salts of acetic acid.[4]

The more recent patents are mainly for modifications of the basic processes in regard to the conditions under which the reaction is carried out. The following examples may be cited:—

H. Dreyfus[5] treats an acetate with chlorides of sulphur (SCl_2, S_2Cl_2, or SCl_3) in such proportions that six atoms of chlorine are present for each eight acetyl radicals. The sulphur chloride is

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[1] H. E. Newton (for Farbenfabr. vorm. F. Bayer & Co.). B.P. 21,560/1900.*

[2] J. Y. Johnson (for Badische Anilin u. Soda Fabr.). B.P. 24,255/1902.*

[3] A.-G. für Anilin Fabr. B.P. 23,923–4/1910.*

[4] W. A. Beatty. B.P. 18,823/1912.*

[5] H. Dreyfus. B.P. 100,450.*

introduced into a suspension of the acetate in a diluent such as acetic anhydride. The product is freed from sulphur by treatment with oxidizing agents. In an addition patent[1] the anhydride is directed to be distilled off at a temperature below 150° C. *in vacuo.*

Boake Roberts & Co., Ltd., and Durrans[2] cover the action of sulphur dioxide and chlorine on an acetate in the presence of small quantities of esters of alcohols or phenols with organic or inorganic acids, or in presence of small quantities of ethers, aldehydes, acetals, phenols, or hydrocarbons.

In the process of making acetic anhydride by the action of sulphur trioxide on an acetate or acetates, Dreyfus recommends that the salt be treated at a low temperature with sulphur trioxide in gaseous form, diluted with inert gases (0– –20° C. or lower).[3]

Leach and the United Alkali Co., in 1919, described a modification of the process of producing acetic anhydride by the action of phosgene on an acetate, in which the reaction bodies are simultaneously introduced into acetic anhydride. The mixture is kept well cooled and stirred. When the reaction is complete, a portion of the mixture is withdrawn and the acetic anhydride completely removed from it by distillation *in vacuo.* The remainder of the reaction mixture serves for the interaction of further quantities of phosgene and sodium acetate, thereby making the process continuous.[4]

Quite recently the Société des Brevets Étrangers Lefranc et Cie stated that acetates of the alkaline earth metals may be used for the production of acetic anhydride by treating them with sulphuryl chloride or with sulphur dioxide and chlorine (with or without a catalyst, and/or solvent) provided they are mixed with sand or other inert powder. An acid absorber such as lime is preferably added.[5]

In addition to the three principal reactions and their modifications described above, a few other reactions have been suggested from time to time for the production of acetic anhydride from salts of acetic acid; thus in 1905 R. Sommer[6] described the production of anhydride from anhydrous acetates by the action of silicon

[1] H. Dreyfus. B.P. 100,452.*

[2] Boake Roberts & Co., Ltd., and T. H. Durrans. B.P. 130,399.*

[3] H. Dreyfus. B.P. 130,660.

[4] Leach and United Alkali Co., Ltd. B.P. 137,701.*

[5] Soc. des Brevets Étrangers Lefranc et Cie. B.P. 344,116.

[6] R. Sommer. B.P. 11,058/1905.*

tetrafluoride, and in 1914 the Deutsche Celluloid Fabrik covered the action of nitrogen pentoxide alone, or other nitrogen oxides mixed with air or oxygen upon dry acetates in the solid state or suspended in a liquid. The resulting anhydride may be freed from the nitrate formed by heating *in vacuo* or by extraction.[1] Neither of these patents is in force. Acetic anhydride may also be prepared from its salts by the action of the acid chloride :—

$$CH_3COONa + CH_3COCl = (CH_3CO)_2O + NaCl$$

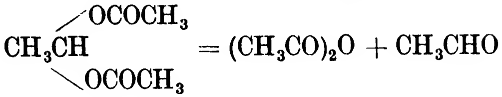
In a modification of this process the I.G. Farbenind. A.-G.[2] produce the acid chloride in situ, the source of chlorine being the chloride of silicon, tin, or titanium. In an example acetic anhydride is made by mixing glacial acetic acid with dry sodium acetate in a closed vessel and adding silicon chloride while stirring. When the pressure (which rises) becomes normal, the mixture is distilled, preferably under reduced pressure.

With the advent of satisfactory methods for the economical concentration of acetic acid, the necessity for processes starting from a salt of the acid no longer exists, and it is probable that the greater proportion of the acetic anhydride produced at the present time not only in cellulose acetate factories, but for general purposes, is made from concentrated acetic acid by suitable treatment, e.g. with a dehydrating catalyst. Where power is cheap, processes depending upon acetylene as the starting material have found favour. If a mixture of acetylene gas and the vapour of acetic acid are passed together over suitable catalysts a mixture of acetic esters of ethylidene glycol, and of vinyl alcohol are produced. For example, if equal volumes of acetylene and acetic acid vapour are passed at a temperature of 200° C. over charcoal impregnated with cadmium acetate, a mixture of ethylidene diacetate and vinyl acetate are produced and may be separated by fractional distillation.[3] Mercury compounds[4] and later mercuric acetate, together with aromatic or aliphatic sulphonic acids,[5] have also been suggested as catalysts for the reaction.

Both these esters are highly reactive and unstable. Thus

[1] R. Müller and Deutsche Celluloid Fabr. B.P. 5,773/1914.*
[2] W. Carpmael (for I.G. Farbenind. A.-G.). B.P. 289,959.
[3] Consortium für Elektrochem. Ind. G.m.b.H. B.P. 182,112.
[4] Chem. Fabr. Griesheim Elektron. B.P. 14,246/1913.*
[5] Soc. Chim. des Usines du Rhône. B.P. 112,765–6.††

ethylidene diacetate is readily decomposed when heated giving a mixture of acetic anhydride and acetaldehyde :—



$$CH_3CH\begin{matrix}\diagup OCOCH_3\\ \diagdown OCOCH_3\end{matrix} = (CH_3CO)_2O + CH_3CHO$$

In the case of vinyl acetate, if it is heated with acetic acid under reflux, it yields a similar mixture :—

$$CH_2{:}CH.OCOCH_3 + CH_3COOH = (CH_3CO)_2O + CH_3CHO$$

The first of these reactions was patented in 1914 by the Bosnische Electricitäts A.-G. with or without the use of catalysts such as sulphuric acid or mercuric sulphate.[1] A similar process was later covered by the Société Chimique des Usines du Rhône, who used sodium pyrosulphate, monosodium orthophosphate, metaboric acid, and sulphacetic acid as catalysts.[2] The same firm also patented a process carried out under reduced pressure in presence of acids or acid salts acting as catalysts.[3] In an example a mixture of ethylidene diacetate and sulphuric acid was heated at 70–80° C. under 100 mm. pressure. Heating the reaction mixture alone, or in presence of depolymerizing agents, converts the paraldehyde formed into aldehyde, and the mixture of aldehyde and anhydride is separated into its constituents by fractional distillation. In a later patent the use of halogen compounds of zinc as catalysts in the thermal decomposition of ethylidene diacetate was claimed by the same firm.[4] For example, a small amount of an acetic acid solution of zinc chloride is added to ethylidene diacetate which is then slowly introduced into a flask provided with a column. On heating, the escaping vapours meet zinc shavings, ribbon, etc., in the column, whereby most of the escaping halogen is returned to the flask. The vapours pass through a second column in which a mixture of ethylidene diacetate and acetic anhydride is condensed. Acetaldehyde is condensed from the residual vapours by cooling with ice and salt. The mixture of ethylidene diacetate and acetic anhydride is fractionated as well as the liquid remaining in the distillation flask, a substance such as potassium acetate being added

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[1] Bosnisches Electricitäts A.-G. B.P. 23,190/1914.*

[2] Soc. Chim. des Usines du Rhône. B.P. 131,399.*

[3] Ibid. B.P. 110,906.†

[4] Ibid. B.P. 238,825.

to the latter before distillation, to prevent further catalytic decomposition. Compounds such as acetyl chloride or bromide which form halogen derivatives with zinc may be used in place of the halogen derivatives themselves. About four years later the same firm described a method of preventing the polymerization of the aldehyde formed in the above process, by passing the reaction vapours before condensation through organic acid salts, preferably acetates of alkalies, alkaline earths, or organic bases in suspension in a mixture of ethylidene diacetate and acetic anhydride and, if desired, acetic acid. The organic salts remove halogen or other substance derived from the dissociation catalyst, and the aldehyde produced has no tendency to polymerize.[1]

The reaction between vinyl acetate and acetic acid was described by the Consortium für Elektrochem Ind. A.-G.[2] in 1928. They recommended the use of a catalyst which converts paraldehyde into aldehyde, e.g. sulphuric, phosphoric, or benzene sulphonic acid. In an example, vinyl acetate is boiled under reflux with acetic acid and a little sulphuric acid, when acetic anhydride is obtained in about 70 per cent yield. A continuous process of production is described.

Another interesting substance in this connection is ketene. This substance, $CH_2:CO$ was first obtained by Wilsmore[3] by heating acetic anhydride, acetic ester, or acetone by means of a glowing platinum wire. It was later prepared by Schmidlin[4] by passing acetone vapour through a red-hot tube :

$$CH_3.CO.CH_3 = CH_2 : CO + CH_4$$

Ketene is a colourless gas with a suffocating odour, and gives rise to painful headaches if inhaled. It has the interesting property of reacting with acetic acid to form acetic anhydride. The production of ketene on a large scale was described by the Ketoid Co. (Assignees of D. A. Nightingale) in 1924, who made use of the thermal decomposition of acetone in presence of metallic sulphates which are not decomposed at a temperature of 700° C., e.g. sulphates of chromium, manganese, aluminium, calcium, barium, strontium, magnesium, and silver. Of these, aluminium sulphate

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[1] Soc. Chim. des Usines du Rhône. B.P. 218,960.*

[2] Consortium für Elektrochem. Ind. G.m.b.H. B.P. 288,549.

[3] Wilsmore. *J.C.S.*, 1907, **91**, 1938.

[4] Schmidlin. *Ber.*, 1910, **43**, 2821.

was said to be the most effective, at a temperature of 635° C.[1] In a further patent, the same firm described the production of acetic anhydride by passing the ketene into acetic acid.[2] They also claimed [3] that cellulose acetate could be prepared by treating cellulose with ketene, either alone or in presence of an inert solvent, such as benzene, or of glacial acetic acid or acetic anhydride, which serves to moisten the cellulose before addition of the ketene. A small proportion of a catalyst such as zinc chloride, chlorsulphonic acid, etc., could also be present. These reactions are very interesting and suggestive. To make them commercially realizable, however, the price of acetone would have to be reduced very considerably, or else an alternative method of producing ketene would have to be found. These three patents are no longer in force, but they evidently stimulated research, for in 1927 H. Dreyfus described a process for the production of ketene from acetaldehyde.[4] The aldehyde is subjected to a temperature of 150–300° C. in presence of a catalyst such as nickel, copper, or zinc, at atmospheric pressure, but the temperature may be as high as 500° C. and a pressure of 5–50 atmospheres be used, particularly if the catalyst is omitted. He claims that the ketene may be collected in the gaseous state and used in acetylation, or it may be used to form acetic acid or anhydride. Another process for obtaining ketene from acetone was described by Kodak, Ltd.,[5] and the patent is still in force. The acetone vapour is passed through a reaction chamber containing a sponge-like structure of metal, free from iron or nickel, and having a high thermal conductivity. Copper, silver, and copper alloys are suitable metals. The optimum time of contact in the case of acetone does not exceed five seconds. In an example, acetone vapour is passed through a copper tube packed with copper turnings and heated to 650–70° C.

Although the thermal decomposition of acetic acid with production of acetic anhydride and water was described in British patent literature as long ago as 1901 by Behrens,[6] the manipulative difficulties arising in connection with the separation of the anhydride and water prevented the commercial development of such processes,

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[1] Ketoid Co. (Assignees of D. A. Nightingale). B.P. 237,573.*
[2] Ibid. B.P. 237,574.*
[3] Ibid. B.P. 237,591.*
[4] H. Dreyfus. B.P. 273,622.
[5] Kodak, Ltd. B.P. 309,577.
[6] J. Behrens. B.P. 3,392/1901.*

and the use of catalysts, which promote the formation of anhydride by binding the water set free in the reaction, does not appear to have been considered seriously for quite twenty years after that date.

When acetic acid is heated to a high temperature, 600–800° C., water is split off with the formation of ketene, which then reacts with a further quantity of acetic acid to form acetic anhydride. The manufacture of anhydride by this means was proposed by the Consortium für Elektrochemische Industrie, G.m.b.H.,[1] who mentioned a temperature of 400–800° C., and stated that catalysts such as compounds of iron, which have the effect of bringing about an undesirable decomposition of the acid,[2] or nickel and copper, which in a state of fine division have been found by Sabatier to decompose acetic acid with the formation of carbon dioxide and methane at a temperature of 300° C.,[3] should be absent. Catalysts which favour production of the anhydride were recommended, as, for example, chlorides and sulphates of alkali and alkaline earth metals or boric acid and borates. In 1924 the same firm described the use of phosphates, preferably of metals of the second or third group of the periodic table, as being specially useful catalysts for this reaction.[4] The anhydride is prepared by passing acetic acid vapour over a heated phosphate, preferably a metaphosphate of sodium, potassium, or lithium, or mixtures of these salts, mounted on a suitable carrier such as silicon or carborundum. Silicates are unsuitable as carriers, since at the high temperatures employed, the phosphate attacks the silicate. The activity of sodium phosphate is said to be improved by heating it beforehand to a temperature of 700–900° C. This is attributed to the formation of salts of polymerized metaphosphoric acid, which are more active than the ordinary sodium phosphate. In an example, 45 parts of carborundum of suitably sized grain are mixed with a solution of 14·9 parts of crystallized disodium hydrogen phosphate and 4·9 parts of orthophosphoric acid of 84 per cent strength in 50 parts of water; the water is evaporated so that there is left carborundum coated with sodium phosphate, which is then heated at 900° C. for an hour. The product obtained is heated to 600° C.

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[1] Consortium für Elektrochem. Ind. G.m.b.H. B.P. 194,719.

[2] Gmelin. *Handbuch der Org. Chem.*, IV Aufl., vol. i, 624.

[3] Sabatier. *La Catalyse*, 1920, p. 328.

[4] Consortium für Elektrochem. Ind. G.m.b.H. B.P. 230,063.

and maintained at that temperature while acetic acid vapour is passed over it.

Certain mixtures of phosphates melt below the temperature at which the anhydride forming reaction takes place. This is advantageous, since the vapour of the acetic acid can be blown through the liquid mass, with improved heat transmission, particularly if the mass is kept in a state of agitation, and consequently the output is increased. In a second example, 102 parts of lithium carbonate, 793 parts of disodium hydrogen phosphate (crystallized), and 405 parts of orthophosphoric acid are heated together at 850° C. Through the resulting melt, which is maintained at 630° C. and constantly stirred, is passed a rapid current of acetic acid vapour.

The catalyst gradually loses its activity due to the deposition of carbon. It may be regenerated by blowing air through at high temperature, or it may be necessary to dissolve in water and filter from the carbon before the phosphates are used again (the composition having been adjusted if necessary).

A later specification [1] after drawing attention to the undesirability of using certain materials such as iron in the construction of the plant used, states that in certain reactions (e.g. the second example above) it is unnecessary to select the material of the vessel from the standpoint of its action on acetic acid, since the highly heated portion of the surface of the vessel is protected from direct contact with the acetic acid vapour by the molten catalyst, and the vapour only comes into contact with parts of the vessel which are at much lower temperatures. The patent covers the use of a number of materials for the construction of the plant, which normally have a strongly decomposing action on acetic acid such as copper, alloys rich in copper, silicon, silicon carbide, and in particular, acid resisting alloys containing chromium or nickel. In an example acetic acid vapour is conducted in a rapid current through a copper tube heated electrically to 700° C., and containing as catalyst, aluminium metaphosphate mounted on a carrier. It is stated that more than half the acetic acid is converted into anhydride and water. The formation of by-products is said to be particularly small when such materials as Krupp's "V 2 A", "V 7 M", or similar alloys containing chromium are used. These alloys have the further advantage that deposited carbon can be removed by passing

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[1] Consortium für Elektrochem. Ind. G.m.b.H. B.P. 272,923.

air or steam with the materials at a red heat, without risk of damage.

A further specification[1] recommends preheating the acetic acid vapour to a temperature of 400–800° C. By this means the output, when using molten alkali phosphate as catalyst, is increased tenfold.

As described by the Consortium für Elektrochemische Industrie G.m.b.H., the process is fully continuous, concentrated acetic vapour being passed into the apparatus in an unbroken stream, and anhydride of about 90 per cent strength issuing continuously. The water dissociated from the acetic acid appears in the form of dilute acetic acid, which can be concentrated in the acetic acid recovery plant or put to other uses. Beyond the small quantity of catalysts used no other reagents are required, and the catalyst has a long life and is inexpensive. The plant is automatic, requiring a minimum of supervision, and the outlay on salaries and wages is consequently small. The product is very pure and, of course, free from chlorine and sulphur compounds. Heat requirements are rather less than 3 Kw. per hour, or if coal is used for heating, at most 0·9 Kg. is consumed per kilo of end-product, while the steam consumption is about 5–6 Kg. per kilo.

According to H. Dreyfus[2] acetic anhydride may be prepared by heating acetic acid vapour in presence of a phosphoric acid or mixture of such acids, either alone or mixed with porous substances, and preferably at a temperature above the boiling point of acetic anhydride, e.g. 100–400° C. A later specification[3] describes a process in which the acetic acid in liquid form is heated with a phosphoric acid of lower degree of hydration than the ortho acid, or with an alkali or alkaline earth salt of such an acid, with or without a non-aqueous diluent such as acetic acid or anhydride. A temperature of 100–250° C. is recommended, and the reaction may be effected under pressure if desired.

The I.G. Farbenind. A.-G. have more recently[4] covered the use of an alkali phosphate containing boron phosphate at a temperature of 600–700° C. as a catalyst for the conversion of acetic acid into the anhydride.

The submission of the mixture of acetic anhydride, acetic acid,

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[1] Consortium für Elektrochem. Ind. G.m.b.H. B.P. 272,951.

[2] H. Dreyfus. B.P. 280,972.

[3] British Celanese, Ltd., Dreyfus and Bader. B.P. 299,342.

[4] I.G. Farbinend. A.-G. B.P. 330,537.

and water obtained when acetic acid is heated to a high temperature with or without a catalyst, to the action of "water-binding" agents such as bisulphates or pyrosulphates of alkali or alkaline earth metals, zinc or calcium chloride, etc., has also been described.[1]

Another method of separating acetic anhydride from the water vapour associated with it in reactions such as have been described above, has been covered by the I.G. Farbenind. A.-G.[2] and consists in passing the vapours through a porous tube heated to a high temperature, and surrounded by a quartz tube to which vaccum is applied, when the vapours are separated by diffusion. In an example, a graphite tube containing the catalyst at 600° C. and surrounded by a partially evacuated quartz tube is used for this purpose.

An interesting specification due to British Celanese, Limited,[3] states that acetic anhydride may be obtained by heating the vapour of the acid, glacial or dilute, and condensing the anhydride while carrying away the water by means of an entraining liquid such as carbon tetrachloride, petrol, benzene, mixtures of two or more of these liquids, or mixtures of ether and petroleum ether, but excluding liquids which are solvents for acetic anhydride and have higher boiling points than water. The vapour of the entraining liquid may be added at any stage of the process.

Another process of producing anhydride which has been patented by British Celanese, Limited, consists in mixing the acid in the form of vapour or spray with an inert gas such as steam, superheated steam, or nitrogen or hydrogen, heated to 600–1,200° C., the acid being preheated to 150–300° C.[4]

H. Dreyfus has described the preparation of acetic anhydride by heating the vapour of the acid mixed with from 2–20 per cent of its weight of sulphur dioxide, and in presence of contact or filling materials such as carborundum, pumice, etc., in a silica or fireclay tube.[5] In an example, sulphur dioxide is passed through boiling acetic acid, and the mixed vapour is passed through a fireclay or fused silica tube filled with balls of pumice or kieselguhr and heated to 450–600° C., the reaction gases being then passed over sodium pyrosulphate or bisulphate at 150–350° C. In a later specification

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[1] H. Dreyfus. B.P. 289,972.

[2] W. Carpmael (for I.G. Farbenind. A.-G.). B.P. 301,562.*

[3] British Celanese, Ltd., Dreyfus and Haney. B.P. 303,772.

[4] Ibid. B.P. 304,156.

[5] H. Dreyfus. B.P. 313,418.

Dreyfus covers a process in which the acetic acid vapour is mixed with at least 2 per cent of a hydrohalide acid and heated to 100–900° C., with or without catalysts.[1] In an example 120 parts of acetic acid and 36 parts of hydrochloric acid are passed rapidly in admixture through a fireclay or silica tube at a temperature of 500–600° C.; the vapours are then passed over sodium acetate, and finally through a fractionating column maintained at a temperature between the boiling points of acetic anhydride and water.

Dreyfus has also described a method of making anhydride from acetic acid,[2] by heating the acid vapour in admixture with or in presence of non-metallic inorganic or organic bases such as ammonia, primary, secondary, or tertiary alkylamines, pyridine, quinoline, aniline, etc., or their salts. The reaction is effected at 200–700° C. in fireclay, silica, copper, or other tubes, and the base may be used in the solid liquid or vapour state. Catalysts may also be used. In a later specification [3] the acid is heated in presence of an aliphatic acid substituted in the alkyl group by a halogen or sulphonic acid group, or in the hydroxyl group by phosphoric acid residues such as mono- or poly-sulphoacetic or acetylphosphoric acids. The reaction is effected at 250–1,000° C. at reduced, ordinary, or increased pressures in tubes of copper, silica, earthenware, etc. Other catalysts mentioned by Dreyfus include phenols or aliphatic acetyl derivatives of phenols,[4] and polyhydric alcohols and their aliphatic acidyl derivatives, such as glycerol or the acetins.[5]

A very interesting reaction has been described by Ewan, Roberts, and Imperial Chemical Industries, Limited.[6] To quote the specification: "In readily reversible reactions involving the splitting of water in which the elements of water are present in the compound or compounds undergoing the reaction it is known that the concentration of the water should be kept low as otherwise a reversal of the process tends to occur. It is also known to employ catalysts or other substances to fix physically or chemically the water produced in such reactions and to ensure a steady production of the desired compounds. We have now found that a specially advantageous method of carrying out dehydrating reactions, i.e. reactions of the type described above in the gaseous phase

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[1] H. Dreyfus. B.P. 314,132.
[2] Ibid. B.P. 317,907.
[3] Ibid. B.P. 318,662.
[4] Ibid. B.P. 318,663.
[5] Ibid. B.P. 318,664.
[6] Ewan, Roberts, and I.C.I., Ltd. B.P. 316,898.

consists in adding carbon monoxide or gases containing same, to the substance or mixture of substances about to undergo the dehydrating reaction, the temperature being maintained in the range wherein the reaction $CO + H_2O = H_2 + CO_2$ is known to occur to a far-reaching extent, namely, from 300-500° C. A catalyst is employed for the dehydrating reaction and also a catalyst promoting the conversion of carbon monoxide with steam is present. Suitable dehydrating catalysts are oxides of aluminium, thorium, or zirconium, aluminium phosphate or silicate, phosphoric acid, etc. One or more of such catalysts may be mixed with a catalyst which favours the CO/steam reaction, but preferably the two catalysts are used in succession.

" In some cases the temperature which is most suitable for the dehydration differs materially from that which is best for the carbon monoxide-steam reaction, or the catalyst for the latter reaction may bring about further undesired changes in the substances undergoing dehydration or in the products of the dehydrating reaction.

" In such cases it is preferable to conduct the process in two stages in which the substance or substances entering into the dehydrating reaction is or are first passed over a dehydrating catalyst at a temperature suitable for the dehydration reaction and then over a catalyst for the CO/steam reaction at a temperature which is more suitable for that reaction.

" In general the second catalyst will be at a lower temperature than the first. The space velocities of the gases may also, if necessary, be different.

" In the above described two-stage process of effecting dehydrating reactions it is not strictly necessary that carbon monoxide should be present in the first stage, as it may be added after the passage of the gases over the first catalyst and before the second stage. It is, however, preferred to add carbon monoxide from the start although additional amounts may be introduced during the course of the operation, particularly for the purpose of cooling the resultant gases from the first catalysis to the lower temperature required for the second.

" EXAMPLE

" Acetic acid was vaporized in a stream of carbon monoxide and the mixed gases passed over sodium metaphosphate at a temperature of 500–600° C. and then over a catalyst prepared by heating manganous carbonate in a current of carbon monoxide at a temperature of 300–500° C. until no further change took place. The temperature of the second catalyst was kept at about 350° C. On cooling the reaction gases a mixture of acetic acid and acetic anhydride which was almost free from water was obtained.

" The invention is also applicable to the formation of esters in the gaseous phase. . . ."

" In working with acetic acid iron should be excluded from the reaction system on account of its deleterious action on acetic acid vapour and the temperature of the second catalyst should be kept as low as possible consistent with reasonable reaction at reasonable space velocities to diminish the tendency to decomposition."

Other catalysts which have been suggested for the dehydration of acetic acid include tungstic acid and/or tungstates at 550–650° C.[1] ; alkaline earth tungstate mixed with copper turnings at 400–700° C.[2] ; oxides or acids of arsenic and antimony or their salts at 350–700° C.[3] ; silica gel, with or without other catalysts, such as calcium tungstate, at 550–650° C.[4]

It has also been proposed to pass the vapour mixture resulting from the thermal decomposition of acetic acid over activated carbon, when the anhydride and some of the acid are adsorbed, while the water and remaining acid pass on. The acid and anhydride may be recovered by raising the temperature and reducing the pressure.[5]

Whatever process is adopted for the conversion of acetic acid into anhydride, such conversion need not necessarily be complete, since the mixture of acid and anhydride obtained can be analysed and adjusted to the correct composition for the acetylation process.

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[1] British Celanese, Ltd., Green and Widdowson. B.P. 314,555.

[2] H. Dreyfus. B.P. 334,533.

[3] Ibid. B.P. 336,960.

[4] British Celanese, Ltd., Oxley and Fallows. B.P. 340,484.

[5] I.C.I., Ltd., Hepworth and Leicester. B.P. 334,968.

CHAPTER VI

THE FACTORY AND PRODUCTION METHODS

The manufacturer of to-day is much more favoured in regard to the choice of a site for his factory than was his predecessor of a century ago. The need for cheap power, which was then synonymous with coal, compelled the latter to seek a location on or near one of the coal-fields. It was this centralization of industry which gave rise to the large industrial cities and areas of to-day, cities and areas which grew organically as crystals about their nuclei—each new factory attracting workers from the countryside, thus building up the new working classes, and at the same time creating fresh facilities for industry in the shape of railways and canals, with the consequent attraction of other manufacturing concerns.

While this centralization of industry was perhaps inevitable, resulting as it did in undeniable economies, we have gradually come to realize that in many respects its results are deplorable. Apart from moral issues, the overcrowding and bad housing conditions in our large towns have reduced the efficiency of the population. Brought up and continuing to live in confined spaces, and in an atmosphere polluted with smoke and fumes, the industrial worker has degenerated physically from generation to generation. From time to time attempts have been made to solve this problem, in some cases with a considerable measure of success, as witness the activities of Lever Brothers at Port Sunlight and of Cadbury Brothers at Bournville.

Coeval with the reduced efficiency of the workers, there has been a corresponding reduction in the efficiency of plant and machinery, and for very similar reasons; the adaptation of unsuitable premises, the lack of foresight displayed by plant designers, with the resulting confusion in the arrangement of plant and machinery, and the general lack of scientific organization in our industrial life have all contributed to this result.

To-day we stand at the beginning of a new industrial era, an era of decentralization to which we have been led by the more widespread distribution of that vital force of industry—electricity—and to some extent by the remarkable development which has taken place during the last twenty years in the sphere of road transport, with the result that the manufacturer now has the widest freedom of choice when seeking a site for a new factory. In other words, industry has been liberated from the shackles of the coal-fields and there is every prospect of improved conditions both for man and machine. This improvement cannot fail to bring about a corresponding increase in our industrial efficiency.

In choosing the site for an acetate factory, there are certain points which must be considered with great care. The arrangement of the various departments, and the manner in which the plant is laid out therein, are of such importance that it is useless to consider the adaptation of existing premises which were designed for some entirely different industry, and although in every other respect the site may be very desirable, it is better to abandon it altogether than to attempt reconditioning, or the installation of plant in existing buildings. In such a case demolition is the only true economy. Assuming that entirely new buildings are to be erected, the primary considerations governing the choice of a site are as follows :—

(*a*) The site should be as level as possible, and have a firm subsoil capable of bearing the weight of buildings and plant, without the necessity for expensive piling.

(*b*) A plentiful supply of pure water should be available.

(*c*) There should be suitable means for disposing of effluents.

(*d*) A reliable supply of cheap power is necessary.

(*e*) A supply of intelligent labour, male and female is desirable.

(*f*) Transport facilities including railway sidings and good roads are very necessary.

(*g*) The site should be of such an extent that there is ample room for expansion of the factory.

All these points are of almost equal importance, a site possessing all of them except a good water supply or easy means of effluent disposal, for example, being quite useless.

The first point requires no amplification or explanation.

As regards (*b*), two things have to be taken into consideration : boiler feed water and water for processes. In both cases the water should be as pure as possible, and full advantage should be taken of condensers and cooling plant in economizing heat requirements. The most satisfactory source of supply is a deep well on the site itself. Such water, obtained by boring through impervious strata to a porous bed saturated with water by percolation and infiltration, is generally of consistent composition, and unlike river water is unaffected by seasonal variations. A preliminary analysis of water obtained from an existing well on a neighbouring site will indicate the degree of softening or other treatment required and so enable the designers to estimate the capacity of the plant required for these purposes. Regarding boiler feed water, further information may be obtained by consulting one of the standard works on the subject, such as *Boiler Chemistry and Feed Water Supplies*, by J. H. Paul, 2nd ed., 1923.

Process water must be of a high degree of purity, and free from all but a trace of hardness. The principal uses of water in the processes are in—

(*a*) Washing and stabilizing cellulose acetate.
(*b*) Dyeing and processing the rayon yarns and fabrics.

In the first case any hardness present in the water will result in the formation of calcium sulphate in the pores of the fibrous acetate, due to combination with free and combined sulphuric acid, and this may give rise to difficulties in the spinning process. Traces of metallic impurities, especially iron, are also very deleterious and must be removed. Hard waters are also unsuitable for dyeing and processing, so that in general the same water may be used for all purposes in the factory after it has been suitably softened and deironized. In the case of very hard waters it is advisable to treat first by the lime-soda process, followed if necessary by treatment by a base-exchange process such as the Permutit.

The readiest means of effluent disposal is by direct discharge into a river. For a production of 10 tons of cellulose acetate weekly, upwards of 1,000,000 gallons of effluent will be produced. This will contain traces of acetic acid, and of cellulose acetate and degradation products of cellulose. The effluent is derived from three sources: washings from the precipitation department; washings from the stabilizing department; and sludge and still washings from the acetic acid recovery plant. The second item is comparatively harmless since it consists of extremely dilute acetic acid containing traces of sulphuric acid and can therefore be discharged directly into a river without fear of pollution; the first and third are distinctly acid and should be neutralized with lime and allowed to settle before discharging. Effluent disposal in the case of an acetate factory is not, of course, the serious problem met with in the viscose industry, and provided common sense is used no trouble need be anticipated.

Railway sidings giving direct communication with a main line are very desirable, to enable raw materials to be brought to the desired place with a minimum of labour, and the finished products to be dispatched rapidly and efficiently. Good roads, both approaching and on the site itself, are very necessary; too frequently in modern factories provision is made on the plans for excellent concrete or metalled roads, while in practice such roads as there are may be little better than cart tracks which become traps for motor transport in bad weather.

Finally, sufficient land must be acquired to allow for the expansion which will follow the successful introduction of the product on the market. Since it is no longer necessary—nor even desirable—to seek a site near a large town, the initial cost of land need not be great, thus allowing a larger margin for the provision of buildings and plant, and for reserve.

Buildings.—The buildings required for an acetate factory may conveniently be divided into three groups:—

(*a*) The acetate section including acetic acid recovery and anhydride plants.

(*b*) The spinning section including solvent recovery plant.

(*c*) The processing section comprising winding, weaving, dyeing, finishing, etc.

Since the acetate section emits acid vapours it should preferably be placed at some distance from the rest of the factory on the leeward side of the site, i.e. in this country, generally to the north-east of the other sections. This is necessary in order to prevent deterioration of the rayon, and for the same reason the boiler house should also be to leeward. In setting out the various buildings due regard must be paid to these points and also to the provision of room for expansion, and to easy means of transport from one section to another so that materials in process may flow easily without being held up by " bottle necks ".

(*a*) **Acetate Section.**—The departments comprising the acetate section are usually eight in number and consist of: linters preparation; acetylation; ripening; precipitation; stabilizing; drying; acetic acid recovery; and acetic anhydride production. A convenient sized unit of acetate making should be capable of producing 10 tons of cellulose acetate per week; such a unit is not too small for economical working, nor too large for the preliminary period of the factory's existence, and it will therefore be adopted as the standard unit in discussing the lay out of the plant.

An acetate factory arranged on the gravity flow system is not altogether practicable. It would involve, for example, an elevated acetylation department, and taking into consideration the great weight of the plant and materials, the substructure would have to be strong out of all proportion to the rest of the building, and the initial expense would not be justified by any saving achieved in subsequent operations, especially as excellent systems of runways can now be installed at low cost. In general, the most satisfactory buildings for the acetate making section are a series of ground-floor departments. with roof lights, provision for flow of materials being made by means of suitable overhead runways.

Linters Preparation Department.—This department should be large enough to house the opening and drying machine described in Chapter III (p. 34) and also to accommodate the stocks of linters, in bales and prepared for acetylation. The process of preparation has already been described in Chapter III. As soon as the cotton has been dried to the required extent, it should be packed in suitable receptacles, and stored in a section of the department in which the air is maintained at a temperature and relative humidity which will not affect the moisture content of the prepared linters.

Acetylation Department.—For a weekly production of 10 tons of cellulose acetate eight acetylizers will be necessary, each having a capacity of 50–60 cubic feet. The acetylizer is a copper lined mixing machine fitted with gun-metal stirrers of the well-known kneading type, and provided with a cast-iron outer jacket for the circulation of brine or water. The machine illustrated in Fig. 28 is fitted with double spur gearing and reversing pulleys for belt drive, which is the form usually employed, so that the motors may be housed outside the department to protect them from acid vapours. Now that satisfactory enclosed motors can be obtained, however, there is no reason why individual drive with all its advantages should not be employed in the acetylation department. A type of motor suitable for the purpose is shown in Fig. 29. It is a frame cooled squirrel-cage motor, the shell consisting of a double walled casting, the annular space between the walls being divided into sections by longitudinal ribs to form ventilating ducts, which are arranged to give two separate circuits. Air is blown around the internal circuit by a fan at the driving end and a second fan forces a continual flow of cool air through the adjacent external ducts, so that heat is transferred from the totally enclosed part of the motor to the external ducts and carried away. The makers state that the machine is capable of maintaining a 50 per cent overload in torque for one minute, or a 100 per cent overload in torque for 15 seconds. In cases where the air contains acid fumes which may impair insulation varnishes and materials, special

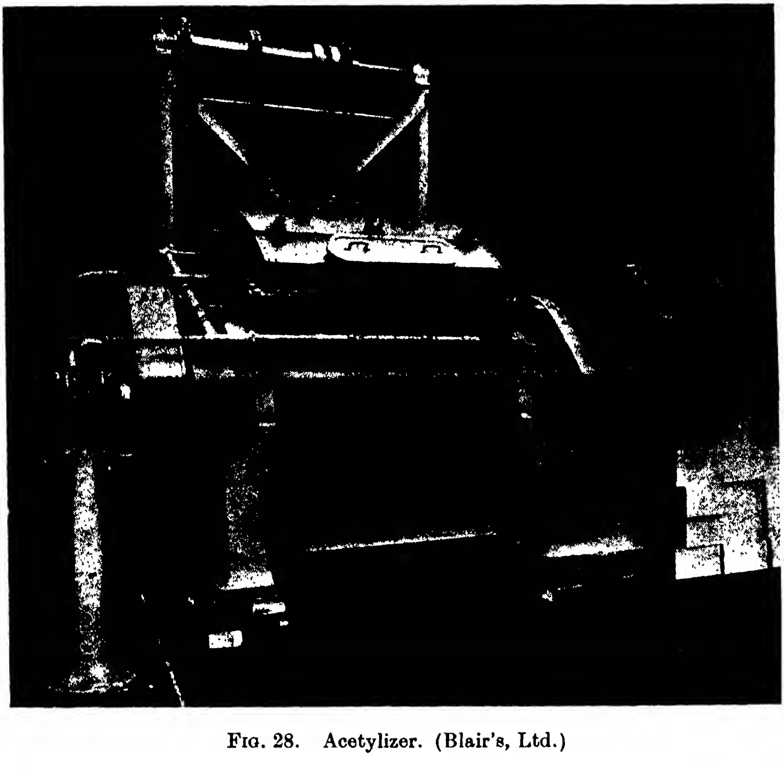

FIG. 28. Acetylizer. (Blair's, Ltd.)

insulation is used which will withstand the action of the fumes satisfactorily. Should it be preferred to use outside air for cooling the motor, a machine arranged for this type of cooling can be obtained.

The acetylizers are best arranged back to back with a clear space of at least 3 feet between neighbouring machines. Two large mixing vessels of aluminium, fitted with stirrers, should be provided for mixing acetic acid and anhydride, and they should be arranged at a suitable height above the acetylizers. The capacity of each vessel should be from 1,200 to 1,400 gallons, and they should be connected by aluminium piping to a main, also of aluminium, which serves to distribute the mixed acids to four aluminium measuring vessels, symmetrically arranged ; these vessels should be fitted with gauge glasses and calibrated to deliver the amount of mixed acids required for an acetylation. All the cocks used should be of gun-metal. The bottom of each measuring vessel should be connected to a cooling vessel, made of copper and provided with a brine jacket. The mixed acids are cooled in these vessels before the addition of the catalyst, and again before transferring to the acetylizers ; these vessels could be dispensed with, the cooling and mixing being done in the acetylizer itself. All tubing for the

FIG. 29. Squirrel Cage Motor (Frame Cooled).
(General Electric Co., Ltd.)

transport of acetic acid, anhydride, or mixed acids should be of chemically pure aluminium, and have a diameter of about 2 inches.

The glacial acetic acid storage tanks in the acid recovery department, and the anhydride storage tanks in the anhydride production department should be connected to the mixing vessels in the acetylation department by aluminium mains, the one conveying acetic acid having a ½ inch steam pipe running beside it, both pipes being lagged together. This serves to prevent freezing in cold weather. Provision should also be made for pumping acid or anhydride from drums in case of a breakdown in either of these departments.

Sulphuric acid may be stored in an iron egg in the acetylation department, and drawn off as required into a lead measuring vessel. Should outside storage be used for sulphuric acid in bulk, the vessel should be lagged and provided with some form of heating to prevent the acid from freezing in cold weather.

The jackets of all the acetylizers should be connected to mains for the circulation of brine from the refrigeration plant, and of hot and cold water, and provision should also be made for the return of brine to the refrigerator in case it is found necessary at any time to drain the jacket of an acetylizer and fill up with warm water to liberate the stirrers if they have become fixed owing to the freezing of the mixture.

Ripening Department.—This should be situated between two other buildings so that it is insulated from sudden changes in the outside temperature. There should be no windows in the department and all doorways should be in duplicate so as to afford an airlock, thus preventing sudden inrushes of air which is cooler or warmer than the air in the department. The temperature should be suitably controlled, preferably automatically. For a weekly production of 10 tons of cellulose acetate, the ripening department should be large enough to accommodate 50–55 ripening vessels.

Precipitation Department.—This is perhaps the most difficult department of an acetate factory to design satisfactorily. Attempts to make the layout of the plant too compact result in overcrowding and congestion, with consequent cramping of the space in which the operatives require to move. Enough precipitators must be provided to cope with the maximum number of batches likely to require precipitation at any one time. As indicated in Chapter III, the ripening time does not vary very much provided the nature of the raw materials and the details of the acetylation and ripening processes are the same throughout. This period is about seventy-two hours at 21° C. It will therefore be necessary to provide four precipitators for a 10 ton plant.

FIG. 30. Hydro-Extractor. (Thos. Broadbent & Sons, Ltd.)

A cellulose acetate precipitator is a cylindrical copper vessel about 4 feet in diameter and from 5–6 feet deep, fitted with vertical stirring gear consisting of two sets of gun-metal blades on a gun-metal shaft. The usual form of drive is by spur gear below the vessel. As there is a large amount of resistance to the action of the stirrers during the process, a large amount of power is required, and the bearings of the stirrers must be rigid. The drive may be by means of a common shaft, with clutch and gear for each precipitator, or individual drive of the type described under acetylation may be employed ; in this case, however, as reversing is unnecessary, a slipring motor may be used.

The best arrangement for the precipitation department is to have three floors, the precipitators being on the upper floor, the hydro-extractors on the first floor, and the tanks for receiving the dilute acetic acid being on the ground floor.

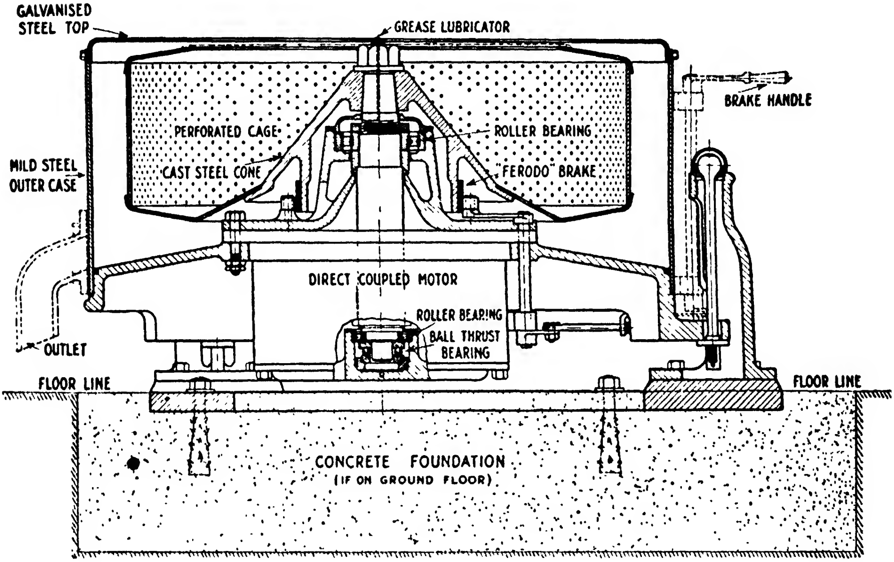

FIG. 31. Hydro-Extractor (Section). (Thomas Broadbent & Sons, Ltd.)

A hydro-extractor suitable for removing acetic acid from the precipitated acetate is shown in Fig. 30. Fig. 31 is a section of the machine used for extracting water from rayon yarn in bundles. The extractor used for acetate is exactly similar in design, but it has a copper cage and copper-lined outer case in order to resist the attack of the acetic acid. The machine illustrated is for A.C. supply only ; if D.C. supply is used, the motor protrudes through the bottom of the machine and it is necessary to have a pit in the foundation to accommodate it, and to facilitate inspection of the switch gear. The A.C. hydro-extractor attains full speed in about 60 seconds and can be stopped by means of the Ferrodo lined brake in about 30 seconds. Roller bearings are fitted throughout, so that maintenance costs are reduced to a minimum. The diameter of the cage of the machine usually employed for freshly precipitated acetate is 60 inches, and its capacity is 13·8 cub. ft. net and 24·7 cub. ft. gross.

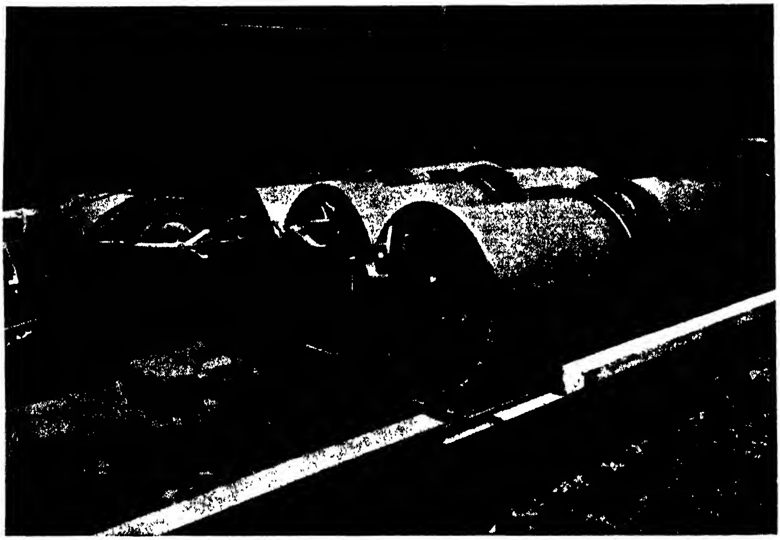

FIG. 32. Stills for dilute Acetic Acid. (Blair's, Ltd.)

The usual procedure is to drain off the acid from the precipitated acetate through the hydro-extractor, and then to allow the batch to follow in two portions, dealing with each portion separately. The basket of the extractor is lined, of course, with a suitable lining material. The machine is started up and allowed to run at a medium speed till all the acid is removed from the cellulose acetate. If the machine is run at full speed at this stage, the acetate packs very tightly and the subsequent washing process is rendered more difficult. With the machine still running at moderate speed, the contents are then washed with a jet of water until the acidity of the effluent is satisfactory. The speed is then increased and the machine is allowed to run until all the water is extracted, after which the batch is removed to the washing and stabilizing department. The outlets from the hydro-extractors should be arranged to discharge into a common trough made of hard wood lined with acid-resisting material such as Haveg, so that the dilute acid may be distributed to the desired storage vat or to waste.

For the storage of the weak acetic acid, cypress wood vats are very serviceable, but a very convenient alternative form of storage consists of excavated reservoirs bricked and lined with acid resisting material. The vats or reservoirs are linked up to pumps by copper piping, so that the acid may be transferred to the stills (Fig. 32) or, if the acid does not undergo preliminary distillation, to the blending vats, which are necessary in either case to ensure the supply of an acid of reasonable constant strength to the recovery plant. The amount of weak acid at 30 to 35 per cent strength per batch of cellulose acetate made is about 300 gallons, or a total of 25,000–30,000 gallons per 10 ton week. It will be necessary to provide storage capacity for at least two weeks' production so that the acetic acid recovery plant may be operated continuously, since frequent stoppages, both there and in the anhydride plant,

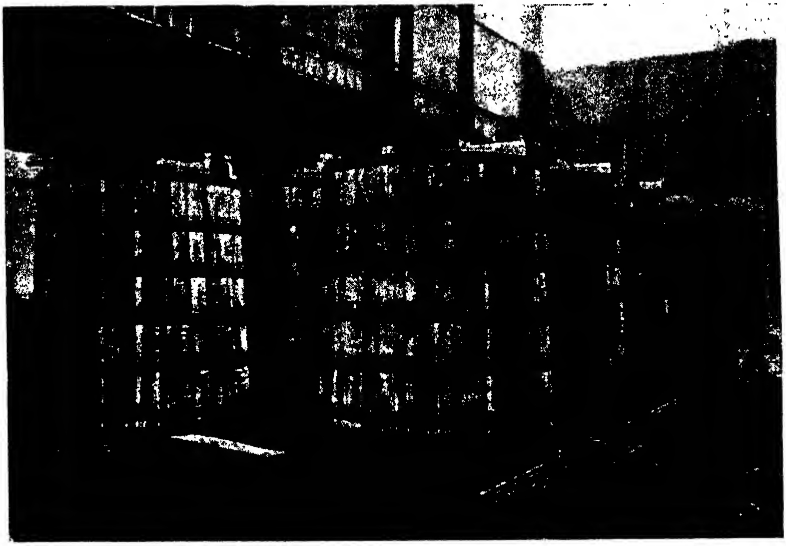

Fig. 33. Washing Vats for Cellulose Acetate. (Blair's, Ltd.)

will lead to corrosion and depreciation. The pumps used for weak acid are usually of the centrifugal type and are constructed of acid-resisting materials.

Washing and Stabilizing Department.—Washing and stabilizing are usually carried out in vats made of cypress or other hard wood, a convenient size being 6 feet in diameter and 7–8 feet deep, the wood being 2½ inches in thickness. A group of such vats ready for erection is illustrated in Fig. 33. The vats are fitted with a vertical shaft having gun-metal stirrers and a bevel drive. The most convenient arrangement is to have the vats erected on girders at a height of about 8 feet from the floor of the department, and a mezzanine floor should be fitted around the vats for attendance purposes. For a 10 ton production six vats will be necessary. Three hydro-extractors of the type described above should be placed below the vats, so that the finished acetate can be discharged directly into them from the traps provided in the bottoms of the vats. The water outlets from the vats are surrounded by a copper gauze strainer to prevent loss of acetate. A special catch box should be fitted in the main drain of this department to collect

Fig. 34. Cellulose Acetate Drier. (Blair's, Ltd.)

finely divided acetate, which would otherwise be lost. At the end of each working day this should be emptied and the cellulose acetate washed, dried, analysed, and blended off.

Drying Department.—A convenient form of drying apparatus is illustrated in Fig. 34. The acetate is placed in copper trays having perforated bottoms, covered with madapolam, and placed in the cabinet on the left of the apparatus. Heated air is then blown through the acetate until it is dried to the desired degree. The air is controlled by means of a slide valve on the cabinet, and also on the return duct of the fan. The latter is of the centrifugal type with full-housed steel casing and the heater is of the welded tube type, requiring steam at about 50 lb. pressure.

Fig. 35. Cellulose Acetate Grinder and Blender. (Blair's, Ltd.)

This department may also house the grinding and blending plant (Fig. 35), which consists of an elevator, disintegrator, dust collector, exhaust fan, sifter, and blender. As indicated in the chapter dealing with spinning, it is not usually necessary to grind the batches if they have been properly precipitated.

Acetic Acid Recovery and Anhydride Plants.—The acetic acid recovery plant will be housed in a building of which the design will depend upon the method of recovery used. In general, there will be a number of floors, and for convenience in dismantling columns for the purpose of overhauling them, as well as from the point of view of economy, a steel framed building with chequer plate floors and brick walls is to be recommended. Similar considerations apply to the anhydride plant.

(*b*) **Spinning Section.**—The spinning plant is described later in Chapter VIII. The dope mixers should be situated on an upper floor, the acetate being taken up by elevator, and the dope descending by gravity to the press room. The spinning cabinets and frames are best situated on the ground floor. The solvent recovery plant should be at some distance, say 50–100 yards from the spinning building proper to minimize the risk of fire.

(*c*) **Processing Section.**—This will follow the layout usually adopted in textile factories. All parts should be kept clean and should be well lighted.

Laboratories.—The general and research laboratories are conveniently housed in one building, but control laboratories should be adjacent to the corresponding departments, and provision should be made for transferring samples and materials by means of wicket windows between laboratory and department.

Organization of Production.—The organization and control of production in an acetate factory is of vital importance to the success of the undertaking. The manufacture of cellulose acetate readily lends itself to scientific methods of control. It has already been indicated in Chapter IV how the ripening and stabilizing processes may be controlled by the routine laboratories as far as the chemical side is concerned. For successful working it is necessary to employ similar methods of checking throughout the plant, i.e. the manager of each section of the factory should know exactly what materials enter and leave the departments under his control. This is of special importance in the case of the acetate-making section of the factory.

The foreman of each department should be responsible for making a report to the works manager at the end of his shift. This report will include such details as the weight of materials processed during the shift, the number of machines in use, and the number of men engaged. The following details should be included in the case of the department concerned :—

Linters Preparation.—Raw linters in stock ; prepared linters in hand ; total weight processed during shift.

Acetylation.—Cotton linters received and on hand ; batches acetylized, differentiating between those started by the previous shift and by the shift in question ; stocks of mixed acetic acid and anhydride and of sulphuric acid at beginning and end of shift ; number of acetylizers in use ; number of men engaged ; short details of any abnormal acetylation ; acetic acid received from recovery plant ; anhydride received.

Ripening.—There should be one man per shift responsible for this department, who could combine the work with other duties such as those of storekeeper, liftman, etc. He will furnish details of the number of batches in the department ; number of batches received from acetylation ; number of batches discharged to precipitation ; and remarks concerning any variations in temperature.

Precipitation.—Number of batches precipitated ; stock of weak acid at beginning and end of shift ; weak acid released to recovery department ; cellulose acetate released to washing and stabilizing department ; number of precipitators in use ; number of men engaged.

Washing and Stabilizing.—Number of batches received from precipitation ; number of batches stabilized ; number of batches stabilizing ; number of batches released to drying department ; number of vats in use ; number of men engaged.

Drying and Blending.—Number of batches received from stabilizing ; number of batches dried ; number of blends prepared, with details of the batches used in their preparation ; blends released to spinning department.

Acetic Acid Recovery.—Stocks of weak and glacial acid at beginning and end of shift ; amount of weak acid treated and of glacial acid recovered ; details concerning any abnormalities.

Anhydride Plant.—Stocks of glacial acetic acid and of anhydride at beginning and end of shift ; amount of anhydride made ; amount of anhydride released to acetylation ; amount of weak acid returned to recovery.

At first sight the details mentioned above appear a somewhat formidable array; if, however, printed forms are provided for making the returns, the extra work entailed is trifling and should not occupy more than a quarter of an hour of the foreman's time. The value of such reports is incalculable, provided they are properly analysed and scrutinized. They enable the works manager to estimate correctly the efficiency of every unit under his control and to gauge the maximum output possible with the plant installed. They provide a ready means for allocating the costs to the proper departments, especially if steam and power meters are fitted in the various sections of the plant, and render it possible to achieve the fullest economy in production.

As regards the staff of the factory, a system of returns such as that outlined above is of great value in indicating which are the most efficient foremen, and they form a basis for computing wage rates and bonuses. They also exercise a valuable moral effect on the personnel of the factory.

In the case of spinning and acetone recovery a similar report system can readily be put into operation. The matter is not so easy in the processing departments, since here the work ceases to be mass production, owing to the variations introduced in the product. Even in these cases, however, a well-conceived system of daily reports properly analysed will serve to keep the responsible managers in touch with every phase of the work in progress.

The information obtained by means of the above system will form the basis of a weekly flow-sheet for the information of the general manager, who will thus be able to see at a glance how the production programme stands.

CHAPTER VII

LABORATORY CONTROL AND METHODS OF ANALYSIS

The manufacture of cellulose acetate is essentially a chemical industry; although the engineer and the technician have important parts to play, the ultimate court of appeal is the laboratory, and adequate measures of chemical and physical control, together with constructive research, are absolutely essential to the success of a company which sets out to manufacture cellulose acetate products.

The organization of the chemical and physical work of the factory falls naturally into three groups: General, Control, and Research. The work of all three groups will usually be under the direction of a chief chemist, who should be a member of the management committee, and preferably of the board of directors, since he is in a position to provide that contact between the board and the factory which is so necessary in a chemical industry. In any case the closest touch should be maintained between the chief chemist and the board and management, so that on the one hand he may be able to advise on matters connected with production, and on the other hand, as a result of his close acquaintance with the policy of the board, he will be able to organize the work of the laboratories with due regard to market conditions and the general requirements of the business. He must also maintain a close contact with the heads of the various sections, general, control, and research, each of which should be under the direction of an experienced man, and be provided with suitable laboratories and adequate staffs made up of both qualified and unqualified men. In general the latter will be recruited from youths who have received a secondary education, and have passed either the Matriculation examination of the University of London or some equivalent examination; they will usually be posted to the general or control sections, and a few months' observation will decide whether they will prove useful members of the staff or otherwise, and also if they have any aptitude for research work. In the case of such unqualified assistants, every facility should be given for attendance at evening classes with a view to their proceeding to a degree in science, or to the Associateship of the Institutes of Chemistry or Physics.

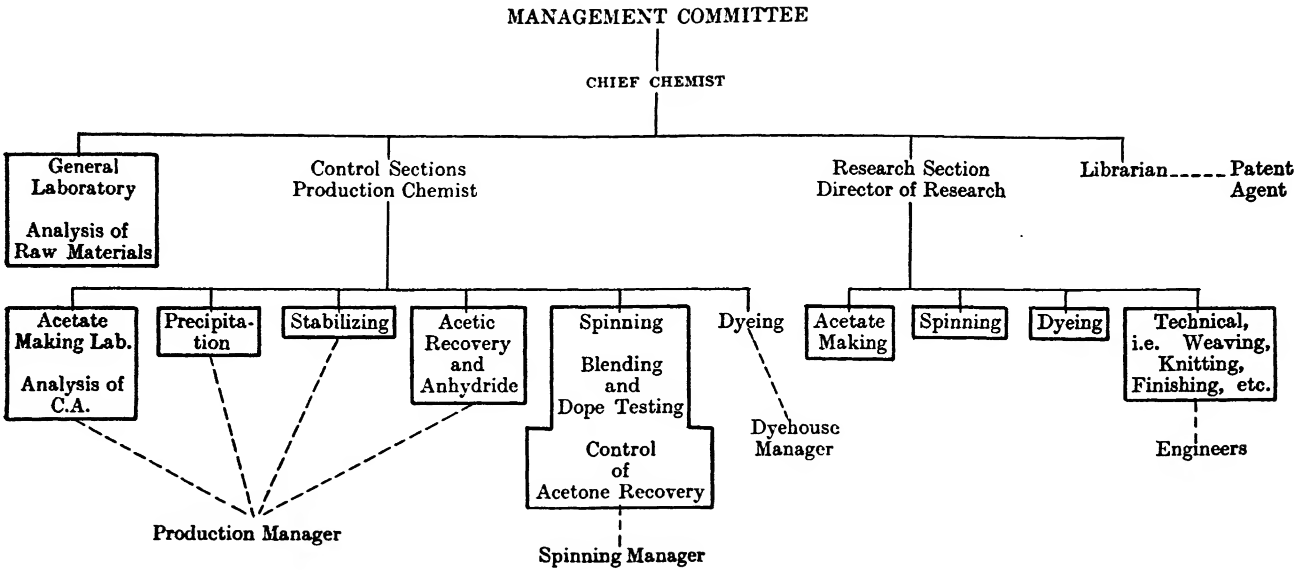

Fig. 36. Liaison Chart.

The chart (Fig. 36) suggests a scheme of liaison between the various departments. This cannot, of course, be regarded as rigid, but the fullest co-operation between chemical and technical staffs is essential if the best use is to be made of the results obtained in the laboratories.

General Laboratory.—This laboratory is usually responsible for the analysis of buying samples and raw materials, viz. cotton linters, acetic acid, and anhydride, sulphuric acid, chemicals for water softening, dyestuffs, coal, oil, water, etc. The chemist in charge, in addition to supervising and controlling the work of the laboratory, will be responsible that all the materials analysed are in accordance with the available standards, and will usually take any action necessary in the case of defective samples. It is desirable that he should keep the chief chemist informed of the work of the laboratory, and this can be done quite readily by means of a periodical report (weekly or fortnightly), showing the numbers of samples of the various materials examined, and whether passed or rejected; if the latter, a brief statement should be made of the reasons for rejection. In addition to the above work, the general laboratory usually deals with all complaints such as defective dyeing, faults in fabrics, etc., passing them on for attention to the appropriate section.

Control Section.—The manufacture of cellulose acetate lends itself admirably to mass production methods—indeed, it is only by the application of such methods that the industry can be made profitable. And mass production in a chemical industry calls for the rigorous control of every operation. The methods of control adopted must be as simple as possible, since they will be carried out by unqualified routine workers, and capable of giving rapid results if the control is to be effective. The control section of a factory manufacturing cellulose acetate and rayon is conveniently divided into raw materials and finished acetate laboratory; ripening and precipitation laboratories, and stabilizing laboratory. The whole section should be controlled by an experienced chemist, with one or two qualified assistants to supervise and check the work of the routine staff. For convenience, the work of the section will be described in the order in which it applies to the processes, a reference being made in each instance to the laboratory in which the work is carried out.

Linters Preparation.—As often as required the chemist in charge of the control section should compile a list of batches of raw cotton linters suitable for blending, based on the returns made to him by the general laboratory. This list will pass to the production manager of the acetate-making department, and he will prepare blends of dried linters in accordance with it. The blends will be sampled to the raw materials and finished acetate laboratory, and their moisture content determined before they are released to the acetylation department. It is convenient to attach a slip to the linters containers, green in colour if passed, and red if the linters are to be redried ; the moisture content should be noted on the slip, also batch number, weight, and other relevant particulars. As soon as the cotton enters the acetylation department, and the particulars have been entered on the acetylation form, the slip should be completed with the number of the acetylation batch, and after initialling by the foreman, be returned to the office of the production chemist. This serves to check the details entered on the acetylation form.

Shift.......... Date ....

Samples to be taken : Batch No.
Time

Samples washing :
Samples drying :
Stock of reagents :
do. do. apparatus :
Remarks :

Signed..........................Old shift.
..........................New Shift.

FIG. 37.

Acetylation.—The tests required for the control of the acetylation process are sufficiently simple to be carried out by intelligent foremen or charge hands. It should always be remembered, however, that the control chemist is responsible for these tests, and he should satisfy himself by periodical checks that the tests are being carried out in an efficient manner. These tests have already been described (Chapter IV).

Ripening and Precipitation.—This laboratory should be situated as close as possible to the departments concerned. As soon as a batch is acetylized the acetylation form should be completed with the time at which the batch was placed in the ripening room and should be handed to the assistant in charge of this laboratory. The batch number and time and date of the commencement of ripening should then be entered in the record of precipitation tests, and the time at which the first test is to be made should also be recorded. As each test is completed, the result should be entered

PRECIPITATION LABORATORY

Batch No. .... Date ....
Ripening Vessel No. .... Precipitate at..................
(Time)
Signed............................
Lab. Supervisor.

RIPENING DEPARTMENT

Batch No. .... Released to precipitation department at ....
Ripening Vessel No............. (Time)
Foreman..................

PRECIPITATION DEPARTMENT

Batch No. .... Received at ....
(Time)
Ripening Vessel No. ....
Precipitator No. .... Sodium acetate .... lb.
Precipitated at .... Discharged to Washing Dept. at
(Time) ....
(Time)
Foreman (precipitation).................
Batch No.....received at ....
Foreman (wash and stabilize)...........

FIG. 38. Precipitation Form

in this record by the assistant who carried it out. A suitable form for recording these tests is that shown in Fig. 22 (p. 67).

So that the work may not be delayed, the assistant in charge should acquaint his successor, when the shifts change over, of the exact state of all samples ; this is conveniently done by means of a log-book as shown in Fig. 37.

As soon as a batch of acetate is ready for precipitation the assistant in charge should complete a suitable form (Fig. 38), keeping a duplicate, and hand the original to the foreman of the precipitation department. This form should be retained by the latter until the charge is released to the stabilizing department, and be returned when completed by the foreman of the stabilizing department.

The precipitation laboratory can conveniently be combined with the acetic acid recovery and anhydride control laboratory, although the work of the two sections should be kept under separate control. The work of precipitation and acetic acid recovery control is sufficiently simple to be carried out by unqualified assistants, but the analysis of the anhydride produced requires great care and attention, and should be entrusted only to a senior assistant, who can also take charge of the shift.

Acetic Acid Recovery and Acetic Anhydride.—The washing tests described on p. 70 in connection with the precipitation process can, like the acetylation tests, be carried out by foremen or charge-hands, but here again the production chemist should satisfy himself that the tests are properly performed. Mistakes will not only lead to trouble in the succeeding processes, but may also result in loss of acetic acid.

The duties of this section comprise the following :—

Analysis of weak acetic acid before it is passed to the acetic acid recovery plant.

Hourly determinations of the strength of the recovered acid, and tests for its purity.

Hourly analyses of the anhydride produced.

Should the concentration of acetic acid or anhydride vary outside the limits laid down, the foreman in charge of the plant concerned should be notified at once. The results of these tests should be entered in a record book in a suitable manner. From the results of the analyses of weak acetic acid, the production chemist will arrange for suitable blends to be transferred to the recovery plant.

Stabilizing.—The details of each batch as received in the stabilizing department should be entered on the appropriate form (Fig. 39) by the assistant in charge of the shift in the stabilizing laboratory. The alkalinity of the water to be used should be determined for each batch, unless experience shows that it does not vary a great deal, in which case it should be determined once only and that at the commencement of each shift. The methods of testing employed in the stabilizing process have already been described (p. 72). The results of the tests should be entered on the form (Fig. 39), which should be frequently inspected by the assistant in charge of the shift, who will be responsible for all orders issued to the stabilizing department.

A log-book showing work in progress should be kept as in the case of the precipitation laboratory.

STABILIZING LABORATORY

Date .... Batch No................ Vat No. ....
Alkalinity of water ....c.c. N/10 acid per 250 c.c. water.

Sample No.	Time.	Hours boiling.	Fibre Tests.			Acidity.	Orders to department.
			Acetone.	Chloroform.	A/B		

FIG. 39. Stabilizing Form

Drying and Blending.—Once the conditions have been established very little control should be necessary in the drying department, unless the fibrous nature of the batches varies very considerably. A coarse batch, for example, will dry more rapidly than a finer one having fibres of a closer texture. The workers in this department will soon become accustomed to the appearance of the batches, and be able to judge the time required for drying to the required degree. There should not, however, be much variation in the charges if the precipitation process is carried out correctly.

As soon as a batch is dry it should be sampled to the finished acetate laboratory in an air-tight container (glass jar with screw cap and waxed wad is suitable). In order to obtain representative samples, a large sample, a quarter of the contents of a drying tray or other container, should be taken from 10 per cent of the total trays comprising the batch. For example, if the batch is spread out over fifty trays, five samples will be obtained; these should be well mixed and quartered as in the case of other dry materials. The batch should, of course, be allowed to cool before sampling. The final samples are sent to the finished acetate laboratory for analysis, and when this is complete the production chemist should prepare a list of batches for blending when required and pass it to the production manager, as in the case of cotton linters. When the blends are prepared they also are sampled to the laboratory, and the viscosity and moisture content determined.

Finished Acetate Laboratory.—The work of this laboratory will normally comprise the following details :—

(*a*) Analysis of finished acetate and of blends.

(*b*) Analysis of recovered acetic acid—bulk lots.

(*c*) Analysis of acetic anhydride made by the anhydride plant.

(*d*) Moisture tests on dried linters.

(*e*) Analysis and control of mixed acids for the acetylation department.

(*f*) Preparation and issue of standard solutions to the control laboratories and departments using them.

The results obtained in this laboratory may be recorded as follows :—

(*a*) Analyses of all batches should be entered in two books, one of which is retained in the production chemist's charge for his information in connection with the preparation of blends, and the other should be kept by the chief chemist for record purposes. The former will be completed at the end of each shift, but the latter need only be entered up weekly.

(*b*) As soon as a storage vat is filled with recovered acetic acid, the strength should be determined and recorded.

(*c*) As for (*b*).

(*d*) Already dealt with under linters preparation.

(*e*) Each batch of mixed acids prepared in the acetylation department will be analysed, and its composition corrected, if necessary.

(*f*) The following reagents are required by the various laboratories and departments :—

Dry chloroform (alcohol free)	Precipitation and Stabilizing Laboratories.
Dry Benzene	ditto.
Absolute Alcohol	ditto.
N/10 Sulphuric Acid	Stabilizing Laboratory.
N/10 Soda.	ditto.
2N Soda.	Precipitation Department.

Spinning.—One laboratory is sufficient for this section and should take charge of the following :—

(*a*) Spinning solution : Viscosity ; total solids ; check on clarity.

(*b*) Tensile strength and elongation of rayon produced.

(*c*) Microscopical examination for faults, including regular examination of cross-sections of the rayon.

(*d*) Acetone recovery. The work required from the laboratory will vary with the process of recovery used, but a determination of water in the recovered acetone, and of the acetone content of the exhaust gases will be required in all cases.

Dyeing.—In this laboratory tests of the rayon should be made from time to time by standard methods to make certain that the dyeing properties remain constant. Any variation may give rise to serious difficulties in the dyeing processes. All dyestuffs and chemicals used in the dyehouse should be kept in the laboratory, and issued in the necessary doses on requisition from the dyehouse manager. Careful records should be kept so that a complete check can be obtained from beginning to end of production.

Research Section.—This section falls naturally into four divisions, viz. : Acetate making ; Spinning ; Dyeing ; and Technical.

In addition to the necessary chemical and physical laboratories, the research section should include small scale plant covering every section of the factory in which trial batches can be made under the closest possible approximation to practical conditions. The work of the section includes investigation of difficulties and failures occurring in the manufacturing departments of the factory ; constant efforts to improve existing processes ; and the evolution and testing of new processes and of new methods of carrying out existing processes with a view to realizing economies in production.

With regard to the staff of the research section, the chemist in charge should possess a considerable measure of imagination coupled with sound business instincts, in order that difficulties may be met by intelligent anticipation and at the same time practical objects may be kept in view. It is important that the other members of the staff should have had practical experience in the sections of the factory with which they are concerned. This is necessary both from the point of view of realizing the plant conditions and limitations, and so that they may be able to introduce improvements or initiate new processes in the departments themselves.

Acetate Making.—This section should study the acetylation process both from the technical and purely academic points of view. There are numerous questions which would repay attention devoted to them, for example, the effect of variations in the acetylation process, such as moisture content of cotton linters, proportion of acetic acid and anhydride used, and the nature and quantity of the catalyst employed. In the last connection an exhaustive study of the mechanism of the acetylation process and of the function of the catalyst would yield valuable results.

A study of the ripening process is also worth consideration, for although there are many patents dealing with the production of acetone soluble cellulose acetate, the field has been by no means exhausted.

With regard to precipitation, the methods in use are of an empirical nature, and it might be described as an art rather than as a scientific operation; here the exact conditions necessary to give the most suitable form of acetate for the purpose required could be determined. In addition, the question of the solubility of cellulose acetate in the weak acetic acid produced during precipitation should also be studied with a view to minimizing losses.

The stabilizing process is also empirical in its nature; a clearer understanding of the underlying principles would be of great value in establishing the most efficient way of achieving the desired end.

In spite of the numerous patents relating to the recovery of acetic acid, this subject still offers a fruitful field of research. The production of acetic anhydride and also of acetone by catalytic processes have been well exploited, but the nature of the catalysts and the conditions under which the various processes are conducted do not appear to have been made the subject of extensive systematic study.

Spinning.—This process offers scope for research from the point of view of (*a*) production of more uniform filaments, having the maximum strength, and even dyeing properties; here the desired results will doubtless be obtained by some process which will give the optimum arrangement of the micellæ—a result already partly achieved by the methods of stretch spinning; (*b*) the nature of the solvents used; and (*c*) processes of solvent recovery. Many problems also offer themselves in connection with such matters as the lustre of the threads, weighting and processing, etc.

Dyeing.—The dyeing of acetate rayon has been made the subject of considerable study during the last twelve years, and such advances have been made in the production of dyestuffs for this purpose, and in their practical application, that there would seem to be but little left for research to achieve. It must be remembered, however, that our knowledge of the mechanism of the dyeing process is still very scanty, and that even minor improvements in technique may result in considerable economies.

Technical.—This section scarcely comes within the province of the research chemist or physicist, since it is concerned with the mechanical problems of winding, weaving, knitting, etc. At the same time, it is well for both the chemical and technical sides of the research programme of an acetate factory to be co-ordinated, and the results obtained by the one section should be freely available to the other.

A very important function of the research section, not already mentioned, is the examination of methods described in the patent specifications of competing firms, both at home and abroad. For this purpose the librarian should keep the department supplied with abstracts from the current patent journals, and the British Specifications at least should be available in the library. It is obvious from a survey of the patent literature of any manufacture, that firms which are interested in the same products study the work of their rivals, and proceed to surround their inventions with hedge patents in order to protect their own position. Although the method may not appeal to all, it seems legitimate that a concern which has discovered a valuable process and has used it as a trade secret, should use this means of protecting their interests against their competitors.

An additional research section which might be considered is the analytical one. Routine workers in the general and control laboratories, and research workers proper cannot usefully devote their time to improving old methods of analysis and to evolving new ones; and in general analytical problems call for a different type of mind from that found among control or research chemists. In this section particularly, and throughout the laboratories the workers should be encouraged by being allowed to publish their results when they are suitable, and if the interests of the firm allow it. In the case of patents, it is usual for the name of the actual inventor to appear as well as that of the firm—indeed, in English patent law a Company may not be the sole applicant for a patent, except in the case of inventions communicated from abroad. The service agreements of chemists usually contain a clause by which they contract to assign all inventions to their employers without reward other than their ordinary remuneration. Besides being just, it is a wise policy to supplement the salaries of such workers by bonuses according to the value of the inventions which they make, since this provides a stimulus to further effort.

The Library.—This is a most important department in any industrial concern depending upon scientific principles. Standard works of reference and analysis, covering the particular type of work will, of course, be found in all the laboratories. In addition to these, the following classes of literature must necessarily find a place in the technical library of a cellulose acetate factory :—

(*a*) Textbooks and standard works of reference, not only of a technical, but also of an academic nature. Examples of these are given in Appendix I.

(*b*) Current Journals—scientific and technical.

(*c*) Ditto—patents.

Among the leading British and American journals of a scientific and technical nature which will prove of great service are the *Journal of the Society of Chemical Industry*, together with *British Chemical Abstracts A and B*, *Journal of the Society of Dyers and Colourists*, *Journal of the Textile Institute*, *Industrial and Engineering Chemistry*, *Chemical Abstracts*, *Rayon Record*, *Silk Journal*; and among continental journals may be mentioned *Berichte der Deutschen Chemischen Gesellschaft*, *Cellulosechemie*, *Zeitschrift für angewandte Chemie*, *Zellstoff und Papier*, *Kunstseide*, *Melliand's Textilberichte*, *Chimie et Industrie*, and the *Japanese Journal of the Cellulose Industry, Tokyo.*

A scheme of technical reading should be instituted among the more responsible members of the chemical staff, and they should mark any articles of outstanding interest so that the librarian may index them. In addition to the reference to the journal, it is well to include a very brief abstract of the paper in the card index.

With regard to patents, although these are regularly abstracted in the leading scientific journals, the abstracts do not appear for some considerable time after the specifications have been published, and it is therefore advisable for the library to receive regularly the leading patent journals, i.e.: British: *Illustrated Official Journal*; U.S.A.: *Official Gazette*; Canada: *Canadian Patent Office Record*, etc. These journals, of course, contain specification references on every imaginable subject, so it is as well to have a preliminary survey made in the library, all the relevant matter being marked. The journals should then be abstracted, preferably on cards, and the abstracts should be sent on to the heads of the departments concerned, including the technical staffs concerned with weaving, etc., and the engineering section. If the specification is considered sufficiently important, a copy of the complete specification is obtained for further investigation.

The publications of the British Patent Office are particularly useful. In addition to the *Official Journal*, which formerly contained abridgments of specifications accepted, as well as lists of applications for patents, of complete specifications open to inspection, of patents, sealed and void, and the details of proceedings in opposition to the grant of patents, illustrated abridgments of specifications are published in three series as follows:—

Series A: 146 volumes for each of the following periods:—

1855–66 1867–76 1877–83 1884–8
1889–92 1893–6 1897–1900 1901–4 1905–8

Series B: 271 volumes for each of the following periods:—

1909–15 1921–25
1916–20 1926–30

Series C: Commencing with the year 1931 (Specification No. 340,001) the publication of abridgments of specifications in the *Illustrated Official Journal* was discontinued, and instead the abridgments are now published, in volumes classified in forty groups (one volume to each group), each series of forty group volumes comprising the abridgments of 20,000 specifications. The volumes in course of publication can be obtained sheet by sheet as they appear.

The classes which are of interest to the acetate factory are set out in Appendix II.

Laboratory Buildings.—These have been dealt with briefly in Chapter VI, which describes the layout of the factory generally.

METHODS OF ANALYSIS

Raw Materials.—These include cotton, acetic acid, acetic anhydride, sulphuric acid, sodium acetate, and acetone.

Cotton Linters.—The most important determinations and tests required in connection with cotton linters are the moisture content, viscosity by some standard method, e.g. cuprammonium, α cellulose, estimation of the proportion of dust and dirt, and trial acetylation. A representative sample of each delivery should be tested.

Moisture.—10 grams of the sample are heated in a shallow metal or glass dish at 100–103° C. until the weight becomes constant. This usually requires 2–3 hours. The loss in weight represents the moisture content.

Viscosity.—It has been satisfactorily established that there is a definite relationship between the viscosity of cuprammonium solutions of cellulose, properly prepared, and that of its esters. The method of determining the viscosity of a cuprammonium solution of the cotton cellulose should be agreed between supplier and buyer, for very slight differences in the mode of preparation of the solution or in the methods used for determining the viscosity may lead to serious discrepancies. A tentative standard method was described by a committee on the viscosity of cellulose, Division of Cellulose Chemistry, American Chemical Society, in the Analytical Edition of *Industrial and Engineering Chemistry* in 1929,[1] and although it is rather complicated, it is doubtful whether a simplified method would give sufficiently accurate results. The method is as follows :—

Solvent for the Cellulose.—Clean copper turnings are placed in a glass tube about 66 cm. long and from 10–15 cm. in diameter.

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[1] *I. and E.C* (Anal. Edn.), 1929, 1, 49–51.

Strong ammonia water (26–28 per cent NH_3) containing 10 gm. per litre of sucrose is then poured in until the tube is nearly full, and air is bubbled up through it for several hours, during which time the tube is preferably cooled in ice. When the copper concentration is more than 3 per cent, as shown by rough analysis, the solution is analysed for copper and ammonia. To determine when the concentration is high enough for analysis, about 0·5 c.c. of the cuprammonia solution is added to 50 c.c. of the ammonia water, and the colour of the resulting liquid is compared with that in another tube prepared from a standard copper solution in the same manner. The original solution is then diluted to the standard concentration, with water containing 10 gm. per litre of sucrose, and the calculated amount of ammonia. The standard concentration is 30 ± 2 gm. of copper, 165 ± 2 gm. of ammonia, and 10 gm. of sucrose per litre. If the solution is stored in a cool dark place in a well-stoppered bottle, it will keep for a month. Before use it should be analysed for copper by electrolysis or by weighing as CuO after evaporation and ignition according to standard practice. It is analysed for ammonia by the addition of strong alkali to a measured volume, followed by distillation into excess of standard acid.

The committee state that a solution prepared as above will peptize a wider variety of celluloses in a greater range of concentrations than one which has been prepared from dry cupric hydroxide. Also since the amount of copper present affects the viscosity, it is better to have one fixed amount as in the solution type of solvent, rather than variable amounts as is sometimes necessary when using the powder method. A slight variation in copper concentration has no appreciable effect on viscosity when that concentration is 3 per cent, but the effect is much greater with lower concentrations such as are used with the powdered cupric hydroxide.

Sampling.—The usual precautions to obtain a representative sample should be observed, i.e. at least 10 per cent of the packages should be sampled, the samples being drawn from various parts of the bales, followed by thorough mixing and quartering until a sample of suitable size is obtained. In some cases where a consignment is very variable a larger proportion of the packages will have to be sampled.

Concentration of Cellulose.—The falling sphere viscometer recommended by the committee can be used with liquids having viscosities between 30 and 300,000 centipoises. Celluloses vary so widely in character that it is not possible to lay down a limit for the concentration to be used in order to give a viscosity lying in the above range. It is customary in some laboratories to use 2·5 gm. of cotton per 100 c.c. of cuprammonia solution in the case of ordinary cottons, 5·0 gm. per 100 c.c. in the case of very low viscosity cottons, and 1·0 gm. for high viscosity cottons. The viscosities of the 5·0 and 1·0 gm. concentrations are then converted to the corresponding values for 2·5 gm. concentration by the application of the Arrhenius formula suggested by Joyner,[1] which states that—

$$\log \eta = \theta \mathrm{C},$$

where η is the ratio : viscosity solution/viscosity solvent, C is the concentration, expressed most accurately as grams of solute per 100 gm. of solvent, and θ is a constant depending on the nature of the cellulose used and is equal to—

$$\frac{\log\ (\text{viscosity of solution}) - \log\ (\text{viscosity of solvent})}{\mathrm{C}}$$

The committee, however, prefer to use a single concentration, so avoiding any uncertainty. They recommend 2·5 gm. per 100 c.c. solvent, except in the case of very high viscosity cotton, when 1·0 gm. of cotton per 100 c.c. is preferred. The viscosities which are too low to be measured by the falling sphere viscometer are obtained by means of a special pipette which is described later.

Allowance for Moisture in Cotton.—Drying cotton by heating diminishes the viscosity in an irregular manner, and drying in a desiccator is a lengthy operation; the committee, therefore, recommend an allowance of 5 per cent for moisture when weighing out the cotton. If the relative humidity varies between 35 and 60 per cent, the moisture content of cotton will vary between 4 and 6 per cent, which would introduce an error in viscosity reading of about 3 per cent. If the room humidity is higher than 60 per cent, or lower than 35 per cent, the committee recommend that samples should be stored in a cabinet kept at a constant humidity of 50 per cent. They also state that a determination of the moisture content on the samples requires too long to be of service ;

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[1] Joyner. *J.C.S.*, 1922, **121**, 1523.

the author prefers to do this, however, and to apply the necessary correction when weighing out the cotton for the viscosity determination.

Dissolving Bulb.—A convenient form of bulb for peptizing the cellulose is shown in Fig. 40. It is about 80 cm. long and about 4 cm. in diameter, with ends drawn out into tubes, one being 2 cm. long, and 1·3 cm. inside diameter, and the other 2 cm. long, and 0·6 cm. in diameter.

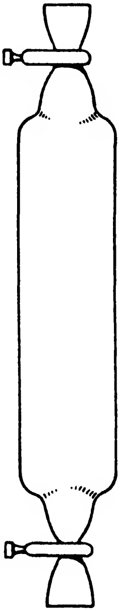

Fig. 40. Dissolving Bulb. (Cuprammonium Method.)

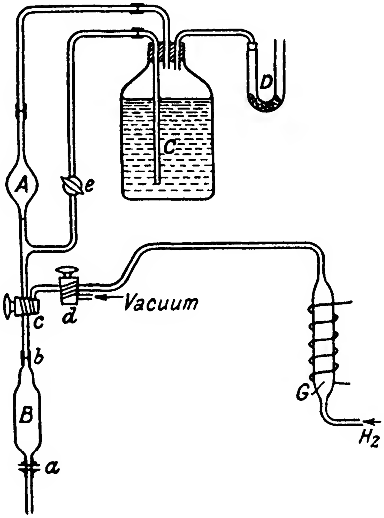

Fig. 41. Evacuating and Filling Apparatus. (Cuprammonium Method.)

Filling the Bulb in Absence of Air.—The sample is placed in the bulb *B*, Fig. 41. Pieces of heavy-walled rubber tubing are slipped over the ends and securely wired. The end *a* is clamped, and the other end is fastened to the evacuating and filling apparatus by slipping the rubber tube on to opening *b*. By manipulating the stop-cocks *c* and *d*, the filling bulb is evacuated and flushed three or more times with hydrogen which has been purified by passing through the heated tube *G* containing platinized asbestos. After again evacuating, 100 c.c. of cuprammonium hydroxide are allowed to enter the bulb *B*, and a slight pressure is applied by turning cocks *c* and *d* to the hydrogen. The rubber tubing of *b* is then clamped shut, and the bulb slipped off the apparatus. It is then tumbled on a wheel rotating at about 10 r.p.m. until the cellulose is dissolved. Cock *c* should be specially ground as the solution tends to eat through the grease applied to lubricate.

It is necessary to purify the hydrogen because there is usually a slight amount of oxygen left in the hydrogen, whether it is from a tank or generator. Experiments conducted with purified and unpurified hydrogen, using cotton linters from the same batch, indicated that the viscosity may be lowered by as much as 15 per cent by using hydrogen direct from a tank, rather than purified hydrogen. If hydrogen from a tank is used, a mercury sealed safety valve will safeguard the apparatus from excessive pressures. Nitrogen carefully freed from oxygen may be used in place of hydrogen if preferred.

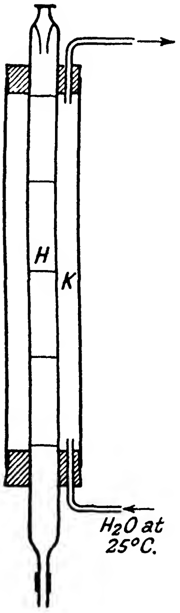

FIG. 42. Viscometer. (Cuprammonium Method).

Falling Sphere Viscometer.—(Fig. 42.) This consists of a tube 30 cm. long and 1·4 ± 0·05[1] cm. inside diameter, with the lower 4 cm. drawn down to 1 cm. outside diameter. It is etched every 5 cm. and placed inside a larger tube, which serves as a water jacket. Water is pumped through this jacket from a constant temperature bath maintained at 25° ± 0·1° C. The readings are easier to take, if two 200 watt lamps are placed behind the tube with sheets of pasteboard having vertical slits, slightly narrower, than the tube itself, placed on either side of the tube so as to cut off the surplus light. A blue colour filter is also recommended, since it removes the mottled appearance of the solution and gives a sharper outline to the sphere. The light should be switched on only for a few seconds at a time, when actually required to take a reading, since strong light causes a decrease in viscosity, attributed to the photochemical action of the

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[1] It would be preferable to use a tube having an internal diameter of 3·2 cm. as in the case of viscosity of cellulose acetate (see p. 150), since this will eliminate wall-effect.

blue and ultra-violet (?) light, and to the heating effect of the infra-red rays.

Spheres.—The spheres used are glass beads, $3 \cdot 175 \pm 0 \cdot 05$ mm. in diameter (so defined by the committee !) and as nearly spherical as possible. Their specific gravity should lie between 2·4 and 2·6. They are calibrated in the viscometer with a liquid of known viscosity, and their constants calculated. Glass spheres are preferred to steel because they are more easily seen in a dark solution.

Calibration of Spheres.—The viscometer is filled with the standard liquid (castor-oil is suitable—see p. 150), the temperature adjusted to 25° C., and the spheres allowed to fall. They are timed through the middle 15 cm. of the tube. The factor K is determined from the equation :—

$$\eta = \mathrm{Kt(D\text{-}d)},$$

where η is the viscosity of the liquid, t is the time taken by the sphere to fall through 15 cm., D is the density of the sphere, and d that of the liquid.

When one sphere has been selected, it should be weighed, and the other spheres chosen so as to nearly equal it in weight. All are then calibrated, and only those selected which have the same constant within the limits of error demanded by the precision required in the subsequent determinations.

Measurement of Viscosity.—The falling sphere viscometer is filled by connecting the dissolving bulb and the bottom of the viscometer tube by means of a U-tube and then applying air-pressure to the bulb. It has been shown that air does no harm at this stage.[1] The spheres are dropped through a small centring tube *L*, which extends a short distance below the surface of the liquid. This ensures the spheres entering without air bubbles. Care must be taken to have the axis of the viscosity tube vertical. The times required for the spheres to fall through 15 cm. of the solution are observed, and after averaging, the result is multiplied by the constant for the spheres, and by the difference in density between the spheres and the liquid. This is preferred to stating the viscosity in seconds or other arbitrary units. The variations in the walls of the viscosity tube and in the spheres are taken care of by this method because of the calibration, except in so far as the plasticity of the solution may come into play, whereas they are neglected when the

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[1] Joyner. *J.C.S.*, 1922, **121**, 1516.

viscosities are expressed in terms of the seconds required for the spheres to fall a definite distance.

Viscosity Pipette.—For the measurement of very low viscosities, the pipette shown in Fig. 43 is used. The dimensions have been determined empirically, so that the shearing force *F* applied by the falling sphere and the pipette are nearly the same, thus making it possible to obtain the same apparent viscosity on a single solution by both methods of measurement.

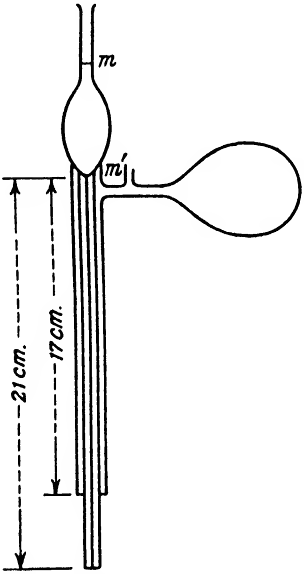

FIG. 43. Cuprammonium Pipette.

The pipette is inserted through the rubber tube at the upper end of the dissolving bulb until the lower end of the outer tube *T* is in exact contact with the liquid level. By pressing the rubber bulb *R* while the thumb is held over the outlet *O*, the solution can be raised in the bulb *S*. The time taken for the liquid to fall from one etched mark *m* to the other *m'*, is the measure of the viscosity. It is converted into centipoises by means of the same formula as used in calibrating the pipette. The end of the tube *T* is crimped in to prevent side play of the tube and to avoid breakage at the junction of the bulb.

Calibration of Pipette.—By timing the outflow of a liquid of known viscosity, a constant K is obtained by application of the equation:

$$\eta = \mathrm{Kdt}.$$

In using the pipette, the bulbs containing the cellulose solution are placed in a thermostat at 25° C., slight variations due to the pipette not being controlled as regards temperature do not appear to affect the results.

The method outlined above does not give a measure of the plasticity, but no evidence has been produced to show that plasticity measurements are significant.

Determinations should agree within 1 per cent.

a **Cellulose.**—Various methods of determining *a* cellulose have been published from time to time, the general principle of them all depending upon the fact that α cellulose is insoluble in 17·5 per cent aqueous caustic soda, while β and γ celluloses are soluble at this concentration. It is necessary to employ a standardized method, since variations in the experimental conditions may lead to serious discrepancies in the results obtained.

The standard method for the determination of α cellulose recommended by the sub-committee of the American Chemical Society is a useful method, although it is not entirely free from features which may lead to errors. However, provided the details are strictly adhered to, the method is sufficiently accurate for the testing of cotton linters for acetate manufacture. The method is as follows[1] :—

3 gm. of the sample is weighed into a 250 c.c. Pyrex beaker, and 35 c.c. of 17·5 per cent caustic soda solution (free from carbon dioxide) are added. After standing for 5 minutes, the material is macerated for 10 minutes with a glass rod, flattened at the ends into a disc, 1 cm. in diameter, and during this period a further 40 c.c. of the caustic soda solution are added in portions of 10 c.c. The temperature of the solution, and of the mixture in the beaker should be maintained at 20° C. The beaker is covered with a watch-glass, and placed in a thermostat at 20° C. for 30 minutes, at the end of which time 75 c.c. of distilled water are added. The whole is filtered through a Gooch having fine perforations : the cellulose forms its own mat, and the solution is refiltered if necessary. The cellulose is then washed, with 75 c.c. distilled water at 20° C. with suction, after which, 40 c.c. of 10 per cent acetic acid are added, and allowed to stand for 5 minutes. The acid is then removed by suction, the α cellulose washed with distilled water till free from acid, sucked dry, and placed in a tared, flat form, glass-stoppered weighing bottle, opened out and dried for 6 hours at 105° C. The first constant consecutive weight after heating intervals of one hour, following the initial drying, is taken as the correct figure. The α cellulose content is calculated on the oven dry weight of the material.

The various times recommended are important and especially the time taken for washing, which is not mentioned in the above method. According to Schmidt,[2] variations in the temperature of the mercerizing (17·5 per cent) solution have a negligible effect on

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[1] *J. Soc. Dyers and Col.*, 1929, **45**, 122.

[2] Schmidt. *Papier Fabr.*, 1929, **27**, 249.

the result obtained, but the temperature of the 8 per cent solution used for washing is very important. The lower the temperature the lower the apparent α cellulose, and the results obtained at 5° C. may be as much as 8 per cent lower than those obtained at 30° C. The time of washing is also very important according to Schmidt, prolongation of the time from 10 to 60 minutes resulting in a loss of about 20 per cent of the α cellulose.

Ash.—5–10 gm. of cotton is weighed into a silica or platinum dish, and ignited gently, so that it chars without flame or violent gas evolution. When charring is complete, the dish and contents are allowed to cool, 5 c.c. of hydrogen peroxide is added, and the whole taken to dryness on the water bath. The dish and contents are then heated to dull redness, and after cooling in a desiccator, weighed. The ash should not exceed 0·10 per cent on the dry weight of the cotton; high ash indicates contamination with sandy and other inorganic impurities.

Solvent Extraction.—It is desirable, especially when examining cotton linters from fresh sources of supply, to make sure that the degreasing process has been carried out satisfactorily. The most comprehensive solvent for the extraction of fats, waxes, and resins from cotton is chloroform, and the most suitable method of carrying out the determination according to A. J. Hall[1] is that of Fargher, Higginbotham, and others,[2] which is as follows: 100 gm. of cotton are extracted for 6 hours in a hot Soxhlet apparatus, the chloroform being maintained in active ebullition throughout the determination. If the amount of material available for analysis is small, 20 gm. of cotton may be extracted for three hours. The solvent is then distilled from the extract, and the residue is dried to constant weight at 80° C. *in vacuo*, as produced by a water pump.

If it is desired to ascertain the fat and wax content separately the chloroform should be replaced by carbon tetrachloride, which has been twice distilled over paraffin wax to remove traces of other chlorinated products. The resins are not appreciably soluble in this solvent, so that a fairly approximate value for the fat and wax content can be obtained.

The chloroform extract of cotton linters which have been satisfactorily degreased should not exceed 0·5 per cent.

Laboratory Trial Acetylation.—The method used should follow

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[1] A. J. Hall. *Cotton Cellulose*, London, 1924, p. 212.

[2] Fargher, Higginbotham, and others. *J. Text. Inst.*, 1924, **15**, 75 and 120.

as closely as possible the one which is practised on the large scale in the factory. It is, however, necessary when acetylating small quantities of cotton or other cellulose, to use a greater excess of acetic anhydride than in large scale acetylations. It is not possible satisfactorily to ripen these small batches of cellulose acetate, so that a laboratory acetylation gives no quantitative information as to the viscosity and acetyl content which can be expected when the same sample is acetylated and ripened on the large scale. The test, however, gives an indication of the reactivity of the cotton, and of the clarity of the final product. It may be carried out as follows :—

A mixture of 100 c.c. of glacial acetic acid, 80 c.c. of acetic anhydride, and 2 c.c. of concentrated sulphuric acid is prepared in a cylindrical copper vessel of about 2 litres capacity, the anhydride being added to the acid, and after cooling in ice, the sulphuric acid is added to the mixture. The vessel is placed in a freezing mixture, and cooled with stirring, until the liquid appears full of small crystals (about 5° C.). 25 gm. of the cotton linters dried to 2 per cent moisture are then added gradually over a period of about 10 minutes, each addition being well beaten with a flat-ended glass rod before adding more. When all the cotton has been added, the course of the acetylation should follow as closely as possible that laid down for the large scale process in Chapter IV. The reaction should be complete in about eight hours, and at the end of that time a sample should be examined microscopically for unacetylated fibres, dirt, etc. The reactivity and the colour and clarity of the solution should also be noted. With experience, it is possible to form a rough idea of the viscosity of the solution, by allowing it to flow from the end of the glass rod.

The colour of the acetylated solution can be determined by diluting a suitable weight with acetic acid to a convenient volume, and comparing it with standard glasses in a Lovibond Tintometer.

The clarity is determined by diluting a second portion of the acetylated solution with acetic acid, and examining it in the apparatus described under the analysis of cellulose acetate (p. 155).

Acetic Acid.—As indicated in Chapter III, glacial acetic acid of a high degree of purity can readily be obtained. The most important determinations in this connection are acetic acid content, traces of iron, silica, and alumina, and in the case of acetic acid derived from pyroligneous acid, tests for absence of pyroligneous matter.

Determination of Acetic Acid.—Owing to the volatility of the acid and the unsatisfactory nature of the end-point obtained, the direct titration of acetic acid with standard alkali gives unreliable results. These difficulties can be overcome by adding a known weight of the acid to an excess of standard alkali contained in a stoppered flask, and after well mixing and allowing to stand for about 15 minutes, determining the excess of alkali by titration with standard acid. The usual precautions must be taken, i.e. all solutions and distilled water used must be free from carbon dioxide, and all glass apparatus must be resistant to alkali.

The above method is not sufficiently rapid for routine purposes as, for example, in the testing of the glacial acetic acid from the acetic acid recovery plant. For such tests a freezing point method is quite satisfactory, the results obtained rarely differing by more than 0·1 per cent from those given by the titration method. Provided the nature and quantity of the impurities present in the acid does not change appreciably, a correction can be found by analysing a number of samples by both methods, and this correction can then be applied to all results obtained by the freezing point method. A useful paper concerned with the relationship between freezing point, specific gravity and percentage of acetic acid present in concentrated acetic acids appeared in the *Analyst* in 1926,[1] and the table here reproduced is taken from that paper. The freezing point of 100 per cent acid is taken as 16·63° C. following Pickering,[2] although Rudorff[3] gives 16·70° C., and Bousfield and Lowry,[4] and de Visser[5] give figures on specially purified acid as 16·60° C. According to Droop Richmond (loc. cit.), the most common impurity in glacial acetic acid which depresses both the

Table. Freezing Points of Acetic Acids

Acid %	0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
99	14·74	14·92	15·10	15·28	15·47	15·65	15·84	16·04	16·24	16·43
98	13·12	13·27	13·43	13·58	13·74	13·90	14·06	14·23	14·40	14·57
97	11·68	11·82	11·96	12·10	12·24	12·38	12·52	12·67	12·82	12·97
96	10·34	10·47	10·61	10·74	10·87	11·00	11·14	11·27	11·40	11·54
95	9·08	9·20	9·32	9·45	9·57	9·70	9·83	9·95	10·08	10·21

[1] Droop, Richmond, and England. *Anal.*, 1926, **51**, 283.
[2] Pickering. *J.C.S.*, 1893, **63**, 998.
[3] Rudorff. *Ber.*, 1870, **3**, 390.
[4] Bousfield and Lowry. *J.C.S.*, 1911, **99**, 1432.
[5] de Visser. *Rec. trav. chim.*, 1893, **12**, 101.

freezing point and the specific gravity is propionic acid, each 1 per cent depressing the freezing point by 0·485° C. on the average.

A suitable method of determining the freezing point of glacial acetic acid is as follows: A large sample of about 250 c.c. should be taken, and 20 c.c. is placed in a dry boiling tube, which is put into cold water at a temperature of about 12° C. The acid is then stirred continuously with a standardized thermometer which can be read to 0·05° C., until crystallization begins, when the temperature is noted. The tube is taken out of the freezing mixture, and the contents are stirred, the temperature being noted every few seconds. The highest temperature recorded before melting begins gives a rough indication of the freezing point, and serves as a guide in the accurate determination. A further 20 c.c. of the acid is placed in a second boiling tube which is put into a bath of water maintained at about 2° C. below the rough freezing point, as indicated by the preliminary experiment. The thermometer is placed in the acid and observed without stirring. When the temperature has fallen to not more than two degrees below the approximate freezing point, a few drops of acetic acid from the first tube, containing small crystals, are added. Crystallization at once begins. The tube is removed from the beaker and placed in an empty flask to protect it from gain or loss of heat. The acid is stirred continuously with the thermometer and the temperature is noted every few seconds. The highest temperature recorded is the freezing point. The mean of at least three concordant results should be taken. It is important to protect the acetic acid from atmospheric moisture during the determination. The following are typical results obtained in this manner:

Sample No.	*Temperature of acid.*				*Freezing point.*	*Acetic acid per cent by*	
						F.P.	*Titration.*
1	14·5	14·7	15·0	15·5	15·9	99·6	99·7
	14·6	14·9	15·2	15·7	15·85		
	14·2	14·6	14·9	15·6	15·9		
2	13·0	13·5	14·0	14·5	14·6	98·9	99·1
	13·7	14·0	14·3	14·6	14·6		
	13·5	13·9	14·1	14·5	14·6		
3	15·0	15·4	15·6	15·6	15·6	99·5	99·6
	14·8	14·9	15·2	15·6	15·65		
	14·6	14·9	15·2	15·6	15·65		

Test for Pyroligneous Matter.—The test given in the *British Pharmacopœia* (1914) is not very sensitive, and the following modification is to be preferred for testing acetic acid for use in the manufacture of cellulose acetate. The test need only be applied to acids derived from pyroligneous sources, or to those which have been concentrated by extraction with solvents derived from wood tar.

9 c.c. of distilled water, 1 c.c. of N/100 sulphuric acid, and 3 drops of a solution of potassium permanganate (containing 1·25 gm. per litre) are mixed. 2 c.c. of the glacial acetic acid are added and mixed in, and after 30 seconds the intensity of the permanganate colour is compared with a blank test prepared in the same way, the acetic acid being replaced by 2 c.c. of distilled water. If the permanganate colour is completely discharged in the time stated, the acid is unsatisfactory. The test solutions should not, of course, be allowed to come into contact with the fingers, as this causes decolorization of the permanganate.

Acetic Anhydride.—Commercial acetic anhydride varies in strength between 94 and 96 per cent. It is essential to determine the anhydride content, and it should also be reasonably free from metallic impurities.

Anhydride Content.—Considerable reliance was formerly placed on the method of Menschutkin and Vasilieff,[1] which depends on the fact that acetic anhydride reacts with aniline to give acetanilide, whereas acetic acid does not. Concordant results can certainly be obtained by this method, but as Treadwell points out,[2] they are from 14 to 16 per cent too high, due to the fact that at the boiling point acetic acid does react with aniline. Thermometric methods have also been suggested, notably one by Richmond and Eggleston,[3] which is based on the same reaction of acetic anhydride with aniline. Unfortunately, the results obtained agree with those from the method of Menschutkin and Vasilieff, which the authors considered to be the most accurate method available. The thermometric method is very promising, but in the light of Treadwell's opinion, Richmond and Eggleston's results would need to be confirmed.

E. Terlinck[4] recommends treating 1 gm. of the sample with 15 c.c. of a 20 per cent solution of dichloraniline in chloroform, and allowing the mixture to stand overnight. The reaction

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[1] Menschutkin and Vasilieff. *J. Russ. Chem. Soc.*, **21**, 190.

[2] Treadwell-Hall. *Quantitative Analysis*, p. 586.

[3] Richmond and Eggleston, *Anal.*, 1926, **51**, 281.

[4] E. Terlinck. *Chem. Ztg.*, 1929, **53**, 814–15, 850–1.

resembles that of aniline and acetic anhydride, 1 molecule of anhydride and 1 molecule of dichloraniline forming 1 molecule each of dichloracetanilide and acetic acid. By determining the acidity before and after the treatment, the anhydride content of the sample may be readily computed. Provided acetic anhydride is without action on dichloraniline, this offers a useful alternative to Menschutkin and Vasilieff's method.

An interesting method was described by A. Rott[1] last year (1930). 10 c.c. are weighed into a stoppered flask and 6 to 7 per cent excess of water is added over what is required to convert the anhydride into acetic acid. The flask is again weighed to determine the amount of water added. After refluxing for one hour, the flask and contents are cooled, and the freezing point of the acid is determined. Then—

$$\%\ Ac_2O = \frac{(\text{Water added} - \text{Water found in final acid})}{\text{Weight of sample}} \times 556{\cdot}67$$

The author claims that impurities such as hydrochloric acid, acetyl chloride, and higher fatty acids do not markedly affect the determination.

The standard method of determining the anhydride content of a given sample, to which all other methods must ultimately be referred, is a modified titration method, similar to that employed for acetic acid, and described above. A known weight of the sample in a stoppered weighing bottle is dropped into an excess of standard alkali in a stoppered flask. The stopper of the weighing bottle is induced to leave the bottle, and the contents of the flask are then well mixed and cooled in water. After half an hour the excess of alkali is determined by titration with standard acid. Great care must be taken in dropping the weighing bottle into the flask to avoid any loss by spirting or splashing, and the flask should be stoppered immediately. During the half hour, the contents of the flask should be well agitated from time to time in order that any anhydride vapour in the flask may be absorbed.

If W gm. is the weight of the sample taken for analysis, x gm. is the weight of anhydride in W gm. of sample, y gm. is the weight of acetic acid in W gm. of sample, Q is the apparent weight of acetic acid in the sample (as found by titration), then :—

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[1] A. Rott. Idem., 1930, **54**, 954–5.

$$W = x + y \quad \ldots\ldots\ldots\ldots \quad 1$$

$$Q = \frac{60x}{51} + y \quad \ldots\ldots\ldots \quad 2$$

$$\text{whence } \% \ Ac_2O = \frac{5{,}100\ (Q\text{-}W)}{9W}$$

The composition of the mixture of acetic acid and anhydride prepared in the acetylation department may be determined in a similar manner.

Sulphuric Acid.—The sulphuric acid used should be of not less than 97 per cent strength. It should also be free from all but traces of metallic impurities.

Determination of Concentration.—The acid is conveniently weighed in a small weighing bottle (tall-form) which is then allowed to slide down the side into a conical flask containing water (boiled and cooled distilled). The acid is then determined by titration with standard alkali.

General Observations on Titration Methods.—As far as possible the conditions, temperature of solutions, concentrations, etc., should be uniform in the standardization of solutions used, and in the actual determinations. The best indicator to use is phenol phthalein, prepared according to the B.P. method, and using three drops in each titration. In the case of acetic acid, acetic anhydride, and mixed acid determinations, it is best not to add the indicator until within a few c.c. of the end-point, otherwise the colour is very faint, and difficult to see. The standard alkali into which the acid material is introduced should be measured out by means of a burette with a water jacket in which water at a suitable constant temperature is circulated (20° C.), and the solution should be allowed to remain in the burette until the temperature is constant. All the ordinary precautions of volumetric analysis should, of course, be observed.

Cellulose Acetate.—In sampling cellulose acetate for analysis care should be taken not to sample until the batch is cooled down to air temperature. At least 10 per cent of the trays or other containers should be sampled, and after mixing the bulk sample should be quartered in the usual way for dry materials.

Moisture.—A crystallizing dish (8 cm. diameter and 4 cm. deep) fitted with a clock glass cover is heated in the oven at 105° C. for half an hour. It is then cooled in a desiccator. When cold it is weighed and 10 gm. of acetate are weighed into it, and the whole is heated at 105° C. to constant weight. Three hours' heating is usually sufficient. After cooling in a desiccator, the dish and contents are reweighed and the result is expressed as a percentage on the original acetate. All weighings should be as rapid as possible, since the dry cellulose acetate is very hygroscopic.

Ash.—A silica crucible is heated to redness, cooled in a desiccator, and weighed. About 3 gm. of dried acetate are weighed into it when cold, and cautiously ignited, care being taken to prevent spitting. The acetate should not be allowed to inflame. The crucible and contents are then heated to dull redness until the ash is free from carbonaceous matter, when they are cooled in a desiccator and weighed. The ash is expressed as a percentage of the dry weight of the cellulose acetate.

Free Acidity.—The determination of the free acidity is a somewhat difficult matter, since the percentage amount is necessarily very low. Shaking or allowing the acetate to stand with distilled water is unsatisfactory, as a very large proportion of the acid is retained by the material, and a low result is consequently obtained. Heating with water is also unsatisfactory, as the cellulose acetate may undergo partial hydrolysis resulting in a high figure for the acidity. The most suitable method is that recommended by the British Engineering Standards Association, and is as follows :—

" 6 gm. shall be shaken in a vessel of chemically resistant glass with 100 c.c. of acetone until solution is complete. The resulting solution shall then be poured slowly and with constant stirring into 100 c.c. of recently boiled and cooled distilled water contained in a suitable bottle (see below). A blank consisting of 100 c.c. of the acetone and 100 c.c. of the distilled water shall also be prepared in a bottle of similar size and manufacture. The bottles containing the solution and the blank shall be shaken mechanically for 30 minutes and an aliquot portion as large as possible of the clear liquid and a similar quantity of the blank shall be taken from the bottles and each titrated with N/100 caustic soda, using phenol phthalein as indicator. *Note*: The bottles used shall be of approximately 250 c.c. capacity and shall comply with the following requirements. They shall be completely filled with recently boiled and cooled distilled water and a few drops of phenol phthalein solution added. After standing overnight at laboratory temperature, the contents of the bottles shall show no distinct coloration."

A suitable shaker for use in this and other tests involving solution of cellulose acetate is shown in Fig. 44.

Total Sulphate.[1]—5 gm. of acetate is weighed into a 250 c.c. conical flask; 35 c.c. of concentrated hydrochloric acid are added, and after warming to 50° C., the mixture is allowed to stand, with occasional shaking, until solution is complete. 6 c.c. of concentrated nitric acid are then added, and the solution is concentrated on the hotplate or sand-bath to a volume of 10 c.c. Should the liquid darken during evaporation, a few drops of nitric acid should be added, and evaporation continued. It is essential that all the nitric acid should be expelled, otherwise barium nitrate is liable to be formed in the subsequent precipitation of the sulphate with barium chloride, and it is impossible to remove this occluded nitrate by washing the sulphate precipitate. If necessary a little more hydrochloric acid must be added and evaporation continued. When evaporation is complete, 80 c.c. of boiling distilled water are added and the solution is boiled for 15 minutes. It is then filtered from traces of precipitated cellulosic matter into a 400 c.c. beaker, and the filtrate and washings are brought to a volume of 150 to 200 c.c. The liquid is then boiled for 5 minutes, and 2·5 c.c. of 10 per cent barium chloride solution is added slowly in a fine stream to the

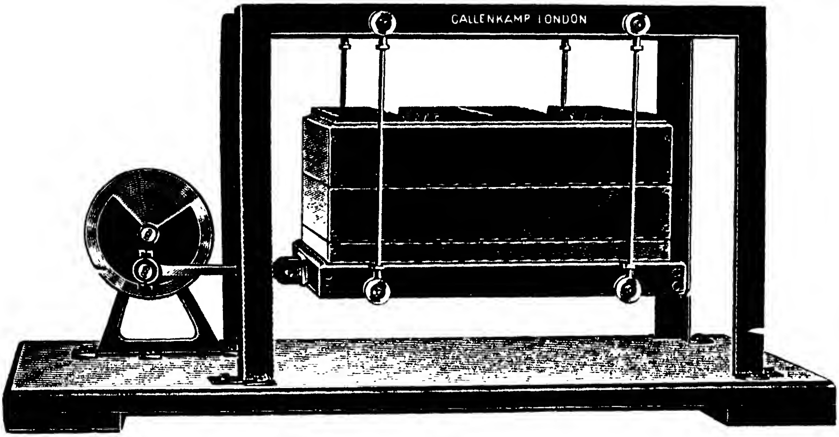

FIG. 44. Mechanical Shaker. (A. Gallenkamp & Co., Ltd.)

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[1] Cf. *Ost. Z. angew. Chem.*, 1919, **32**, 66, 76, 82.

boiling solution, which is boiled for a further 4 minutes. A second 2·5 c.c. of barium chloride solution are then added as before, and the solution is boiled gently for one hour. It is allowed to stand overnight, and the liquid is then decanted through a tared Gooch or sintered glass crucible, the precipitate being twice washed with 10 c.c. portions of boiling distilled water by decantation, before transferring it to the crucible. It is again washed three times with 10 c.c. portions of distilled water (boiling), and the crucible and contents are then dried at 105° C., followed by ignition at a low red heat. The barium sulphate is weighed when cold, and the result is expressed as per cent SO_4 on the dry acetate : $\%SO_4 = (\text{wt. of } BaSO_4 \times 8{\cdot}23)$. A blank test must be performed with the reagents used.

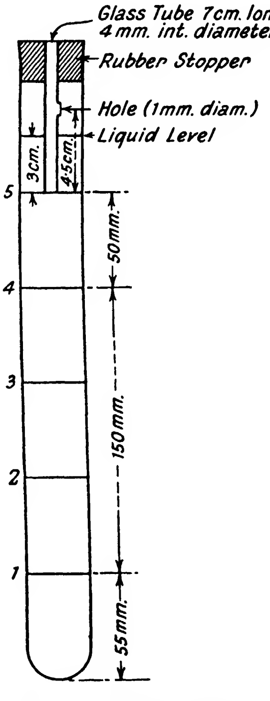

FIG. 45. Falling Sphere Viscometer for Cellulose Acetate Dispersions.

Heat Test.—About 1 inch depth of finely powdered cellulose acetate is packed fairly tightly into a $\frac{5}{8}$ in. hard glass test tube, and immersed in a beaker of paraffin-wax at 150° C. The temperature of the bath is then raised at exactly 2° C. per minute with frequent stirring until the acetate melts or chars. The temperature of melting or charring is noted. It is not necessary to carry the test above 240° C. unless the exact temperature is required, since any charring or melting temperature above 240° C. is satisfactory.

Viscosity.—Cellulose acetate equivalent to 15 gm. of dry material is weighed into a 6 oz. glass bottle having a well-fitting ground stopper. Water is added to make with the water present in the acetate 5 gm. 80 gm. of acetone is then added from a stoppered pipette graduated to deliver that weight of acetone, at 15° C. The stopper is at once inserted tightly in the bottle and tied down with string. The bottle and contents are then shaken in a shaking machine (Fig. 44) until solution is complete.

The viscosity is then determined by means of the falling sphere viscometer shown in Fig. 45. It consists of a glass tube, which has an internal diameter not less than ten times that of the sphere to be employed, in this case 32 mm. as the most useful size sphere is a $\frac{1}{8}$ in. ball bearing. The tube is filled with solution and tightly stoppered and placed in a constant temperature bath at 25° C. A convenient bath for this purpose consists of a cylindrical specimen jar, having an overflow at the top, and supplied with water at 25° C. from a spiral water heater. When a number of determinations are to be made consecutively, the tubes are conveniently stored in a circular copper test-tube holder, which just fits the jar. The tubes of solution should be kept in the bath for at least one hour, to ensure that the contents have attained a uniform temperature of 25° C. When this is the case, the tube containing the solution to be tested is clamped with its axis vertical (the tube being still in the bath), and the cork is replaced by a rubber stopper carrying a glass tube of the dimensions shown in the figure. This serves to centre the sphere, and to ensure that it enters the liquid without accompanying air bubbles. The time taken for a $\frac{3}{8}$ in. steel ball to fall from graduation 4 to graduation 1 is then noted, and the process is repeated until three or more concordant results have been obtained. Lack of agreement may be due to inaccuracy of the stop-watch, poor temperature control or to the fact that the solution is not homogeneous.

The viscosity may be calculated from the following formula :—

$$\eta = \frac{td^2(\delta - \rho)g}{18s\left(1 + \frac{2\cdot 4d}{D}\right)\left(1 + \frac{5d}{3h}\right)}$$

where g = 981 cm/sec^2.
d = diam. of sphere in cm.
δ = density of sphere in gm. per c.c.
ρ = density of cellulose acetate solution.
t = time in seconds taken for the sphere to fall through "s" cm. (i.e. 15 cm.).
D = diameter of tube in cm.
h = height of column of solution in cm.

Alternatively, the ball fall time of pure castor-oil may be noted in the same manner, when the viscosity may be calculated from the following formula :—

$$\frac{\eta_x}{\eta_c} = \frac{(S - \sigma_x)}{(S - \sigma_c)} \times \frac{T_x}{T_c}$$

where T_x = ball fall time for solution under test.
T_c = do. do. castor-oil.
η_x = viscosity of solution under test.
η_c = do. castor-oil.
S = density of steel balls used.
σ_x = do. solution under test.
σ_c = do. castor-oil.

The above method is essentially that described by Gibson and Jacobs[1] in 1920. If accurate results are to be obtained, all the dimensions given must be strictly adhered to. The use of viscosity tubes of less diameter, for example, leads to inaccuracies due to " wall-effect ". Other methods may be used for determining the viscosity of cellulose acetate solutions such as the Ostwald tube, but if a capillary tube method is adopted, less concentrated solutions of the acetate must be used. The method described is rapid and very convenient for routine purposes.

Acetyl Content.—A number of processes for the determination of the combined acetic acid in cellulose acetate have been described. They may be divided into two classes according to whether the preliminary hydrolysis of the acetate is brought about by alkaline or acid reagents.

Alkaline Methods.—The earliest example of an alkaline saponification of cellulose acetate for the determination of the acetic acid content is that of Cross and Bevan. As modified by Woodbridge,[2] it is as follows : 23 cgm. of sodium are dissolved in 2 litres of alcohol. The sample is treated with a quantity of this solution, containing twice the amount of sodium necessary to combine with the acetic acid contained in it, the digestion being continued for six hours in the cold.

Barthélémy[3] introduces 2 gm. of the sample into a 200 c.c. Erlenmeyer flask, and adds to it 40 c.c. of N/1 caustic soda solution ; the flask is then closed with a rubber stopper having a Bunsen valve, to prevent air from entering the flask. The flask is placed in a bath at 85–90° C. and maintained at that temperature for 4 hours,

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[1] Gibson and Jacobs. *J.C.S.*, 1920, **117**, 473.
[2] Woodbridge. *J.A.C.S.*, 1909, **31**, 1008.
[3] Barthélémy. *Monit. Scientif.*, 1913, **78**, 549.

shaking every 15 minutes. It is then kept at 85–90° C. for a further 12 hours. At the end of that time the solution is transferred to a 250 c.c. flask and made up to that volume with distilled water. 50 c.c. of the resulting solution are titrated with sulphuric acid using phenol phthalein or congo red as indicator.

Barnett[1] dissolves the sample in acetone and saponifies by shaking with caustic soda solution. He states that a correction is necessary to allow for the action of the soda on the regenerated cellulose. Other alkaline methods have been described by Schwalbe,[2] Eberstadt,[3] Clément and Rivière,[4] and Knoevenagel and Eberstadt.[5]

Acid Methods.—It has been shown by Ost,[6] that alkaline methods of hydrolysis of cellulose acetate give unreliable results, owing to the action of the alkali upon the cellulose. He has described a method depending upon hydrolysis with 50 per cent by volume sulphuric acid followed by steam distillation to recover the acetic acid set free. While the method is somewhat long, it gives very reliable results (± 0·5 per cent),[7] and has been found suitable for routine purposes when only 10 per cent of the samples are tested. The details are as follows:—

About 1 gm. of the sample is accurately weighed into a 400 c.c. round-bottomed flask, and 15 c.c. of 50 per cent by volume sulphuric acid are added. The flask is well corked, the contents mixed, and allowed to stand 12 hours or overnight. 100 c.c. of boiled and cooled distilled water are then added, and the liquid is steam-distilled with steam from a generator containing well-boiled distilled water. These precautions are necessary to avoid the presence of carbon dioxide in the distillate. The volume of liquid in the distillation flask must be kept constant at 100–125 c.c., if it is allowed to concentrate, the sulphuric acid attacks the cellulosic material and gives rise to volatile acid materials; if the volume is allowed to increase due to condensation of steam, the operation is unduly prolonged. Distillation should be at the rate of 500–600 c.c. per hour. According to Ost, when almost 1 litre has distilled, the

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[1] Barnett. *J.S.C.I.*, 1921, **40**, 8T.

[2] Schwalbe's method. See M. Deschiens. *Chim. et Ind.*, 1929, **21**, 1131.

[3] Eberstadt. *Diss. über Acetylcellulose*, Heidelberg.

[4] Clément and Rivière. See Deschiens (loc. cit.), 1909.

[5] Knoevenagel and Eberstadt. *Kolloidchem. Beih.*, 1921, **13**, 194.

[6] *Ost. Z. angew. Chem.*, 1906, **19**, 995; 1912, **25**, 1467.

[7] Ibid. 1919, **32**, 66, 76, 82.

receiver is removed, the distillate made up to 1 litre, and 250 c.c. is titrated with standard baryta, using phenol phthalein as indicator. It has been found more satisfactory to distill two separate litres, and to titrate the whole of the distillate, with N/5 soda. The acetyl content is expressed as acetic acid per cent on the dry weight of the cellulose acetate taken.

An extremely accurate method of determining the acetyl value is that described by Hess and Weltzien[1] in 1923. Many hundreds of determinations have been carried out by this method, and concordant results have been obtained by various workers. The method is unfortunately too long for routine purposes, but is of great value where an accurate determination of the acetyl value of a sample of cellulose acetate has to be made. As described by Hess in *Die Chemie der Zellulose* (p. 418), the method is as follows:—

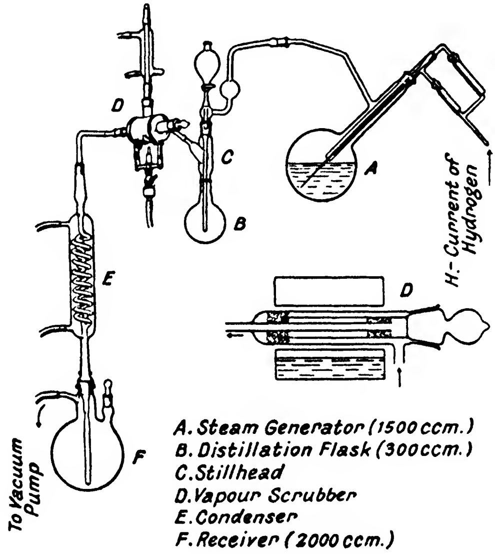

FIG. 46. Apparatus for Determination of Acetyl Content of Cellulose Acetate. (Hess.)

0·2–0·3 gm. of the sample are accurately weighed into the flask *B* (Fig. 46) and mixed therein with 2 c.c. of 50 per cent sulphuric acid with shaking. The flask is then closed with a rubber

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[1] Hess and Weltzien. See Hess, *Die Chemie der Zellulose*, pp. 416–19.

bung and allowed to stand until a clear solution is obtained. This takes from 2–24 hours, according to the solubility of the acetate and the room temperature. The flask is then connected to the still-head *C*, the receiver *F* is filled with water (which has been boiled in a current of carbon dioxide free air) to such a height that the end of the condenser dips into it. A current of hydrogen is now passed through the apparatus, and at the same time the flask is warmed in a boiling water bath to complete the saponification of the acetate ; this requires ten minutes' heating. The flask is then cooled, and 13 c.c. of sodium phosphate solution are added through the dropping funnel (solution prepared by dissolving 1,170 gm. of secondary sodium phosphate and 150 gm. of 84 per cent aqueous phosphoric acid in water, the volume being made up to 900 c.c.). The apparatus is now evacuated, and steam is passed from the generator *A* into the solution in flask *B*. The rate of distillation should be adjusted to suit the capacity of the condenser *E*. When the liquid in *B* approaches dryness, the distillation is interrupted, and just sufficient water is added through the dropping funnel to dissolve the contents, following which distillation is resumed. The process is repeated three times. The function of the purifying apparatus *D*, which is shown in detail in the large inset, is to free the vapour passing from *B* to *F* from traces of mist or spray. This is achieved by keeping the water boiling in the jacket of *D* during a determination. During the last distillation it is necessary to ensure that every trace of vapour is driven from the apparatus between *B* and *F*, by cautious heating with a flame.

When the last distillation has been completed, hydrogen is admitted to the apparatus, and the contents of flask *F* are titrated with N/20 baryta, using phenol phthalein as indicator. This is achieved by using a burette with a long delivery tube which is inserted into the flask *F* through the tubulure (on the right in the diagram).

Control tests have shown that there is no production of volatile acid products through the decomposition of cellulosic matter ; and blank tests indicated that the vapour purifier *D* works well, no trace of acid being detectable in the distillate.

If 0·2–0·3 gm. of acetate are taken, the result is within 0·1–0·3 per cent of the truth, while 0·15 gm. of acetate give a result within 0·3–0·6 per cent of the correct value. The errors of the method are due to traces of acetic acid remaining behind in the apparatus.

Free and Combined Sulphuric Acid.—Vulquin and Entat[1] treat the sample with boiling water under pressure at 125° C. They then measure the potential difference between a polarized platinum electrode dipping into the solution, and a normal electrode immersed in the same solution. A curve is then traced with the quantity of baryta necessary to precipitate the sulphuric acid as abcissæ, and as ordinates the potential difference. At the neutral point, there is a sudden fall in the potential difference and a turning point in the curve. The method is said to be rapid and accurate.

Copper Number. — The copper number of cellulose acetate gives a good indication of the degree of degradation. A method for its determination was described by Deschiens[2] and is as follows: 2 gm. of the sample is digested with 30 c.c. of distilled water in a flat-bottomed flask for 30 minutes, at 60 - 70° C., shaking every five minutes. 100 c.c. of Fehling's solution are then added and the whole is placed on the water-bath for one hour. The liquid is then refluxed for some time, and after standing for ten minutes, the solution is filtered, and the precipitate is washed with hot water till the filtrate is neutral. The copper in the precipitate is then determined by a standard method of analysis.

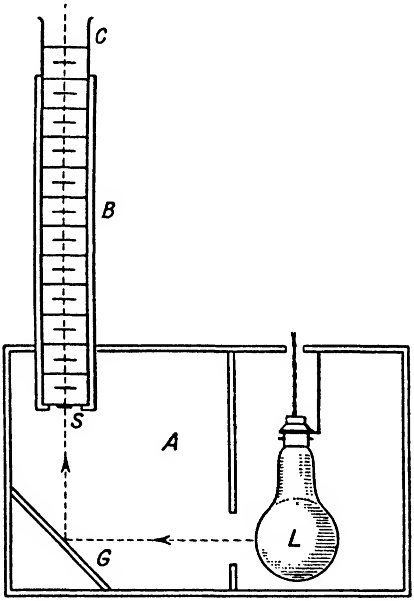

FIG. 47. Apparatus for determining the Clarity of Cellulose Acetate.

Clarity.—10 gm. of the sample is shaken in a 10 oz. bottle with 100 c.c. of acetone until dispersion is complete. A quantitative measure of the clarity of the solution is obtained by means of the apparatus shown in Fig. 47. This consists of a box *A*, painted

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[1] Vulquin and Entat. *Ann. Chim. anal.*, 1922, **27**, 131.
[2] M. Deschiens. *Chim. et Ind.*, 1929, **21**, 1131.

inside with drop black, and having a 60 watt electric lamp *L* at one end. At the other end is an opal glass *G* inclined at an angle of 45°, so that the light from the lamp is projected up through the tube *B*, inside which is a flat-bottomed glass tube *c*, graduated in c.c. and having a small black spot *S*, 5 mm. in diameter at the centre of the bottom. The solution to be examined is poured into the glass tube, until the black spot is just rendered invisible. The number of c.c. required is in inverse proportion to the clarity of the solution. A note should also be made of any foreign matter present in the solution.

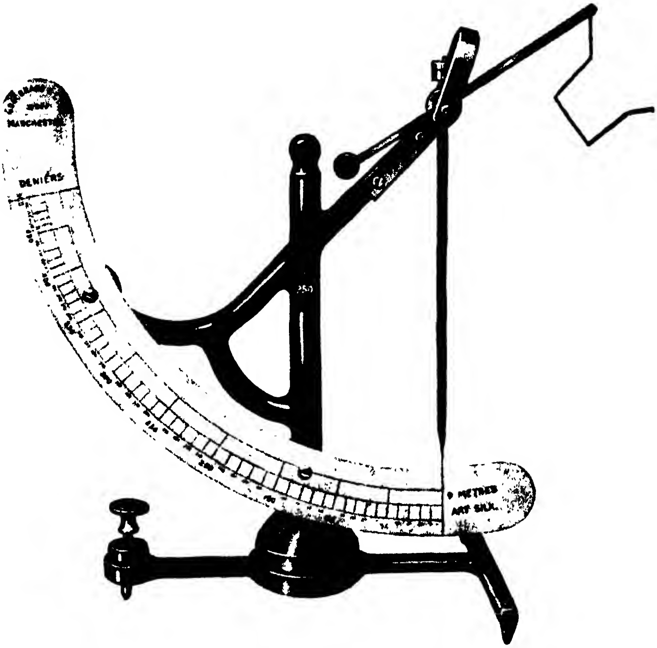

FIG. 48. Quadrant Balance. (Goodbrand & Co., Ltd.)

In the routine examination of cellulose acetate in the factory, the most useful determinations are the following: Moisture, free acidity, total sulphate, heat test, viscosity, and clarity. It is usually sufficient to examine 10 per cent of the samples for acetyl content.

Rayon Tests.—The tests which will usually be required to be made in the laboratory on the rayon yarn include a determination of the titre, and of the tensile strength and elasticity.

Titre.—This is determined by hanging a definite length of yarn on the hook of a quadrant balance of the type shown in Fig. 48. Quadrants may be obtained graduated in deniers to read directly the titre of definite lengths of yarn. The one illustrated is arranged to weigh 9 metres of yarn, and is graduated from 0–500 deniers.

Tensile Strength and Elongation.—Figs. 49 and 50 illustrate machines for testing the tensile strength and elongation of rayon yarns. The machines are similar, except that the first illustration shows a hand-operated machine, while the second is motor driven. In both cases a drum is fitted on which a permanent record in the form of a stress-strain diagram is obtained for each sample tested. When the thread breaks the tensile strength is read off on the dial plate, and the elongation on the stretch indicator at the right hand side. In the case of the power operated machine, the motor is coupled through worm reduction gears to the traverse screw, which is attached to the bottom carriage and yarn grip. When the sample

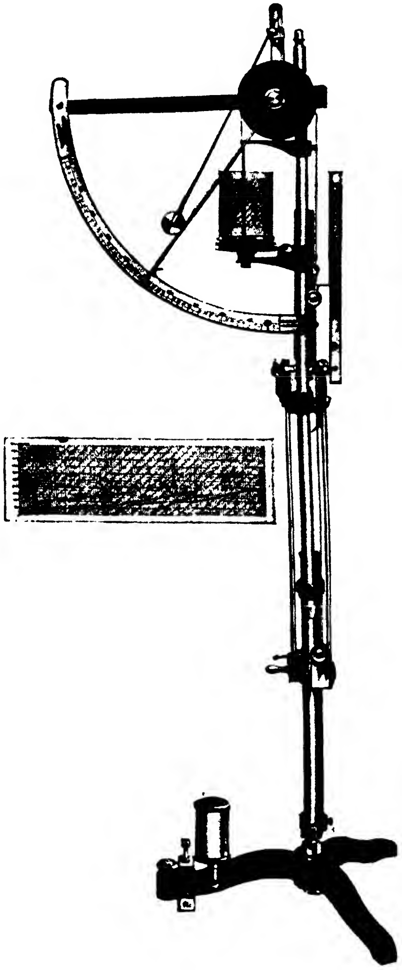

FIG. 49. Yarn Testing Machine—Hand operated. (Goodbrand & Co., Ltd.)

breaks a catch engages with the teeth cut in the main pillar, and this stops the machine instantly. As it is not possible to stop a motor dead, a friction device is incorporated. The carriage is so designed that it always starts at the same position, and when this position is reached, and also when the sample breaks, this frictional device comes into operation, giving the operator plenty of time to reverse or stop the motor.


FIG. 50. Yarn Testing Machine —Motor operated. (Goodbrand and Co., Ltd.)

Twist Testing.—The machine shown in Fig. 51 is designed to determine the amount of twist which has been imparted to a rayon yarn. To make the test, the dial is first set to zero, and the yarn to be tested is secured at one end in a revolving grip, and at the other end it passes through an open sliding grip, over a guide pulley, and is then secured to the tension lever. The sliding grip is then tightened up and the hand wheel is rotated in the correct direction, the threads being meanwhile observed through the lens. The finger on the dial indicates the hundreds, and the mark on the head-stock the units of revolution.

Resistance to Creasing.—An interesting method for determining the resistance of rayon yarns to creasing has been described by A. J. Hall,[1] and is useful in comparing the qualities of acetate yarns made by different processes. The yarn is steeped in cold water for four hours, and allowed to dry without tension ; this treatment removes all effects of stretching due to previous processing. A length of yarn is then wound with minimum tension on a flat card, and is then subjected to a pressure of 20 lb. for five minutes. The yarn is carefully removed from the card and laid on a sheet of highly glazed paper. On gently tapping the paper the yarn takes up a stable form (Fig. 52) which Hall calls the " Crease trace ",

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[1] A. J. Hall. *J. Soc. Dyers and Col.*, 1930, **46**, 257.

the angles in the folds of the yarn being termed the " Crease angle ".

Some interesting results have been obtained by Hall with acetate yarns in the normal condition, and also those which have been submitted to various degrees of stretching, and the following are a selection of the figures obtained :—

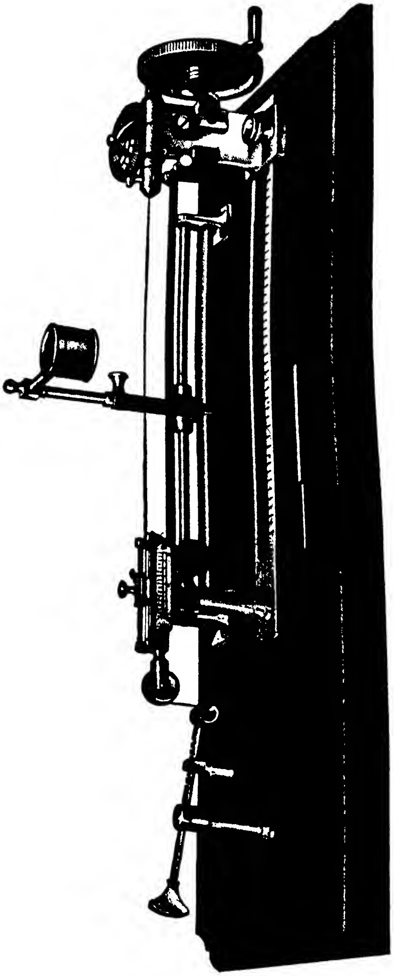

FIG. 51. Twist-testing Machine. (Goodbrand & Co., Ltd.)

Original length of yarn.	*Stretched length of yarn.*	*Length 5 min. after stretch.*	*Original extension %*	*Final extension %*	*Recovery of orig. length.*	*Crease angle.*
60·0	60·0	60·0	0·0	0·0	100·0	170° approx.
60·0	61·5	60·1 60·1	2·5	0·16	94·0	130° 122°
60·0	63·0	60·7 60·6	5·0	1·08	78·0	94° 108°
60·0	66·0	63·2 63·3	10·0	5·41	46·0	68° 65°
60·0	69·0	66·1 66·2	15·0	10·25	32·0	62° 62°
60·0	72·0	69·1 69·2	20·0	15·25	24·0	61° 61°

It will be observed that the yarn gradually loses its power of recovering its original length as the degree of stretching increases.

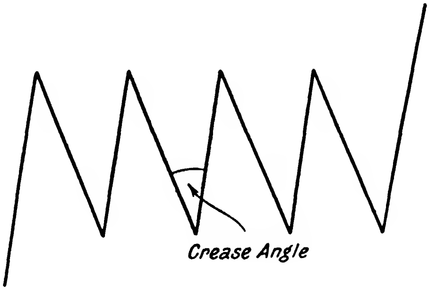

Fig. 52. Crease Trace. (A. J. Hall.)

Softness or Rigidity.—The same author (loc. cit.) has described an approximate method for comparing the rigidity of various yarns. A length of the yarn is laid flat on a smooth tiled surface in front of a vertical card. The middle of the yarn is then lifted vertically and allowed to collapse, and a curve is traced on the vertical card following the trace of the collapsed yarn. This is termed the "Self-supporting curve". By submitting stretched and unstretched yarns to this test, it was found that the softness of acetate rayon is decreased by stretching but to a less extent than is the case with viscose.

Regularity.—The total regularity or uniformity of rayon yarn depends upon uniformity of count, uniformity of tensile strength, and uniformity of elongation. A quantitative measure of these factors may be obtained by a method due to H. Sommer.[1] The

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[1] H. Sommer. *Textilber.*, 1926, 7, 757.

tensile strength (or count or elongation as the case may be) is determined for a number of samples, say ten, and the arithmetical mean of these results is calculated. The sub-mean (mean of all values below the arithmetical mean) is also calculated. Then the irregularity I is defined by

$$I = \frac{(\text{Principal mean} - \text{Sub-mean}) \times 100}{\text{Principal mean}}$$

and the average deviation of all the values from the arithmetical mean is taken as a measure of the irregularity of the yarn for that particular property.

$$\text{Deviation, } D = \frac{2 \times (\text{Number of values below A.M.}) \times \text{Irregularity}}{\text{Number of values determined}}$$

CHAPTER VIII

SPINNING AND SOLVENT RECOVERY

As previously mentioned the principle of spinning acetate rayon is similar to that of the process used by the silkworm in spinning its cocoon, i.e. the solution of cellulose acetate in a suitable solvent is forced through fine orifices or spinnerets. Unlike natural silk, however, cellulose acetate solutions do not coagulate spontaneously in contact with the atmosphere, and a choice must be made of two alternatives : extrusion into a liquid coagulating bath, or extrusion of a solution of the acetate in a volatile solvent into an evaporative atmosphere. The former is known as wet and the latter as dry spinning.

Wet Spinning.—The most obvious method of preparing artificial filaments from cellulose acetate is by the extrusion of the primary solution immediately after acetylation into a suitable coagulating bath. Some of the advantages are obvious, for example, the reduction in the number of stages in the manufacturing process, as compared with the acetone soluble product, leads to a corresponding reduction in labour costs, power consumption, and depreciation ; and the use of costly solvents, the expense of their recovery, and the capital outlay on recovery plant are also avoided. Other advantages, which are not so obvious, include the superior strength of threads derived from the triacetate, since it is less degraded than the product which has undergone a ripening process, and the greater facility with which the stretch principle can be applied. This again leads to increased strength of thread owing to the better orientation of the micellæ, and it also enables much finer counts to be spun.

A serious though probably not insurmountable difficulty is met with in the poor dyeing properties of primary acetate yarns. (This is claimed by Wagner[1] as an advantage in the production of effect threads.) The viscosity of the primary acetate solution

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[1] Wagner. D.R.P. 152,432.

is also poor, which increases the difficulties of the spinning process. Lastly, the fact that such solutions would require to be spun almost at once leads to serious practical difficulties, especially in regard to blending.

An important series of patents due to Zdanowich, and relating to the manufacture of directly spinnable solutions of acetone soluble cellulose acetate, has already been referred to in Chapter IV (p. 47). In addition to those already cited reference may also be made to B.P. 200,186, 203,599, and 227,134. The first related to the stabilizing of such solutions by the addition of formaldehyde; the second is a development of B.P. 139,232 and 190,732, using a weak condensing agent in its ordinary, as distinct from its nascent condition in the first stage of acetylation; and the third covered the stabilizing of the spinning solutions by the addition of water in admixture with methyl, ethyl, or amyl alcohols, lactic or formic acids, chloral hydrate, hydrogen peroxide, or with glycerol. It is claimed that solutions so treated can be kept in a spinnable condition for a considerable time, say for a few weeks, and the cellulose acetate does not suffer any appreciable change in solubility characteristics.

Most of the earlier patents relating to the wet spinning of acetone soluble cellulose acetates, when not entirely worthless, made extravagant claims which could scarcely be maintained. In common with more recent patents they can be divided into two classes, viz. those which cover the spinning of a solution in an organic solvent, soluble in water, into an aqueous spinning bath, and those covering the extrusion of a solution in an organic solvent into a coagulating bath consisting of a non-solvent organic liquid. Both methods present difficulties: in the former a skin is formed on the outside of the filament immediately on extrusion, and this prevents the satisfactory coagulation of the interior of the thread; and in the latter the threads vary considerably in their tensile properties. The Chemische Fabrik van Heyden[1] claimed to have overcome the former difficulty by adding to the spinning solutions some of the liquid used in the coagulating bath, in an amount insufficient to cause precipitation, with the result that the threads were coagulated more rapidly on entering the spinning bath, and presumably the presence of a non-solvent liquid within the fibre facilitated its complete coagulation.

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[1] Chem. Fabr. van Heyden. B.P. 3,972/1911.*

More recently the British Cellulose and Chemical Manufacturing Co., Ltd. (British Celanese)[1] claim to have produced filaments of improved strength and elasticity, and of the fineness of natural silk by coagulating in a bath containing a soluble thiocyanate (which is a swelling agent for cellulose acetate), using comparatively large spinning orifices in conjunction with a stretching process. They later covered a similar method in which aqueous coagulating baths were used, containing solvents or latent solvents for the acetate, which are themselves soluble in or miscible with water, e.g. acetone, diacetone alcohol, alcohol, formic or acetic acids, zinc chloride, etc., but excluding thiocyanates.[2] They state that by this means filaments as fine as 1–2 deniers may be drawn out from spinning jets of relatively large size.

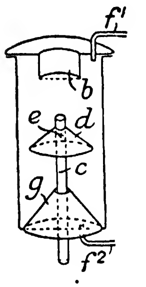

Fig. 53. Wet-Spinning Device. (B.P. 235,852.)

On the other hand, the Farbenfabriken vorm. F. Bayer & Co. makes an addition to the spinning solution of a compound which is extracted more slowly by the salt solution composing the coagulating bath than is the main solvent. For example, a small proportion of benzene-alcohol, benzene, chlorobenzene, ethyl acetate, pyridine, or aniline is added to an acetone solution of cellulose acetate which is to be spun into a calcium chloride bath, while with an acetic acid solution of the acetate and a sodium acetate spinning bath, chloroalcohol or acetylene tetrachloride is a suitable addition. It is also stated that spinning may be so conducted that only a part of the solvent is extracted in the bath, the remainder being evaporated as the filament passes through the air, and that in this manner filaments of the order of 3 deniers may be produced.[3] The same firm later described the manufacture of acetate rayon of low denier by conducting the threads through two superimposed layers of precipitating liquid, the first layer being at a higher temperature than the second ; stretching of the thread takes place in the first layer, while in the second it gradually hardens.[4] In 1925 they obtained a patent for the addition of solvents or swelling agents, such as acetone, acetone alcohol, etc., to aqueous salt coagulating baths, to prevent or minimize breakage

[1] British Cell. and Chem. Mfg. Co., Ltd., Palmer and Dickie. B.P. 177,868.

[2] Br. Cell. and Chem. Mfg. Co., Ltd., Palmer and Dickie. B.P. 179,234.

[3] Farbenfabr. vorm. F. Bayer & Co. B.P. 219,333.

[4] Ibid. B.P. 194,666.*

of the threads during spinning[1] (cf. n. 3, p. 164). They have also described an ingenious arrangement for use in the stretch spinning process as described under 7, above.[2] This is shown in Fig. 53, and consists of an umbrella-shaped shield " d " fitted to the tube " c " or to the funnel through which the filaments pass. This shield obviates the formation of eddies in the precipitating liquid as it rises from the inlet " f^2 " and flows over the edge of the tube. It also serves to collect air bubbles rising through the liquid, and the collected air passes through the aperture " e ", and is carried away by the precipitating liquid.

H. Barthélémy in a patent assigned to the Ruth-Aldo Co. Inc. describes the coagulation of solutions of cellulose acetate in an organic solvent by means of an aqueous solution or emulsion of alcohols, polyalcohols, hydrocarbons, or fatty acids of high molecular weight or their esters, or animal and vegetable oils, the emulsifying agents being alkali oleates, ricinoleates, or stearates, Twitchell's reagent or gum tragacanth.[3]

G. Müller has recently covered the production of fine filaments of high tensile strength by stretch spinning a 12 per cent solution of cellulose acetate, which may be the acetylation reaction mixture, into a concentrated solution of a strong acid, e.g. 40–60 per cent sulphuric acid containing 1 per cent of formaldehyde and if desired salts, solvents, etc., may also be added.[4]

A further series of wet spinning patents is also due to the British Celanese, Ltd. The first [5] covers the extrusion of a 20–25 per cent solution of cellulose acetate in acetone into a liquid containing a high proportion (25–65 per cent) of a solvent for cellulose acetate, such as diacetone alcohol, ethyl tartrate, or lactate together with a volatile solvent such as acetone. Examples given are as follows : Diacetone alcohol : ethyl alcohol :: 1 : 1 ; diacetone alcohol : acetone : water :: 30 ; 15 : 55 ; diacetone alcohol : water :: 60 : 40 ; and water : ethyl lactate :: 45 : 65. The specification states that the filaments may be stretched while still plastic, and that an oil may be mixed with the acetate to improve the lustre. An addition to this patent [6] describes the coagulation or treatment after coagulation with a large proportion of a non-solvent plasticizer such as a triaryl

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[1] Farbenfabr. vorm. F. Bayer & Co. B.P. 233,342. [2] Ibid. B.P. 235,852.*

[3] Ruth-Aldo Co. Inc. (Assignees of H. Barthélémy). B.P. 282,790.†

[4] G. Müller. B.P. 358,501.*

[5] British Celanese, Ltd., Dickie and Sowter. B.P. 340,324.

[6] Ibid. B.P. 340,325 ; Addn. to B.P. 340,324.

phosphate. A further addition[1] recommends the addition to the spinning solution of a solvent such as diacetone alcohol (which is less volatile than the non-solvent ingredient of the coagulating bath) together with a more volatile solvent such as acetone, in order to render the filaments plastic and capable of coalescence so that they can be stretched. Alternatively,[2] instead of adding the above to the spinning solution they may be used as a secondary bath after coagulation.

Among patents of the second class, in which the coagulating bath is an organic liquid which is a non-solvent for cellulose acetate, are a number also due to British Celanese, Ltd. The first[3] covers the use of a spinning solution at a temperature greater than that of the coagulating bath, which enables more concentrated solutions to be spun and smaller jets to be employed. Fine filaments of 1–10 denier or heavy filaments up to 2,000 denier or even higher may be obtained; in the second case slow drawing off speeds are employed, e.g. for 1,000 denier a speed of 1–2 metres per minute is used. In an example a solution of cellulose acetate in 95 per cent acetone is maintained at a temperature of 45° C. and is extruded through jets having orifices of 0·08 mm. diameter, into a bath of kerosene maintained at 25° C. The drawing-off speed is 50 metres per minute, and the immersion in the bath 12 to 16 inches. The second patent[4] describes the production of hollow filaments by extruding a solution of cellulose acetate in a solvent mixture into a coagulating bath in which one constituent at least of the solvent mixture is insoluble or only partly soluble, and the temperature of the spinning bath is kept above the boiling-point of the solvent constituent in question. For example, 25 per cent of cellulose acetate in a mixture of ethylene dichloride and methyl alcohol in the proportions 60 : 40, is extruded through jets having orifices of 0·08 mm. diameter into a kerosene bath at 65° C., the drawing-off speed being 50 metres per minute and the immersion length 12–16 inches. Finally,[5] a solution obtained by heating cellulose acetate with a polyhydric alcohol such as ethylene glycol is coagulated by passing through a liquid such as a polyhydric alcohol (or water is also mentioned) which is maintained at a

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[1] British Celanese Ltd., Dickie & Sowter. B.P. 340,436; Addn. to B.P. 340,324.

[2] Ibid. B.P. 340,437; Addn. to B.P. 340,324.

[3] British Celanese, Ltd. B.P. 341,148.

[4] Ibid. B.P. 341,388.*

[5] Ibid. Dickie and Sowter. B.P. 355,298.

temperature greater than that of the surrounding atmosphere. The spinning bath also contains a solvent or plasticizer, and optionally salts or sugars.

Other inventions relating to wet spinning processes are as follows : W. Harrison [1] treats the filaments after coagulation with a solvent such as aqueous acetone, which causes the core to swell to a greater extent than the outside, thus producing a diametrical expansion of the threads, with consequent arrangement of the crystallites of the outer layers at right angles to the axis of the threads.

Filaments of superior lustre are obtained by the wet spinning process by the addition of a solvent or latent solvent for the cellulose acetate at high temperatures (which is not readily soluble in the spinning bath) to the spinning solution, and the filaments are afterwards heated to 90–125° C. When using an aqueous spinning bath, suitable additions to the spinning solution are dichlorethane, phenyl methyl ketone, butyl tartrate, etc. ; while, with a kerosene bath, diethylene glycol is used.[2]

An interesting patent was granted to Field and Haslett in 1928,[3] which covers the production of a mixed filament of cellulose acetate and regenerated cellulose, by spinning a mixture of cellulose xanthate and acetate dissolved in epichlorhydrin, mono- or dichlorhydrin, an acetin or similar ester of glycerol or in glycerol itself into an acid spinning bath, for example an aqueous solution of hydrochloric acid containing ammonium chloride.

In spite of the large number of valid patents concerned with the wet-spinning of cellulose acetate solutions, it is well known that very little acetate rayon is produced commercially by these methods. Nevertheless it is quite evident that the properties of wet spun rayon are sufficiently attractive to warrant research work, and further developments will be awaited with considerable interest.

Dry Spinning.—In principle the dry spinning process of producing acetate rayon is extremely simple, and closely resembles the method used by the silkworm ; it consists in the extrusion under pressure of the cellulose acetate dissolved in a suitable solvent such as acetone into an evaporative atmosphere. Evaporation of the solvent leaves a lustrous solid filament which is wound on a suitable bobbin. By the use of spinning jets pierced with a number of holes,

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[1] W. Harrison. B.P. 351,527.

[2] British Celanese, Ltd. B.P. 356,343.

[3] Field and Haslett. B.P. 319,294.

several filaments are formed simultaneously, and these can be twisted together before winding to form threads of any desired thickness, depending on the number and diameter of the holes in the jet. In this respect at least Man has improved upon Nature, for the silkworm produces but two threads which are not twisted together, and which require to be treated by a number of processes, scouring, throwing, etc., before they reach a stage corresponding to that represented by acetate rayon as it leaves the spinning frames. In spite of this apparent simplicity, there are, in practice, numerous difficulties to contend with ; for example, the raw cellulose acetate must be of high clarity or filtration difficulties will be experienced ; it must have a suitable viscosity when dissolved in the required solvent, taking into consideration the temperature at which it is extruded ; the threads during coagulation must be suitably protected from air currents, etc., by being enclosed in a casing (Metier casing) or tube through which the warm evaporative medium is circulated, and such an arrangement is also necessary to enable the evaporated solvent to be recovered.

The clarity of the spinning solution depends on the cleanliness of the initial cotton linters used, and more particularly on the efficiency of the acetylation process, since partly acetylated fibres are extremely difficult to remove by filtration owing to the clogging of the filter cloths.

The choice of a solvent for the dry spinning process is limited by the following considerations : It should be as cheap as possible, of a non-poisonous nature, easily recoverable, of good stability and free from corrosive action upon the metallic parts of the apparatus. Above all, it should have a high dispersive power for cellulose acetate in order that the solutions may be as concentrated as possible, with resulting rapidity in the coagulation of the filaments and economy in the use of solvent. The boiling-point should be reasonably low, and the vapour pressure as high as consistent with safety in handling, so that the rayon can be spun at as low a temperature as possible. Solvents such as acetic and formic acids, acetylene tetrachloride, etc., are therefore ruled out (hence the lack of dry spinning processes prior to the discovery of acetone soluble cellulose acetate), and recourse must be had to low boiling ketones such as acetone and its related compounds, either alone or in admixture with other liquids such as alcohol or benzene. In spite of a considerable amount of research having been devoted to the development of cheaper solvents and solvent mixtures, acetone probably remains by far the most important medium in use to-day.

As previously mentioned (p. 10) the earliest successful production of acetate rayon by a dry spinning process was achieved by Eichengrün in 1904, but this method and the one which he described two years later never reached the commercial stage, owing to the high price of the solvents and the absence of a satisfactory method for their recovery.

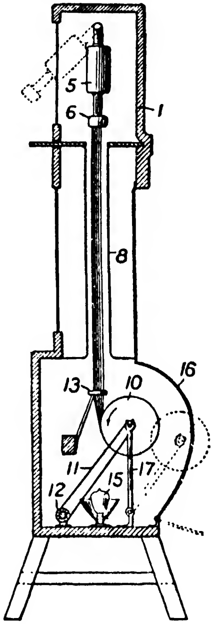

Fig. 54. Bouffe's Spinning Apparatus. (B.P. 160,859.)

The process described by Bouffe[1] in 1919 is very interesting since it is more or less the prototype of those in use to-day. The diagram (Fig. 54) represents the apparatus used ; this is very simple and comprises a casing 1, in the top of which is the spinning nozzle 6 and filter 5. The threads pass downwards from the nozzle through the tube 8 and guide 13 to the reel 10 upon which they are wound. The whole of the working parts are enclosed in the casing, access being had by the door 16, and the casing may contain gases such as sulphur dioxide, carbon dioxide, or air, which may be heated, or the chamber may be exhausted. The method closely resembled that described by von Loewe[2] for the spinning of nitro-cellulose esters, and the patent is no longer in force.

From 1919 onwards the dry spinning process was steadily developed, especially by the outstanding work of the brothers Dreyfus and their co-workers at the factory of the British Cellulose and Chemical Manufacturing Co., Ltd. (later British Celanese, Ltd.) at Spondon, near Derby. According to the claims made in a patent granted to this firm in 1921[3] it had previously been supposed that for the efficient recovery of the solvent and for the maintenance of safe-working conditions in the factory, it was necessary to enclose the winding arrangements

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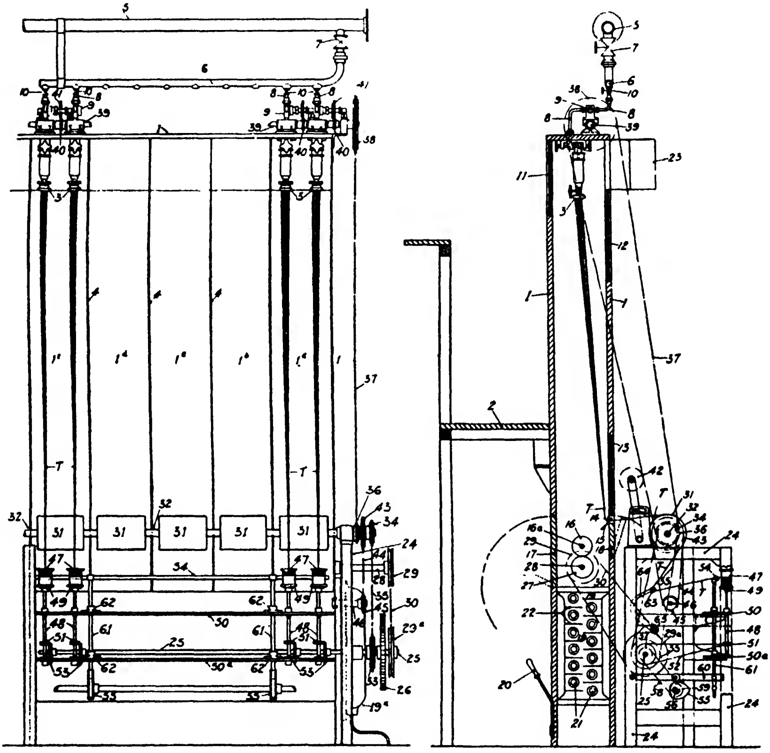
[1] G. F. J. Bouffe. B.P. 160,859.*

[2] von Loewe. D.R.P. 238,160/1909.

[3] British Cell. and Chem. Mfg. Co., Ltd., and H. B. Roy. B.P. 165,519.

within the spinning cell. Such an arrangement was, of course, of an impracticable nature since it necessitated frequent opening of the casing to attend to the filaments, with consequent admission of cold air, causing disturbances in the spinning process and consequent irregularities and breakages in the threads produced.



(a) (b)

Fig. 55. Dry Spinning Apparatus. (B.P. 165,519.)

A suitable form of apparatus is described in the specification, from which the following is abridged.

Fig. 55 (*a*) is a front elevation representing a portion of the metier with the winding apparatus situated outside, the front of the metier casing being removed.

Fig. 55 (*b*) is a section at right angles to Fig. 55 (*a*) through the metier and winding apparatus.

1 represents the metier casing, 2 being a raised platform at the back of the apparatus for the operators attending to the spinning nozzles 3 and the solution feed valves and pumps. The spinning nozzles are mounted in a row in the upper portion of the metier, which is divided into compartments or cells, 1*a*, 1*b*, 1*c*, etc., by vertical partitions 4, each cell containing two or any desired number of nozzles.

The spinning solution supplied by the main or header 5 to the auxiliary header 6 passes through a pipe 8 and pump 9 to each spinning nozzle, a suitable filter being disposed before the nozzle. The individual nozzles may be cut out or controlled by means of the valves 10.

11, 12, and 13 are windows provided in the casing for purposes of inspection, and to give access to the nozzles and filaments.

The newly formed threads pass downwards from the spinning nozzles, meeting in their passage a current of air heated in the chamber 19, the volume of air being controlled by means of dampers. The air laden with solvent vapours is led off through suitable outlets 23 at the top of the metier. The threads after the solvent has been evaporated pass out of the metier casing through an opening 14, having suitable guides or eyes 15, thence over the feed or godet rollers 31, down round the guide rod 64, and over the traversing bar 54 to the bobbins 47, which are changed when filled.

16 (Fig. 55*b*) represents a friction driven waste drum or drums, extending horizontally through all the compartments, and serving to catch and wind up filaments on breakage or during the changing of the bobbins.

The waste drum and feed rollers may be driven at the same speed as that of the extrusion of the filaments, or at a higher speed if it is desired to extend the filaments or threads.

The specification also states that other mechanisms may be disposed outside the casing of the spinning machines between the same and the winding apparatus, e.g. guiding, feeding, drawing, or twisting devices for the filaments.

The specification does not mention any specific solution of cellulose acetate to be used in the spinning process, but indicates in a general manner the use of solutions of cellulose acetate, nitrocellulose, or other cellulose derivatives containing volatile solvents such as acetone, alcohol-benzol, ether-alcohol, and the like. The necessary time of exposure of the filaments to the evaporative atmosphere to effect complete evaporation of the solvent depends, of course, upon the boiling points and quantities of the volatile liquids used in the solutions, the denier of the filaments, and the temperature and speed of the air current, but this time is usually very short. The specification states that in most cases the volatile liquids are sufficiently evaporated and the filaments sufficiently solidified by a travel of one to two seconds exposed to a warm air current of about 30–50° C. in the casing.

Two years later a further improvement was described by the same firm.[1] It was found that the winding and twisting of the thread could be effected simply and economically as a single operation by applying a process known as cap spinning to the thread leaving the metier casing. The travelling thread is led to a point vertically above the cap spinning device, and passes under the lower edge of the cap on to the bobbin on which it is wound. The bobbin is rotated at a higher speed than that at which the thread is fed to it, and hence the thread in passing from a point above the spindle down round the bottom of the cap on to the bobbin, will receive a twist, the amount of which depends upon the difference between the speed of feed of the thread and the speed of the bobbin or winding device. In an example the speed of the bobbins is given at 7,000 to 10,000 revolutions per minute or more.

It is said to be a great advantage to lubricate the threads on their way to the cap spinning devices, an operation which is effected by applying oil or other lubricants in a similar manner to those sometimes practised in spinning or other textile operations, e.g. by causing the threads to pass over lubricated surfaces before they reach the cap spinning devices. Damping of the threads is also said to be advantageous, and this is effected by exposure of the travelling threads to humidified air, or by passing them over a wetted roller or other damp surface.

The invention is not limited to downward dry spinning but may be extended to apparatus in which the threads are spun upwards or otherwise.

An apparatus for applying the invention to downward dry spinning is described in the specification and closely resembles the apparatus of B.P. 165,519 above. It is illustrated in Fig. 56 (*a*),

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[1] British Cell. and Chem. Mfg. Co., Ltd., Palmer and Whitehead. B.P. 198,023.

(*b*), (*c*), (*d*), and (*e*), and the following is an abridgment of the description.

Fig. 56 (*a*) is a diagrammatic front elevation of a portion of the spinning cabinet or metier with the cap spinning device appertaining thereto.

Fig. 56 (*b*) is a diagrammatic side elevation of the metier and cap spinning apparatus with the side of the metier removed.

Fig. 56 (*c*) is a detail sectional elevation taken on line X–X (56*a*), showing one of the cap spindles with its bobbin and bobbin carrier.

Figs. 56 (*d*) and (*e*) are a side elevation and plan of one of the upper thread guides.

In this case each compartment contains only a small number of jets, two being shown, but only one might be employed in each cell. As before, the threads pass down through a current of heated air, and after leaving the cell are carried over feed or godet rollers 7, which are driven at a surface speed greater than the speed of extrusion of the filaments, so as to draw out or extend the threads. The threads then pass back under the feed rollers at an angle, up through the back guide hooks 15, thence up again over the godet rollers, and forwards down through the eyes 44*a* of the thread guides 44, and under the bottom of the caps 20 on to the bobbins, which are rotated at a high speed, for example 10,000 revolutions per minute or more. The bobbins are traversed up and down in order to wind the thread evenly, the spindles and caps remaining stationary; alternatively the spindles and caps may be traversed while the bobbins remain stationary.

Since the peripheral speed of the bobbin is greater than the speed at which the thread is fed to it by the godet roller, it is correspondingly twisted during the winding process, the amount of twist depending on the difference between the speed of feed of the thread and the peripheral speed of the bobbins.

" When a given bobbin has been fully wound it can be stopped by the attendant's hand and removed by swinging up the thread guide, taking off the cap and sliding off the spindle and a fresh bobbin can then be put on to the spindle.

" The amount of twist imparted to the thread can be varied by varying the speed of the godet roller or of the bobbins, or the speed of both, or otherwise as desired.

" The tension of the thread may be varied by adjusting the

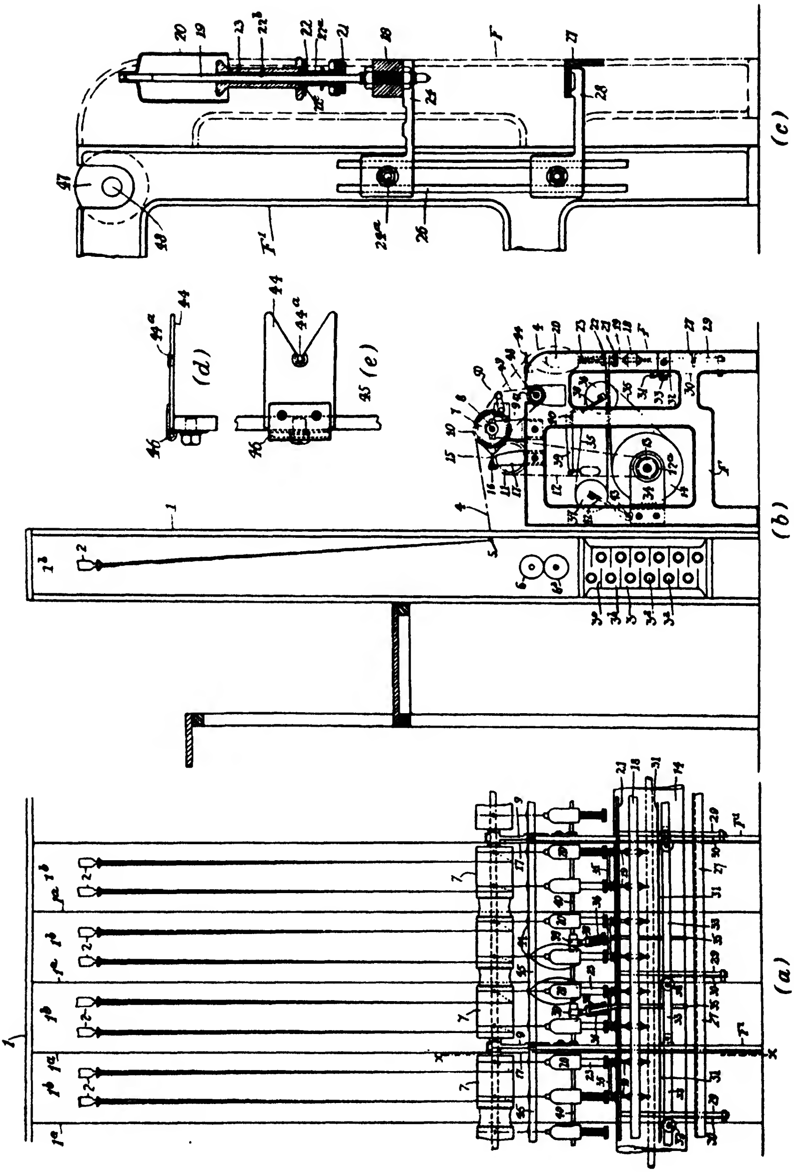

FIG. 56. Dry Spinning Apparatus. (B.P. 198,023.)

height of the thread guides 44, or by employing caps of other diameter, or damping the threads, or in any other way.

" It is desirable, as before mentioned, to lubricate the filaments with oil or other lubricating liquid, on their way to the cap spinning devices. This can be done in any appropriate way, for example by leading them over a pad, roller, or other surface supplied or impregnated with the lubricating liquid and disposed between the metier and the drawing rollers 7. Likewise if it is desired to damp the filaments on their way to the cap spinning devices this can be done in any convenient way, for example by humidifying the air in the room, or by discharging humidified air on to the threads of associated filaments, or causing them to pass over a damp roller or other surface, in their travel between the metier and the drawing roller or the cap spinning devices.

" Further it will be understood that instead of bobbins one may employ tubes or any other desired winding devices for the threads, and that any known or suitable traversing mechanism may be employed according to the type of wind desired, for example a parallel wind, spool wind, bottom bobbin wind, or other desired form of wind.

" Also instead of traversing the bobbins or the like while the cap and spindle remain stationary, the spindle and cap may be traversed up and down through the bobbin or the like while this only revolves without traversing up and down."

Other methods of imparting twist to the threads during spinning include the use of revolving spinning heads,[1] and the adaptation of the centrifugal spinning box method invented by Topham in 1900.[2] The specification mentions that the thread is preferably moistened with a sizing solution before entering the box, and is later withdrawn, either through the reciprocating funnel through which it entered, with the box rotating (to impart further twist) or as a cake, in which case removal is facilitated by heating the box and contents for about 10 minutes at 70° C. More recently the British Celanese, Limited, has made application for patents covering combined lubricating, moistening, or sizing with winding and twisting in a centrifugal box 3–4 inches in diameter, revolving at a speed of 12,000 to 20,000 revolutions per minute.[3]

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[1] Ruth-Aldo Co. Inc. (Assignees of Thénoz). B.P. 283,140.

[2] Courtaulds, Glover and Topham. B.P. 268,455. Cf. B.P. 23,158/1900.*

[3] British Celanese, Ltd., Dreyfus and Taylor. B.P. 340,471, 340,504–5.

An apparatus described by the Société pour la Fabrication de la Soie Rhodiaseta in 1923,[1] is shown in Fig. 57. The spinning nozzles 7^a are placed as usual in the upper part of the cell 1, which is provided with a funnel-shaped portion 11 at the lower end, at the apex of which is the orifice 12 through which the thread is led out of the cell to the winding apparatus. The internal surface of the funnel-shaped portion of the cell is polished to assist the passage of the filaments to the outlet, and the latter is made of bronze and is in two parts, one of which is carried by a door 14 giving access to the filaments. 2, 2*a* are jackets through which hot water is circulated in series or independently so as to obtain equal or different temperatures in different parts of the cell. An inspection window 20 is provided in the upper part of the cell and below the outlet is a waste roller 18. The threads are normally carried to a delivery apparatus 17.

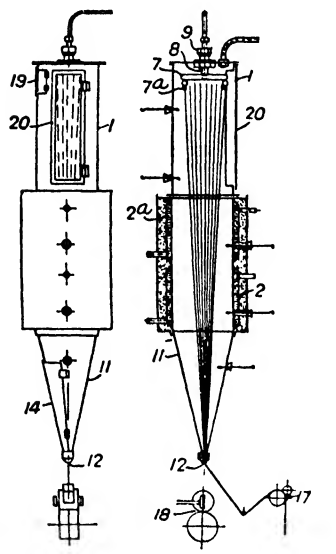

FIG. 57. Dry Spinning Apparatus. (B.P. 218,913.)

The Naamlooze Vennootschap Nederlandsche Kunstzijdefabriek have described a spinning cell[2] which consists of a cylindrical chamber about 2 metres long and 25 cm. in diameter, which is open at the bottom. It is fitted with a jacket for the circulation of a heating medium, the flow of which is so regulated that, when spinning a solution of cellulose acetate in acetone, the temperature falls from 50° C. at the top to 20° C. at the bottom. Air or an inert gas flows slowly upwards (8 cm. per sec.) and is withdrawn through an adjustable outlet near the spinning nozzle. They claim that turbulence is practically eliminated and that sufficient solvent vapour is present in the cell to ensure a uniform cross-section.

In all the methods so far described, the air or other evaporative medium flows in the direction opposed to the travel of the filaments.

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[1] Soc. pour la Fabr. de la Soie Rhodiaseta. B.P. 218,913.

[2] N. V. Nederlandsche Kunstzijdefabriek. B.P. 282,326.

In 1927 A. E. Gull[1] described an interesting apparatus consisting of a tube of gradually decreasing cross-section while a current of heated air or gas passes in the same direction as the travel of the filaments, i.e. from top to bottom of the tube. Consequently the air has a greater velocity at the exit than at the entrance, a factor which should result in the production of filaments of more uniform cross-section.

Solvents for Spinning Solutions.—In addition to the simpler types of solvents and solvent mixtures for acetone soluble cellulose acetate, such as acetone, acetone-water, acetone-alcohol, etc., numerous patents have been granted for other solvents or solvent mixtures used either on account of cheapness, or because they impart to the solutions some special qualities which produce certain desired effects in the rayon produced when they are spun.

It is obvious that the most useful solutions of cellulose acetate for the manufacture of rayon by the dry spinning process are those which possess a viscosity sufficiently low to render filtration easy, and at the same time sufficiently high to prevent the rupture of the threads as they leave the spinning dies, i.e. before they are coagulated by exposure to the evaporative atmosphere. The question of the viscosity of cellulose acetate solutions has been discussed already (p. 25). It will be recalled that the addition of water to an acetone solution of cellulose acetate produces an initial fall in the viscosity, the minimum being reached with a concentration of 4–5 per cent of water in the solvent mixture. It is probable that this is the solvent mixture most generally used for the production of acetate rayon by the dry spinning process. As regards concentration of cellulose acetate, the viscosity of the solutions increases rapidly with the concentration (depending, of course, upon the nature of the cellulose acetate and of the solvent mixture). The concentration of the spinning solution should be as high as possible, consistent with easy filtration and passage through pipes, pumps, and spinning dies. Using a solvent consisting of 96 per cent of acetone and 4 per cent of water, a satisfactory concentration for the cellulose acetate is 20 per cent.

The addition of plastifying agents, usually liquids of high boiling-point, has also been claimed, but except in the production of very fine denier filaments by stretch spinning methods, their use has little to recommend it, and it is conceivable that excessive quantities

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[1] A. E. Gull. B.P. 301,141.

of such liquids remaining in the threads may lead to undesirable results such as uneven tension in later winding and weaving operations.

The use of very low boiling solvents such as formaldehyde and acetaldehyde has been described by Dreyfus.[1] By the use of such solvents spinning can be effected at lower temperatures, and a more regular evaporation of the solvent obtained, with consequently increased regularity in the filaments produced.

Eichengrün [2] claims the use of a compound solvent containing methylene chloride mixed with alcohol or one of its homologues, or with any cellulose acetate solvent. Such solutions can be prepared in the cold, and if the alcohol in the solution does not exceed 30 per cent (or in the case of acetone, 20 per cent) the solution is not inflammable. The use of such solutions is said to permit high spinning speeds with a very short spinning distance, either by the dry or wet process. By varying the conditions, e.g. speed of evaporation and addition of such liquids as dichlorethylene, filaments ranging from the finest to those resembling horse-hair or even hollow tubular filaments may be obtained.

Typical plastifying agents for cellulose acetate include such compounds as liquid mixtures of isomeric xylene monoethyl sulphonamides,[3] o-toluenemonomethyl- or o-toluenemonoethylsulphonamides [4]; benzene monomethylsulphonamide, benzene methylethylsulphonamide; mixtures of o- and p-toluene dimethyl- or diethyl- or methylethylsulphonamides, o-toluenedimethyl- or diethylsulphonamides, or mixtures of isomeric xylene dimethyl or diethyl- or methylethylsulphonamides, or mixtures of these dialkylsulphonamides and the monoalkylsulphonamides referred to above may be used.[5] The use of such agents as triphenyl- or tricresylphosphates, derivatives of urea, di- and triacetin, etc., is no longer protected by patents.

Other non-solvent additions to the spinning solutions include 1–5 per cent of vegetable or animal oil, or a mixture of both having a melting-point of about 30° C. [6]; and acetone solutions containing glycerol or other polyhydric water soluble alcohol to the extent of 1 to 30 per cent of the total solvent are spun under such conditions that a substantial proportion of the alcohol is retained in the threads.

[1] H. Dreyfus. B.P. 182,166.

[2] A. Eichengrün. B.P. 243,350.

[3] H. Dreyfus. B.P. 132,283.

[4] Ibid. B.P. 133,353.

[5] Ibid. B.P. 154,334.

[6] N. V. Nederlandsche Kunstzijdefabriek. B.P. 301,017.

Yarns so made are self-lubricated, and owing to their superior wetting powers are more readily scoured and dyed.[1]

Various concentrations of cellulose acetate have been patented. Thus Dreyfus [2] recommends the use of high concentrations of not less than 20 per cent strength (e.g. 25–30 per cent). By employing these high concentrations the filaments are stronger and of rounder section, show less tendency to crinkle or turn woolly, and do not show " glitter ". Later the same inventor claimed that solutions of less than 20 per cent strength, preferably of 10 or 5 per cent or less, give threads and filaments of round section, with less " glitter " effect than those produced from solutions of about 20 per cent strength. The threads have good covering power and possess increased strength both wet and dry, and do not become woolly when heated with water.[3] More recently British Celanese, Limited,[4] has covered the dry spinning of 25 per cent solutions of cellulose acetate having an acetyl value of 52·5 to 56 per cent—preferably 54·5 per cent—in a mixture of 2–5 per cent or more of methyl alcohol, and at least 70 per cent of acetone. Such a solution has a low viscosity and improved capability of being drawn out. It is spun at 50–60° C. The same firm also claim the manufacture of heavy filaments by the extrusion of a solution of an organic derivative of cellulose, containing 30–40 per cent of such derivative and also 1–12 per cent relative to the cellulose of a resin, particularly a synthetic resin, together with a plasticizer.[5] Both wet and dry spinning are mentioned.

Spinning Jets or Nozzles.—These are small cylindrical metal cups, usually of platinum or one of its alloys, although nickel and silver have been used. The bottom of the jet is usually perfectly flat and is pierced with a number of very fine holes usually slightly larger in diameter than corresponds with the denier of the rayon to be produced, except in the case of stretch spinning processes, when the orifices are much larger. The diameter of the orifices will vary normally from 0·05 to 0·15 mm. A number of patents have been granted for special types of jets, for example: Jets having the orifices at the tip of a hemispherical cap or nipple [6]; conical jets for use in wet or dry spinning and said to give more

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[1] British Celanese, Ltd. B.P. 313,885.

[2] H. Dreyfus. B.P. 210,108.

[3] H. Dreyfus. B.P. 217,287.

[4] British Celanese, Ltd. B.P. 310,046.

[5] Ibid. B.P. 342,340.

[6] Ruth-Aldo Co., Inc. (Assignees of Orioli). B.P. 303,782.

uniform filaments[1]; jets having a number of groups of orifices, the filaments from each group being collected together as separate threads,[2] so increasing the output of the spinning machine; and special jets having an annular depression on the side to which the spinning solution is applied, and on the other side a central circular depression into which engages a reinforcing member to support the centre of the jet and so prevent its distortion.[3]

In addition to the preliminary filtration which the spinning solution undergoes after leaving the mixing vessels, each spinning jet is provided with a special filter. This is usually a filter candle of the type described by Topham[4] or Dreaper.[5] In the former the solution passes from within the candle to without, and conversely in the latter.

Regulation of the Rate of Flow.—One of the principal difficulties encountered in the spinning process is to ensure a perfectly steady flow of solution through the spinning jets, and many devices have been suggested to achieve this end. It is absolutely necessary to provide individual spinning pumps for each jet, either of the gear-wheel or piston type; the former is to be preferred since it gives a perfectly uniform flow of solution, and exercises a thorough mixing action, thus ensuring uniformity. These gear wheel pumps were first suggested in connection with the spinning of rayon by F. Küttner in 1912.[6] They are also simpler and cheaper than the piston type, of which the sole advantage is longer wear.

When first starting spinning with new plant it is necessary to flush out the whole system with spinning solution repeatedly until it issues from the spinning heads in a perfectly clear condition, free from even the slightest traces of mechanical debris. The jets are not, of course, fitted until this cleansing process has been carried out. The starting of a fresh jet is attended with some difficulty and requires considerable experience on the part of the person in charge of the machine. There is a tendency, especially in spinning the finer deniers, for the solution to spread over the face of the jet. Courtauld's overcome this difficulty by applying a sudden extra pressure by means of an auxiliary pump of the plunger type, or alternatively by means of a flexible diaphragm[7]; on the other

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[1] British Celanese, Ltd. B.P. 318,631.

[2] Ibid. and Taylor. B.P. 344,351.

[3] British Celanese, Ltd. B.P. 355,720.

[4] Topham. B.P. 23,157/1900.*

[5] Dreaper. D.R.P. 414,675.

[6] F. Küttner. B.P. 28,320/1912.*

[7] Courtaulds and Topham. B.P. 278,881.

hand British Celanese apply a vacuum to the outer face of the jet until an uninterrupted flow through all the orifices is obtained.[1]

Control of Temperature in the Spinning Cells and Regulation of Flow of Evaporative Atmosphere.—The maintenance of uniform conditions as regards temperature and rate of evaporation, throughout the cells of a given spinning machine is of considerable importance in ensuring a uniform product. Variations in these conditions give rise to variations in the lustre, cross-section, and physical properties of the filaments produced.

The problems arising in this connection have received considerable attention from the Société pour la Fabrication de la Soie Rhodiaseta, and a number of patents have been granted to this firm for various devices and methods designed to achieve and maintain the correct conditions. The first patent granted to this firm has already been mentioned (footnote [1], p. 176), and is concerned with a special type of spinning cell. An interesting specification which appeared the following year describes a method of maintaining uniform conditions in a group of such cells.[2] This is achieved by providing the cells with a double set of temperature controlling elements, identical for the groups of the cells, and through each of which flows a current of temperature controlling fluid in series as regards each of the sets but in reversed sequence in opposite directions relatively in the one set to the other set. These elements may be fitted inside the cells, or they may be arranged to heat the evaporative medium before it enters the cells. The mode of working is to pass hot water, for example, through one set, the temperature gradually falling from one element to the next; through the other set passes in the opposite direction a separate stream of hot water, or the same stream as in the first set, with or without reheating. Here again there is a fall of temperature from element to element, but since this is in the reverse sense from that in the first set, the element of highest temperature of one set is associated with the element of lowest temperature of the other set, and intermediately. In addition to uniformity of temperature, provision is also made for securing uniform evaporation by controlling the flow of gaseous medium in the following manner: The collecting or supply piping is of such dimensions that the loss of head throughout the system is negligible; in the connections to the individual cells of a group

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[1] British Celanese, Ltd., and Taylor. B.P. 320,106.

[2] Soc. pour la Fabr. de la Soie Rhodiaseta and N. Grillet. B.P. 233,384.

devices are fitted which produce a fixed, predetermined, and substantial loss of head, and which are interchangeable but not individually adjustable, such devices being tubes of definite length and small diameter, or plates with perforations of definite diameter. The rate of flow through the cells of a group is adjusted by regulating the head producing the flow in the collecting or supply piping. The flow is produced either by aspiration or by forcing the air through the system.

In spite of the precautions just described, difficulties were apparently experienced due to the frequent rupture of the newly formed filaments inside the cell. A patent due to the Société Chimique des Usines du Rhône describes a method of preventing this occurrence, the chief point of which rests in maintaining the vicinity of the spinning dies at a considerably lower temperature than the rest of the cell.[1] It is pointed out in the specification that this unsteadiness in the spinning causes extra expense, not only on account of the labour required to gather the broken filaments and rejoin them, but also by the irregularities produced in the spinning and solvent recovery processes. The difficulty increases with the fineness of the filaments, and the manufacture of very fine filaments is either prevented entirely, or a considerably reduced spinning speed has to be employed, with consequent reduction in output. The trouble is due to the lowered viscosity of the spinning solution at the high temperature normally obtaining in the neighbourhood of the dies, as a result of which the newly formed fibre, still containing most of its solvent, is very weak and readily ruptured. The method adopted in this patent consists in protecting the region of the dies from the influence of the hot evaporative atmosphere as much as possible by withdrawing the gaseous medium at a point intermediate between the dies and the exit of the threads or filaments. To ensure a proper rate of evaporation, a determined proportion of gaseous medium is admitted in the region of the dies, at the ordinary or lower temperature. The spinning solution may also be cooled before reaching the spinning dies, and a suitable cooling device may be arranged inside or outside the cells in the vicinity of the dies. In examples the spinning of a 16 per cent solution of cellulose acetate in a mixture of acetone and alcohol in the proportions 90 : 10 is described with the production of elementary filaments of 2 to 4 "deniers" by spinning

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[1] Ellis (for Soc. Chim. des Usines du Rhône). B.P. 236,393.

through dies having orifices of 0·1 to 0·12 mm. diameter, the gaseous medium being withdrawn at a point 20–50 cm. below the dies, and external air being introduced near the dies in an amount corresponding to $\frac{1}{4}$ to $\frac{1}{2}$ of the rate of flow of the gaseous medium entering at the bottom of the cell; or by spinning the same solution in a similar manner except that the fresh air introduced near the dies is only one-tenth of that entering at the bottom of the cell, and cooling pipes are provided near the dies, the rate of flow in which is regulated to produce a temperature of 20° C. or thereabouts in the vicinity of the dies. The drawing (Fig. 58) accompanies the specification and represents a perpendicular section of the cell through the axis, in a plane perpendicular to the general direction of the group of cells. It is described as follows :—

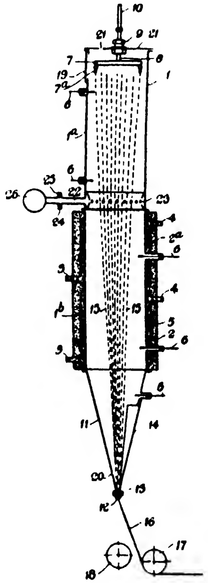

FIG. 58. Dry Spinning Apparatus. (B.P. 236,393.)

" 1 represents the wall of the cell supposed cylindrical and of metal, and formed of sections 1^a and 1^b suitably jointed together with the interposition of a thermally insulating joint, the whole being supported by a suitable framing not shown.

" 2, 2^a represent the two double walls of a hot water jacket, these walls having areas 3, 3, being the hot water inlet pipes and 4, 4 the outlet pipes, these inlets and outlets being in series according to the principles described in Specification 233,384 (footnote 2, p. 181), the said walls and pipes being provided externally with a lagging 5, 5.

" Thermometers 6, 6 placed at different levels allow the temperature inside the cell to be observed.

" 7 represents a spinning die unit, formed of different elementary spinning nozzles 7^a and pivoted about an axis 8 in the stuffing box 9. It receives by means of the pipe 10, from any suitable arrangement adapted for filtration pressure, and other requirements, the solution to be spun, of cellulose acetate in a suitable mixture of ethyl alcohol and acetone.

" 11 represents as in Specification 218,913 (footnote [1], p. 761), a metallic conical member on the polished internal wall of which slide the spun filaments. 12 is the opening for the exit of the thread, provided in a bronze member 13, in two portions, placed at the apex of the said conical member. 14 is a door mounted upon the said conical member, of which door, one of the portions of the bronze member 13 is integral.

"The dotted lines 15, 15 represent isolated filaments, forming by their union the thread 16 which, either before or after passing through the paying-out device 17, proceeds to the bobbining or frame apparatus or other apparatus as may be required. 18 is a roller placed below the orifice 12, and driven in any suitable manner (not shown), on which the thread 16 is wound up when it is broken, outside the cell, either purposely or not. 19 is a small door giving access to the die 7 or to one of its parts.

"The surrounding air penetrates into the cell by the outlet orifice 12 or by openings 20 provided in the conical portion, or simultaneously by both and by openings 21 provided above the dies in the upper portion of the cell.

"The air laden with volatile vapours is sucked by the pipe 22 or several similar pipes opening into an annular chamber 23, so as to avoid the filaments being carried off by the gaseous stream. At that stage it could be exhausted in the atmosphere, for instance on the roof of the shed, but if, as has been supposed it is desired to recover the volatile solvents with which it is laden, the piping 22 will comprise as described in Specification 233,384, a diaphragm 24 placed in a junction 25 and adapted to slide in the said junction to form a closure. The piping 22 opens into a collector 26, common to a certain number of analogous cells. This collector, which will be provided with any accessory devices as may be required, is itself connected to an air pump and to a system of recovery of volatile solvents. . . ."

A further patent to the Rhodiaseta [1] is directed to the prevention of scintillating effects. These increase as the cross-section of the filaments becomes less circular, and more "bone-like". To prevent this an input of heat is provided at the spinning dies, to produce a temperature depending upon the desired cross-section and varying with the nature of the cellulose derivative being spun, the solvent used, the viscosity of the solution, the pressure employed to extrude the solution, the diameter of the spinning orifices, the final diameter of the filaments and the rate of flow of the evaporative medium.

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[1] Ellis (for Rhodiaseta). B.P. 248,696.

More recently[1] the same firm have covered the production of stable threads, showing no scintillating effects, at a spinning speed of 400 metres per minute or more, and of fine denier (1 or even less) by combining the processes of Specifications 236,393 (footnote [1], p. 182) and 248,696 (footnote [1], p. 184), i.e. by heating the spinning solution and introducing a cold, dry atmosphere at 20° C. say, into the spinning cell in the vicinity of the dies.

The proportion of solvent vapour in the evaporative atmosphere of the spinning cells is also a matter of considerable importance. It should, of course, remain constant during spinning, otherwise irregularities in the lustre and cross-section of the threads will result. Rhodiaseta[2] have covered the use of an evaporative medium rich in solvent vapour for the purpose of obtaining filaments of almost circular cross-section. The high concentration of solvent vapour prevents the formation of an initial hard layer on the outside of the filaments, so permitting the free passage of the solvent from the interior and thus facilitating the drying process. It is also mentioned that working in this manner enables the solvents to be recovered with ease. A suitable apparatus for carrying out this method is described in a patent of addition,[3] and in a further addition[4] it is mentioned that the required concentration of vapour is maintained in the cell by gaseous exchange between the heated atmosphere of the cell and that of the cooled solvent condenser through a single large aperture connecting the one with the other.

Syntheta A.-G.[5] go still further and spin into an atmosphere consisting of hot solvent vapour only, the desired concentration being maintained by removal and condensation of the excess of vapour. In this way it is claimed that the difficulty of recovering solvents from dilute mixtures with air is avoided.

Courtauld's[6] obtain uniform conditions in the cells by providing them with heating elements of substantially identical construction, and communicating in parallel with the supply and discharge mains for the heating fluid. These mains are directed to be of such a capacity that the flow of water is sufficiently rapid and plentiful

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[1] Ellis (for Rhodiaseta). B.P. 300,672.

[2] Soc. pour la Fabr. de la Soie Rhodiaseta. B.P. 238,842.

[3] Ibid. B.P. 269,377.

[4] Ibid. B.P. 288,618.

[5] Syntheta A.-G. B.P. 265,577.

[6] Courtaulds, Wood, and Turney. B.P. 281,058.

to limit the temperature drop through the heating elements to about 0·1 to 0·2° C. Further, all the cells are connected to a common aspirator sufficiently large to maintain a constant flow of air through the cells, the connection being made through interchangeable but not individually adjustable outlets of the same size.

British Celanese, Limited,[1] ensure regularity of working in the different units of a spinning machine by providing each cell or compartment with an outlet pipe for the vapour laden air, provided with a flow meter and a valve or other device for regulating or cutting off the flow from any given cell or compartment.

In order to utilize all the evaporative capacity of the evaporative medium, thereby reducing the total volume required for spinning a given amount of rayon, and increasing the solvent content of the exhaust air, the same firm make use of collector devices fitted at the top of the spinning cell.[2] It is also claimed that by working in this manner a stricter control can be exercised over the cross-section of the filaments. A further specification describes a cell open or only partially closed at the end remote from the spinning dies, in order to ensure a more even distribution of the air, and the cell is fitted with collector devices as before.[3] The principle was later applied to special spinning nozzles comprising a line of orifices, the collector devices being of an appropriate shape.[4] Finally,[5] the whole or most of the evaporative medium is caused to pass in the vicinity of the spinning dies solely by means of suction applied to withdraw it from the cell, and additional evaporative medium is also introduced in the neighbourhood of the spinning dies.

Spinning into a closed and heated cell in which the pressure is reduced has been covered by Dreyfus and the British Celanese, Limited.[6] In order to prevent moist air from entering the cell, the thread is led through an aperture of which the diameter can be adjusted so that it does not greatly exceed that of the thread; this aperture is surrounded by a cowl which maintains a supply of dry heated air in the vicinity of the outlet.

In contrast with the methods described by the British Celanese, Limited, in which the evaporative medium is caused to pass in

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[1] British Celanese, Ltd. B.P. 203,092.

[2] Ibid., Kinsella, Bower, Taylor, and Dreyfus. B.P. 300,998.

[3] Br. Celanese Ltd. B.P. 304,674. Addn. to 300,998.

[4] Ibid. B.P. 326,232. Addn. to 300,998,

[5] Ibid. B.P. 352,922. Addn.to 300,998, 304,674, and 326,232.

[6] H. Dreyfus. B.P. 324,061. (With B. Celanese, Ltd., and Taylor. B.P. 343,936.)

the vicinity of the spinning dies before leaving the cell, and in agreement with the views of the Rhodiaseta is an invention due to the Aceta Ges.[1] In the method described the threads pass downwards in an ascending current of warm air in the usual way. The cell, however, is subdivided by an adjustable constriction into upper and lower portions, both parts being connected independently at their upper ends to the suction pipe. The greater portion of the evaporative medium laden with solvent vapour is in this way withdrawn at the upper end of the lower subdivision of the cell, so that only a comparatively small proportion of the air passes the vicinity of the dies.

Similar ideas are embodied in a series of patents assigned to the Ruth Aldo Co. Inc. by M. Klein. The first specification [2] describes a cell divided by one or more diaphragms into an upper zone containing the spinning dies, and lower portions where the thread comes into contact with the heated air. The diaphragms consist of a fixed portion and a central hinged portion, having a triangular notch, partially closed so as to leave only sufficient space for the passage of the thread, thus preventing heated air from entering the upper zone. In the first addition to this patent [3] an inlet for cold air is provided in the upper zone of the cell where the spinning die is situated, and the thread passes down between a series of diaphragms set obliquely in the cell, the hot air and solvent vapours being withdrawn from the lower part of the cell. In a further addition [4] the air circulation is modified, each zone of the cell having its own inlet and outlet so that the circulation of the evaporative medium is independent in each cell. The evaporative medium from one zone may optionally be circulated in another zone after passing through heating, cooling, or other devices.

Both British Celanese, Limited,[5] and the I.G. Farbenindustrie A.-G. [6] describe means for introducing fresh evaporative medium in the immediate vicinity of the spinning dies, doubtless with the purpose of bringing about rapid initial coagulation of the filaments and so preventing or minimizing breakages. Courtauld's [7] propose

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[1] Aceta Ges. B.P. 286,608.
[2] Ruth-Aldo Co. Inc. (Assignees of Klein). B.P. 292,561.
[3] Ibid. B.P. 292,608.
[4] Ibid. B.P. 300,166.
[5] British Celanese, Ltd., Kinsella, Bower, Briggs, and Taylor. B.P. 341,075. Addn. to 325,233.
[6] I.G. Farbenind. A.-G. B.P. 349,793.*
[7] Courtaulds and Diamond. B.P. 353,597.*

to introduce the whole of the evaporative medium in the vicinity and to one side of the spinning dies and to withdraw it from the opposite side, the whole of the evaporative medium being thus drawn across the path of the filaments.

Importance is also attached to the temperature of the spinning solution as it reaches the spinning jets; Courtauld's,[1] for example, state that improved results are obtained if the temperature of the solution is the same as that of the air surrounding the dies. Furthermore, the lustre and to some extent the cross-section of the filaments can be controlled by suitable adjustment of the temperature of the spinning solution; thus, when spinning a 20 per cent solution of cellulose acetate in acetone, with an air flow such that the concentration of acetone in the vicinity of the dies is about 1·5 per cent by volume, the lustre decreases as the temperature of the solution falls from 67 to 62° C., while a further drop in temperature considerably modifies the round section of the filaments. H. Dreyfus [2] also has a specification covering the use of spinning solutions at a predetermined temperature.

Among other specifications relating to the dry spinning of acetate rayon is one by A. E. Gull [3] which describes an apparatus in which the air is drawn into one end of a drying chamber consisting of a central tube surrounded by a large annular space, and is heated by passing through a duct having variable or both variable and invariable electric elements. It then passes down the central tube in contact with and in the same direction as the extruded filaments, the exit end being maintained at a higher temperature than the inlet end. As the cell is constricted towards the lower end, the velocity of the air stream is greater at the exit than at the inlet. The Aceta Ges.[4] have described a spinning cell heated by a fluid or by a resistance coil in the external casing; this is surrounded wholly or partially by a second connecting casing in which the air passing to the spinning cell is heated. Ruzicka [5] uses a jacketed spinning cell, the hot air used as the evaporative medium passing downwards through the jacket and then up through the cell proper. Finally, the Soie de Chatillon [6] have an interesting specification in which a spinning cell is described, having a cooling device consisting of a pipe which is close, and approximately parallel

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[1] Courtaulds and Lewis. B.P. 278,814.

[2] H. Dreyfus. B.P. 320,632.

[3] A. E. Gull. B.P. 303,778 and 303,821.

[4] Aceta Ges. B.P. 308,350.

[5] Ruzicka. B.P. 317,108.

[6] Soie de Chatillon. B.P. 309,158.

to the path of the filaments, and through which flows a stream of cooling liquid. In this way the solvent vapours are condensed and collected in a trap at the bottom of the cell.

Treatment of the Threads during Spinning or Winding.—The application of lubricants to the threads during their travel to the winding devices has already been mentioned in connection with the apparatus of the British Celanese, Limited (footnote [1], p. 172) described above. A further patent by H. Dreyfus[1] covers the application of sizing materials in a similar manner, suitably moistened pads or rollers being used for the purpose, or the threads are passed through a bath of the sizing material, or it may be sprayed on the threads. British Celanese, Limited, also have a patent[2] describing the application of a lubricating dressing to the threads during their travel to the winding devices, in order to prevent "hairing" or "fluffing". This dressing is again applied by means of a pad or roller, or by bath or spray, and consists of such compositions as: equal parts of lard and pale oleic acid; olive oil; medicinal paraffin; an emulsion of olive oil, oleic acid, and caustic potash solution mixed with boiling water, and further diluted with water before use. This latter may be used in its alkaline condition, or after acidifying with formic and tartaric acids.

The threads may also be subjected to all kinds of chemical or physical treatments during spinning or immediately before winding, in order to produce certain desired effects, but these methods will be dealt with in their proper places.

Stretch Spinning.—Although the application of a certain amount of stretching to the filaments is inevitable in the ordinary methods of spinning acetate rayon by the extrusion of a solution of cellulose acetate by means of pressure, it is only quite recently that stretch spinning methods have been applied in the acetate industry with the object of producing finer filaments than is possible by the ordinary processes. A further object of applying stretch to the partially coagulated threads is to bring about a better orientation of the micellæ, with consequent improvement in the mechanical properties of the threads.

The production of very fine filaments by forcing cellulose acetate solutions through minute orifices is impracticable, firstly owing to the difficulty of removing by filtration the smallest particles of

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[1] H. Dreyfus. B.P. 210,266.

[2] British Celanese, Ltd., Riley, Palmer, and Welch. B.P. 215,417.

dirt or fibrous debris, which do not matter when using spinning orifices of normal size, but which would inevitably cause clogging with very fine orifices; and secondly owing to the extremely high pressures necessary to force the viscous acetate solution through these minute orifices, with consequent increase in the expenditure of power, and more rapid depreciation of pumps, etc. With the stretch spinning process, however, these difficulties do not arise, since the filaments may be extruded from dies having normal or even larger than normal orifices, the reduction in diameter of the filaments being brought about by the subsequent stretching process, there being no limit, theoretically, to the fineness of the filaments which can be produced in this way.

The normal denier of the individual filaments of acetate rayon produced by pressure spinning is of the order of 5–10, i.e. a 150 denier yarn may be made up of thirty filaments of 5 denier, 15 filaments of 10 denier or intermediately. Compared with the 15 denier, 25 filament cuprammonium yarn made by the Bemberg stretch spinning process, even the finest acetate yarns are comparatively coarse. The stimulation of research on stretch spinning methods in the acetate industry is no doubt a result of the increasing competition of these fine denier cuprammonium and also viscose yarns, as well as of the demand for the softer, warmer, and less lustrous fabrics produced from fine denier yarns.

The stretching of acetate filaments may be carried out, either while they are still plastic during their travel through the spinning cell; or plasticizers may be incorporated in the spinning solution and stretching is then deferred till the volatile solvent has almost completely evaporated; or again, the threads after coagulation may be subjected to the action of the vapours of solvents or plasticizers, followed by stretching. Thus, British Celanese, Limited,[1] subject the extruded filaments while traversing a countercurrent of evaporative medium in the spinning cell, to a controlled and uniform stretch, by passing the filaments round two or more rollers, the first receiving the threads while still plastic and containing 20–40 per cent of solvent, and the subsequent roller or rollers drawing the filaments at a speed greater than that of the first roller.

H. Dreyfus [2] produces filaments of low denier and high extensi-

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[1] British Celanese, Ltd., H. Dreyfus, and Taylor. B.P. 331,299.
[2] H. Dreyfus. B.P. 353,956.

bility by a stretch spinning process using an acetate solution, containing in addition to the solvent a non-solvent and a high boiling solvent. The ratio recommended between non-solvent and high boiling point solvent is between 2 : 1 and 1 : 2, and the total of non-solvent should be less than 12 per cent. An example of a suitable mixture consists of 80–84 of acetone, 9–7 of water, and 11–9 of diacetone alcohol, ethyl phthalate or the like.

The I.G. Farbenindustrie A.-G.[1] cause the threads while still liquid to enter a chamber filled with the vapour of a swelling agent for cellulose acetate (and free from air). In this way the solvent still remaining in the filaments is replaced by swelling agent and the jelly-like threads are stretched and then dried by a current of air in an adjoining chamber. The same firm[2] later described a spinning cell for the stretch spinning process, in which the upper portion of the cell is partitioned off as a swelling chamber, being fitted internally with a spiral gutter in which a continuous flow of swelling agent is maintained.

A later method due to British Celanese, Limited,[3] consists in extruding the filaments into a vigorous evaporative atmosphere, and after a skin has been formed on the filaments they pass into an atmosphere of solvent or other vapour to soften this outer layer. The softened filaments are stretched by tension throughout their whole length, or wholly or partially in the softened portion, and are afterwards dried in a second evaporative atmosphere followed by further stretching after they have reached the elastic limit.

The same firm has also covered a process in which liquid solvent or swelling agent is applied to the threads after the formation of a skin-like layer (i.e. while still retaining 25–50 per cent of solvent), followed by stretching and completion of the setting process. Swelling agents mentioned include 70 per cent aqueous acetone, 50 per cent alcohol-acetone, or 50–60 per cent aqueous or alcoholic dioxan, diacetone alcohol, or methyl or ethyl lactate.[4]

A method of plastifying the filaments previous to stretching described by the Rhodiaseta[5] consists simply in heating them to a suitable temperature, followed by stretching to a greater extent than the breaking elongation in the dry state. This process is

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[1] I. G. Farbenind. A.-G. B.P. 340,570.

[2] Ibid. B.P. 341,021.

[3] British Celanese, Ltd., Dreyfus, and Taylor. B.P. 340,929.

[4] Br. Celanese, Ltd. B.P. 342,712.

[5] G. B. Ellis (for Rhodiaseta). B.P. 323,846.

claimed to produce threads of very fine denier and of improved mechanical properties.

Although not concerned with stretch spinning a suggestive specification may conveniently be mentioned here. It describes a method which is claimed to bring about an improved orientation of the dispersed particles of cellulose acetate in a spinning solution by submitting the solution immediately before reaching the dies to the action of a high voltage electrical field.[1] The solution flows parallel to a series of electric sparks, and the spinning cell is either evacuated or filled with an inert gas to avoid the risk of explosions. It is not suggested that the above claim is justified, but the specification is interesting as indicating the trend of ideas in this connection. A patent due to British Celanese, Limited,[2] with a similar object states that before extrusion the spinning solution is passed through a number of capillary tubes of uniform cross-section (0·2 to 0·02 per cent of the diameter of the spinning orifices) arranged parallel to one another and to the line of flow of the spinning solution.

Modification of Lustre.—The earlier acetate rayons were characterized by a brilliant glassy lustre, which was liable to be diminished or even destroyed (" blinding ") by certain treatments such as boiling with water or soap solutions. Hence the laundering of fabrics made from this rayon was a difficult matter, especially as the action of dry heat, such as is met with in the process of ironing, tends to restore or increase lustre. The whole question of lustre is more fully discussed in the section devoted to the properties of acetate rayon. In view, however, of the fact that filaments of modified lustre are now produced by modifications of the spinning process to meet the increasing demand for fabric having a subdued lustre, it is necessary to indicate that there are other methods of producing the same or similar effects. The delustring action of hot aqueous liquids probably consists in the rearrangement of the surface micellæ, which were originally parallel to the length of the threads, but are afterwards arranged in an irregular manner; there may also be a certain amount of depolymerization into smaller particles, and the final condition of the threads in relation to their original condition may be compared with sheets of polished and ground glass respectively. That is to say, the diminution in lustre is an optical effect depending

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[1] Iwasaki and Hagiwara. B.P. 288,655.

[2] British Celanese, Ltd., and Welch. B.P. 322,764.

upon the scattering of the incident light. Hence, if a white insoluble substance can be dispersed in a solution of cellulose acetate before spinning, the resulting rayon should have a subdued lustre. It has also been mentioned earlier that the various conditions obtaining in the dry spinning process have their effects in regard to the degree of lustre of the rayon produced.

The methods of producing rayon of subdued lustre from cellulose acetate may be divided broadly into four classes :—

(*a*) Those depending upon the spinning conditions.

(*b*) Those in which a finely divided solid is dispersed in the spinning solution.

(*c*) Those in which a liquid is added to the spinning solution.

(*d*) Those in which the lustre is modified by the application of certain reagents to the threads before they are completely dried.

(*a*) An early patent to the Naamlooze Vennootschap Nederlandsche Kunstzijdefabriek [1] covers spinning in presence of water vapour introduced into the spinning cell, or by treating the threads after spinning, but while they still contain some of the solvent, in a second chamber containing water vapour.

British Celanese, Limited,[2] produce acetate rayon of subdued lustre, or even matt or lustreless filaments by dry spinning a solution of cellulose acetate in acetone or other volatile solvent, or in a mixture of such volatile solvent and a diluent such as water, into an evaporative medium at a higher temperature than the spinning solution, the latter being maintained at 10–20 °C. below the minimum temperature required for the production of rayon of normal lustre.

(*b*) H. Dreyfus describes a method in which finely divided solids such as barium sulphate, zinc oxide, etc., are added to the spinning solution. The substance to be added is ground dry, graded, and again ground with water and a dispersing agent or protective colloid until the particles are less than 0·0025 mm. in diameter, before it is added to the spinning solution.[3]

A similar patent due to J. A. Singmaster [4] covers the addition of fine particles (0·75μ or less) of white inorganic pigments such as zinc or titanium oxides to the spinning solution. A further patent

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[1] N. V. Nederlandsche Kunstzijdefabriek. B.P. 291,067.

[2] British Celanese, Ltd., Taylor, and Roberts. B.P. 334,195. Ibid., Dreyfus, Taylor, and Roberts. B.P. 334,198.

[3] H. Dreyfus. B.P. 338,490.*

[4] J. Singmaster. B.P. 339,603.

to British Celanese, Limited,[1] also mentions titanium dioxide, the particles having a diameter of 0·0001 to 0·00035 mm., and the addition being made in an amount of 0·5 to 4·0 per cent on the weight of the spinning solution. The specification also mentions the use of zinc oxide and barium sulphate, and it is claimed that the opacity is increased by adding 2–6 per cent of boric acid or a borate (calculated on the weight of TiO_2).

H. Dreyfus has covered the addition of finely divided organic, fibrous material to the spinning solution, e.g. cotton, linen, straw, wheat husks, wool, or artificial fibres,[2] and more recently, the addition of high melting organic compounds (water insoluble) in a state of fine division (0·0001 to 0·0005 mm.). Suitable compounds mentioned are diacetyl benzidine or tolidine, dibenzoyl benzidine, dinaphthyloxamide, diphenyloxamide, succinic naphthylamide, etc.[3] Finally, he has also described the wet or dry spinning of solutions containing natural or artificial resins, preferably those which melt above 250° C.[4]

(*c*) E. Heymann describes a method of producing dull lustre acetate rayon by adding to the spinning solution a mixture of a non-volatile substance such as a mineral, animal, or vegetable oil, aniline, etc., with a volatile substance. The thread produced is treated for the removal of part of the added substance by evaporation in air or *in vacuo*, or by means of solvents.[5]

British Celanese, Limited,[6] dry spin a solution of cellulose acetate in a volatile solvent, containing one or more organic precipitants for the ester, e.g. alcohols, hydrocarbons, esters, or ethers ; or the added liquid precipitant may be water. The spinning conditions are so adjusted that the precipitating action is exerted while the filaments are still wet.

Courtauld's add a little animal or vegetable oil such as arachis oil to the spinning solution, and the threads produced are boiled with aqueous soap solution, washed, and dried.[7]

(*d*) British Celanese, Limited,[8] describe the production of acetate rayon of modified lustre by applying a lustre modifying liquid such as xylene, water, etc., to the threads by means of a wick, at

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[1] British Celanese, Ltd., Ryley, Parkinson, and Sims. B.P. 341,897.*

[2] H. Dreyfus. B.P. 344,510.

[3] Ibid. B.P. 346,678.

[4] Ibid. B.P. 346,793.

[5] E. Heymann. B.P. 297,364.*

[6] British Celanese, Ltd., Payne, and Roberts. B.P. 314,404 and 314,414.

[7] Courtaulds and Diamond. B.P. 338,269.*

[8] British Celanese, Ltd., and Taylor. B.P. 327,740.

an early stage in the drying of the filaments, i.e. while they still contain a relatively high proportion of solvent. The effect produced may be an increase or a decrease in the lustre of the threads, depending on the liquid employed and upon the stage of drying reached by the filaments.

Before leaving the subject of spinning acetate rayon of modified lustre, it may be mentioned that the Société Chimique des Usines du Rhône have modified a method of colouring cellulose acetate with mineral pigments, which they patented in 1927, to give a product which, when dissolved and spun gives a rayon of subdued lustre. The original patent states[1] that the reagents necessary to produce a mineral pigment are dissolved in water and added to a solution of cellulose acetate in an organic solvent, and the coloured solution is then precipitated with water. For example, to 100 gm. of cellulose acetate in 800 gm. of acetone is added 5 gm. of ferric chloride in concentrated aqueous solution, followed by an aqueous solution of 6·5 gm. of potassium ferrocyanide. When the reaction is complete the cellulose acetate, containing Prussian Blue in an almost colloidal condition, is precipitated with water, washed and dried. The following year[2] the process was modified by using reagents which give a white precipitate, e.g. barium sulphate.

Production of Hollow Filaments.—The idea of producing rayon filaments which are hollow was first exploited by the viscose manufacturers. The advantages of hollow filaments are reduction in weight for a given covering power, and increased insulating properties of fabrics made from such yarns. Several methods of producing hollow acetate yarns have been patented.

J. Rousset,[3] as long ago as 1921, proposed to make hollow fibres by spinning solutions of cellulose acetate, collodion, viscose, etc., containing air or other fluid maintained in a dissolved state by pressure, and producing an emission of bubbles within the fibre after extrusion, by releasing the pressure or by the action of heat. Alternatively, he states that a substance such as a carbonate, gasoline, or carbon bisulphide, capable of emitting gaseous bubbles by chemical or thermal action, may be incorporated with the solution to be spun. In a further patent in 1925[4] Rousset describes the

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[1] Soc. Chim. des Usines du Rhône. B.P. 275,553.

[2] Ibid. B.P. 294,623.

[3] J. Rousset. B.P. 189,973.

[4] Ibid. B.P. 267,187.

production of hollow filaments from the usual solutions of cellulose acetate, e.g. in acetone-alcohol, by spinning into a cell containing air at a temperature substantially greater than the boiling-point of the solvent used, and a comparatively high rate of flow is maintained in order to produce active superficial evaporation from the filaments as they emerge from the orifices.

Dreyfus and the British Celanese, Limited, have several patents relating to the production of hollow filaments. For example,[1] Dreyfus claims that hollow filaments of good strength and capable of being stretched for the production of low deniers may be made by introducing into the spinning solution high boiling solvents or plasticizers, in the amount of 3–80 per cent of the weight of the cellulose acetate used, the actual quantity depending on the volatility of the liquid in question. Compounds recommended are diacetone alcohol, acetophenone, di- or triacetin, ethyl phthalate, alkyl ethers of ethylene glycol, etc. The plasticizer remaining in the threads after spinning is removed by the action of water or other suitable solvent. In a second specification[2] the same result is achieved by dry spinning a solution in a mixed solvent, the components of which differ in B.P. by 35–100° C. or more. The temperature of the spinning cell is maintained below or not much above the boiling point of the higher boiling constituent of the solvent mixture. The less the difference in boiling point of the constituents, the greater the proportion of the lower boiling constituent, and the lower the spinning temperature. In an example the spinning solution consists of a 20·7 per cent solution of cellulose acetate in a mixture of acetone and formaldehyde in the proportion of 1 : 3, and the spinning temperature is 65° C.

The collector devices of B.P. 300,998 are applied in the manufacture of hollow filaments, to concentrate sufficient heat near the point of extrusion to prevent the lowering of the temperature which accompanies rapid superficial evaporation.[3]

In a further specification the British Celanese, Limited, extrude a solution of cellulose acetate into an atmosphere having a low evaporative power, which gives a slow initial solidification, following which the threads pass through a vigorous evaporative atmosphere.[4]

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[1] H. Dreyfus. B.P. 317,097.

[2] Ibid. B.P. 317,098.

[3] British Celanese, Ltd., Dreyfus, and Roberts. B.P. 324,899.

[4] British Celanese, Ltd. B.P. 318,629.

The Cellulose Acetate Silk Company, Limited, state that hollow filaments may be produced by extruding a solution of cellulose acetate through special dies, having conical holes tapering to a greater diameter on the outer face of the die. For example, if the face of the die is 0·4 to 0·5 mm. thick, the holes may be 0·05 to 0·07 mm. diameter on the inside, and 0·09 to 0·11 mm. diameter on the outside of the die.[1]

Recently the I.G. Farbenindustrie A.-G. [2] have described a process in which a solution of cellulose acetate in a solvent such as acetone, which contains at least 20 per cent of a non-solvent such as toluene (and excluding alcohol), is extruded under such conditions that it is subjected to accelerated but weakened evaporation.

Although hollow acetate rayon would probably find a ready demand, it does not seem to have found its way on to the market as yet, due no doubt to various difficulties which have been experienced in its production. It is a difficult enough matter to establish and maintain correct conditions for the manufacture of ordinary threads, so that the extra care and attention called for by hollow yarns, in the present state of the knowledge concerning them, probably render the cost of production prohibitive.

Saponification Processes.—Although the saponification process of dyeing cellulose acetate is practically obsolete, processes are still described from time to time, which have for their object the superficial hydrolysis of acetate filaments during the spinning operations, in order to modify the dyeing properties of the yarn produced. These processes are frequently directed to obtaining effects as a result of variable saponification along the length of the threads.

This partial hydrolysis may be achieved by treatment of the filaments with an alcoholic or aqueous solution of caustic alkalies or ammonia. Thus, British Celanese, Limited,[3] treat the threads while still swollen with such a solution. In the case of wet spinning the swollen condition required is brought about by the addition of a high boiling solvent to the spinning solution or the coagulating bath, or the threads may be treated with the solvent after the spinning process proper. In the case of dry spinning the high boiling point solvent is added to the spinning solution.

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[1] Cellulose Acetate Silk Co., Ltd., and H. C. Curtis. B.P. 353,042.

[2] I.G. Farbenind. A.-G. B.P. 356,327.*

[3] British Celanese, Ltd., Dickie, and Sowter. B.P. 330,950.

In a further patent British Celanese, Limited,[1] apply a suitable saponifying agent, such as caustic soda or potash, or alkali carbonates, silicates, or phosphates, intermittently to the threads during production. In this way multi-coloured or cross-dyed effects may be obtained by using dyes having different affinities for the saponified and unsaponified portions of the fibres.

The process of saponifying materials made from acetate rayon by the application of a suitable paste or solution [2] was later extended to the treatment of the filaments during their travel from the spinning cabinet to the collector device. This treatment is followed by immediate drying with the aid of heat, followed by steaming.[3] The materials so produced are claimed to have higher safe ironing temperatures than the untreated material, and to retain their affinity for cellulose acetate dyes.

Acetate yarns exhibiting different degrees of resistance to saponifying agents may be produced by suitable variation in the spinning conditions. Thus, British Celanese, Limited,[4] have found that an increase in the concentration of acetone vapour in the vicinity of the spinning nozzles renders the fibres produced more resistant to saponification. For example, a 25 per cent solution of cellulose acetate in acetone is dry spun while the acetone content of the air near the dies is from 2–3 per cent. The solvent concentration may be increased to the required amount by injecting vapour near the nozzles, or by decreasing the flow of air. The yarn produced is afterwards treated with saponifying agents either wholly or in parts, and is mixed with cotton, wool, silk, etc., for the production of effects.

More recently the British Celanese, Limited,[5] have covered the production of acetate yarns having a high moisture regain (of about 7 per cent), a safe ironing point 20–30° C. above the normal value, and an increased affinity for dyestuffs, by spinning a solution of cellulose acetate containing less than two acetyl groups per $C_6H_{10}O_5$ residue, for example, an acetate containing 45–48 per cent of combined acetic acid.

Miscellaneous Patents relating to Dry Spinning.—Among the various other patents relating to the dry spinning of cellulose

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[1] British Celanese, Ltd., and Taylor. B.P. 332,263.

[2] British Celanese, Ltd. B.P. 316,521; 318,468.

[3] Ibid. B.P. 351,417.

[4] Ibid. and Roberts. B.P. 343,953.

[5] British Celanese, Ltd. B.P. 356,170.

acetate, and directed towards obtaining special effects of one kind or another, the following may be mentioned :—

Sever and Speakman[1] impart wave or curl to acetate filaments by setting up a swirling or eddying motion in the evaporative atmosphere of the cell.

British Celanese, Limited, claim to have produced acetate threads of very regular character by causing them to traverse a longer path in the spinning cell (3–6 yards). Loss of solvent by evaporation from the threads after they leave the cell is also prevented or minimized.[2] They have also covered the production of yarns having improved strength and elasticity by treating them during or after spinning with " organo-mineral " acids.[3] Examples given are 30–45 per cent solutions of sulphoacetic acid, sulphonic acids, or phosphinic acids. Such treatment also results in modifications in lustre.

Dreyfus[4] describes the spinning of acetate rayon containing metallic residues by the extrusion of an acetate solution containing a soluble metallic salt, such as stannic or ferric chloride, zinc chloride, aluminium thiocyanate, etc., followed by treatment with a precipitating agent such as tannic acid, ammonia, etc.

The production of fibres having a large cross-section by causing the individual filaments in a bundle to merge into a single filament of large cross-section, followed by stretching, is covered by British Celanese, Limited.[5]

Various effects may also be obtained by the use of yarns which vary systematically in denier. Such variations may be brought about by varying the speed of the spinning pumps,[6] by producing pulsations by vibration or the reciprocating action of a diaphragm or piston in contact with the spinning dies[7]; by varying the linear speed of the filaments by means of a roller which is driven at a greater peripheral speed than the speed of extrusion, and which is provided with means of varying periodically the frictional force exerted on the threads[8]; and by varying the spinning conditions.[9]

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[1] W. Sever and J. B. Speakman. B.P. 300,221.*

[2] British Celanese, Ltd., and Dreyfus. B.P. 315,729. Addn. to 165,519.

[3] H. Dreyfus. B.P. 334,853.

[4] Ibid. B.P. 336,621.

[5] British Celanese, Ltd., and Taylor. B.P. 349,999.

[6] British Celanese, Ltd., Dreyfus, Dickie, and Taylor. B.P. 326,777.

[7] Ibid. B.P. 326,778.

[8] Ibid. B.P. 346,354.

[9] British Celanese, Ltd., and Roberts. B.P. 343,973.

SPINNING PLANT AND PROCESS

Preparation of Solution.—The mixing vessels in which the cellulose acetate is dissolved in the solvent are usually made of welded steel, galvanized internally, and provided with rotating stirrers. Copper vessels may also be used, but present no advantages and are, of course, more expensive. A suitable capacity is from 1200 to 1500 gallons. The vessels are air-tight and tested to withstand the pressure necessary to blow the solution to the blending vessels. Two typical "dope" mixers are shown in Fig. 59. It will be noted that they are fitted with gauge glasses, manhole for the introduction of the materials, pressure gauge, and the drive for the stirrers is by belt, the fast pulley actuating the stirrers through a helical gear. There are also three sampling cocks at the

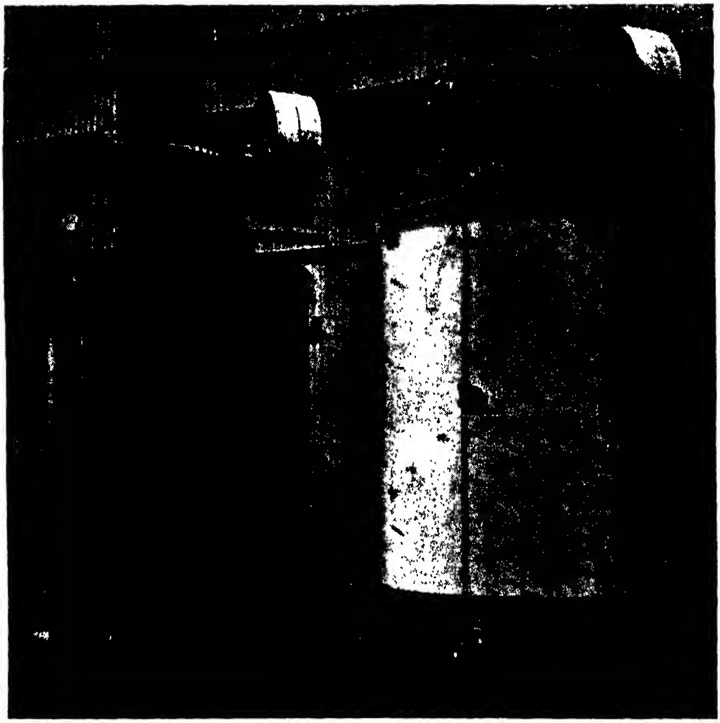

FIG. 59. "Dope" Mixers. (Blair's, Ltd.)

top, middle, and bottom of the vessel, so that the course of the mixing may be followed.

To ensure thorough uniformity of the spinning solution continuously during spinning, the solution prepared in the mixing vessels is blended in larger vessels of a similar type. These have a capacity of 4000–6000 gallons.

For ease in dissolving, the cellulose acetate is best used in the form of small fibrous masses, rather than as a powder; with the latter " balling-up " takes place when it is stirred with the solvent, and the process of solution is thereby considerably lengthened. The best method of preparing the solution is to place the necessary volume of solvent in the mixing vessel and to add the correct amount of cellulose acetate gradually, with continuous stirring; in this way all the acetate becomes thoroughly wetted with solvent and dissolution proceeds smoothly and reasonably quickly. A suitable solution is made up from 900 Kg. of blended acetate added to a mixture of 3500 Kg. of acetone and 145 Kg. of water. When the acetate is completely dissolved, the viscosity of the solution is determined, and the batch is suitably blended with other batches in the blending vessels.

The blended spinning solution is again tested for viscosity and adjusted if necessary, and the total solids should also be determined. The solution is allowed to stand until all the air bubbles held in suspension have risen to the top, and it is then blown by compressed air to hydraulic compressors, from which it is forced through filter presses. It then passes to the main delivery pipe to the spinning machines. Although the solution has been filtered it still contains sufficient debris and dirt to clog the fine orifices of the spinning dies; also if it were delivered direct from filter presses to dies, the variations in pressure would produce uneven filaments. Consequently each spinning head is provided with an individual pump, generally of the gear-wheel type, and a candle filter. The air required for evaporating the solvent may either be introduced by blowing, or drawn through the system by means of exhaust fans, and it is heated by passage through steam coils in the lower part of the cabinet and other steam coils are arranged at various points inside the cabinet according to requirements. Fig. 60 shows the spinning frame (cabinet not shown). The height of the cabinet is usually such as to allow of the filaments travelling two to three yards before leaving by a guide and porcelain eye at the bottom, after which they travel as a single thread over the godet rollers which are driven at such a speed as to exert an extending effect on the threads. The threads then pass to the bobbin on the spindle where they are simultaneously twisted and wound. The spinning frames are usually made up to 100 spindles, 6 inch pitch; a usual spindle speed is 10,000 revolutions per minute, so that, assuming the plant is working continuously, and allowing for stoppages due to breakages and changing of bobbins, and for breakdowns, the output of a 100 spindle machine spinning a medium denier, e.g. 150, will be about 4 tons of acetate rayon per day of 24 hours. Such a machine would require about 12 horsepower. Although spinning machines are sometimes driven by shafting and belts, it is much more satisfactory to employ a separate motor for each machine. The motor shown in Fig. 61 is very suitable for this purpose, as well as in all other parts of the spinning section where the atmosphere is liable to contain acetone or other inflammable vapours. This is a slipring machine, the sliprings being enclosed in explosion proof covers.

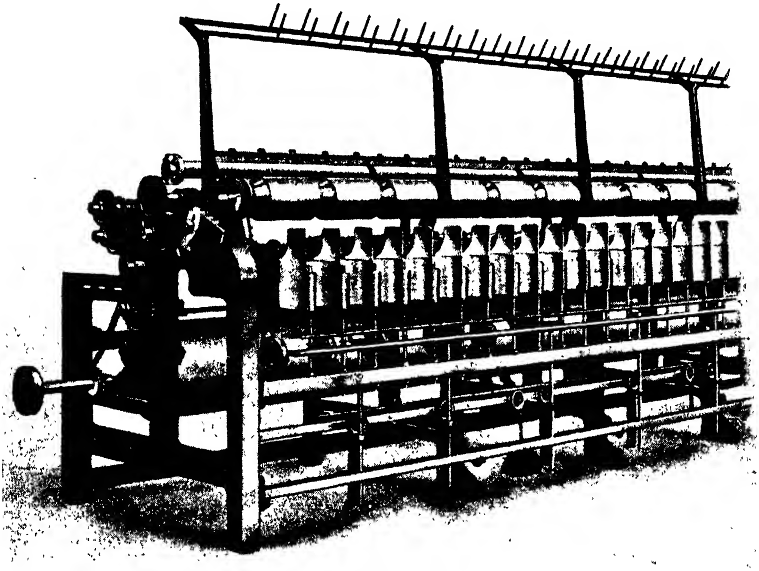

FIG. 60. Acetate Spinning Frame. (Prince Smith & Stells, Ltd.)

The sizes of the orifices in the spinning dies depend upon the denier of the yarn to be produced, and upon the degree of stretching applied to the threads during their travel to the winding devices. The dies need frequent attention in the way of cleaning. This is best done by immersing them (if made of noble metals) in heated chromic acid solution, which may be prepared by dissolving sodium dichromate in water and adding strong sulphuric acid until the chromic acid commences to precipitate. Sufficient water is then added to redissolve any precipitate.

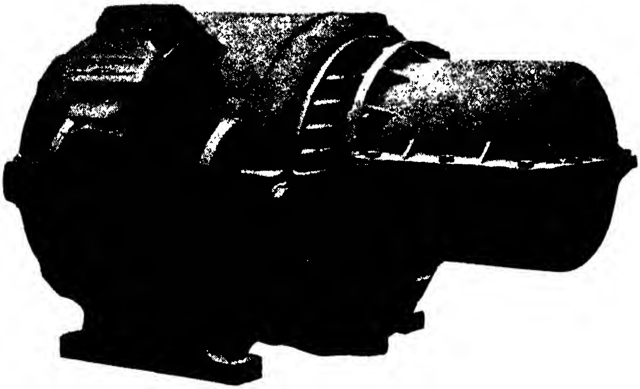

Fig. 61. Explosion Proof Motor. (General Electric Co., Ltd.)

The spinning cabinets are connected at the top to an exhaust main of galvanized iron, which passes to the solvent recovery plant.

SOLVENT RECOVERY

The successful production of rayon from cellulose acetate on a commercial scale depends upon a cheap and efficient method of recovering the solvent evaporated during spinning. Various methods have been devised for this purpose with varying degrees of success ; these methods may be divided into three classes, viz. :

(*a*) Condensation methods.
(*b*) Absorption in liquid media.
(*c*) Adsorption in solid materials such as carbon or silica gel.

The second class may be subdivided, according to whether the absorption is a purely physical one, or whether there is chemical combination between solvent and absorbent.

The process of simple condensation by cooling even if very low temperatures are employed, when applied to the exhausted air from the spinning cabinets, which is very poor in acetone vapour, gives a low percentage recovery, and is no longer used, except perhaps as a first stage in combination with other processes. Used alone, such a process has an efficiency of less than 40 per cent, and the risk of explosion and fire is very considerable. Condensation processes have also been combined with compression of the gases, or compression followed by expansion to give a sudden cooling, but with little success.

Acetone may be recovered by absorption in water, but the efficiency is low, and the concentration of acetone in the resulting water-acetone mixture rarely exceeds 2 per cent, so that a considerable expenditure on rectification is necessary.

With regard to sulphuric acid as an absorbent, it is doubtful whether it is of any value for acetone, although Ormandy has mentioned it in a patent.[1] The concentration claimed in particular is from 130–110 Tw. and he also mentions phosphoric acid of 130–150 Tw. The specification claims that concentrations of acetone of 10, 20, 30, and 40 per cent of the acid used may be obtained when the air contains 1·8, 4·6, 8·5, and 14·2 gm. of acetone per cub. m. The plant for carrying out extraction with sulphuric acid would, however, be very costly.

Robertson and Rintoul have proposed the use of bisulphite solutions as absorbents for acetone. The efficiency of such solutions will doubtless be greater than that of water, but the difficulty of recovering the acetone from the bisulphite compound formed is very great.

The use of cresols as absorbents for acetone, which forms the basis of the Brégéat process, is the only practicable absorption method available to-day for use in the acetate rayon industry. According to Brégéat the process has an overall efficiency of 95 per cent, i.e. from air containing 25–30 gm. of acetone per cub. m., 95 of every 100 Kg. of acetone present is recovered. Of this 95 per cent he allows 7 per cent to cover costs of the process, giving a net efficiency of 88 per cent. One of the greatest objections to the Brégéat process is the resinification or polymerization of the cresols which

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[1] Ormandy. B.P. 308,885.

takes place owing to the large volumes of air which are treated.[1] It has been shown that this is not entirely due to the action of the air, for resinification still occurred when the cresols were distilled *in vacuo* at 70° C. instead of at 140° C. in air (loc. cit.). It is stated that naphthalene or tetralin lessens this tendency to polymerize, but the use of the former in any quantity may lead to blockages in the plant, while the latter decreases the absorptive capacity of the cresols.

As an adsorption medium for volatile solvents silica gel is very efficient. Unfortunately a very high temperature is necessary to drive out the adsorbed acetone, and at such temperatures the catalytic effect of the gel leads to very serious decomposition of the acetone.

The activated carbon process for the recovery of volatile solvents was developed during the war by Bayer of Leverkusen. At that time it was applied in connection with the manufacture of explosives, but has since been used for a variety of purposes including the recovery of solvents used in the dry spinning of acetate rayon. The process depends upon adsorption in the vast number of capillaries in the activated carbon used. A schematic arrangement of the plant is shown in Fig. 62. It consists of the adsorbers A1, A2, etc., filled with the active carbon, which is supported on sieve plates; the gas inlet pipe G for the mixture of air and solvent vapour from the spinning plant—this gaseous mixture is impelled through the adsorbers by the blower G1; the steam inlet pipe D; the condenser K which is connected to the adsorbers by the distillate and steam pipe D and to the cooling water Wa; and the pipe L for drying and cooling air, the heater E, and the air blower L1. The plant is also fitted with a meter. The plant is operated as follows:—

The solvent laden air is forced through the adsorber A1 by the blower, and during its passage the solvent is adsorbed by the carbon practically quantitatively. When the carbon is fully charged the solvent-air mixture is switched over to the second adsorber A2. According to Liddle [2] active carbon will take up a high charge even at low concentrations, and for this reason a great deal of latitude is possible in regard to the quantity of air mixed with the solvent. The normal concentration is from 15 to 20 gm. per cub. m., whereas

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[1] *Chem. Ztg.*, 1927, **51**, 101–3.

[2] J. C. Liddle. *J.S.C.I.*, 1932, **51**, 3–4.

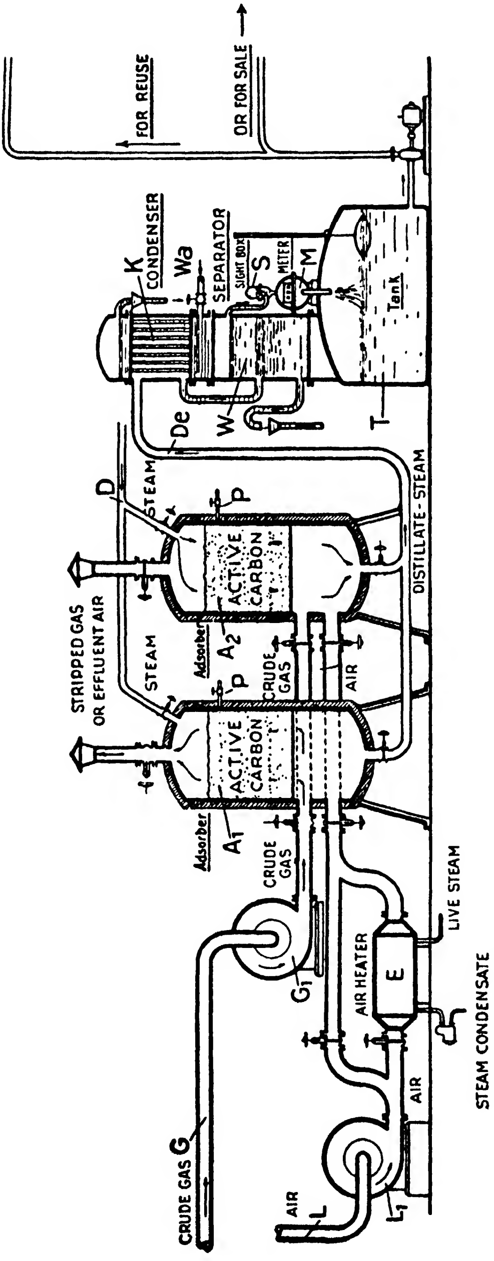

Fig. 62. Schematic Arrangement of the British Carbo Union Plant for Acetone Recovery.

the lower explosive or inflammable limit in the case of acetone is about 74 gm. per cub. m., which allows a wide margin of safety.

When the adsorber A1 is fully charged, steam is passed through the loaded carbon. The heating effect combined with the rinsing action of the steam sets free the solvent vapours which distill off along with some of the steam and are condensed in the condenser K. After steaming out the solvent, the carbon is dried with hot air or other gas, and is then cooled by blowing cold air through it, when it is ready for a further charge. The acetone is rectified in the usual way, the concentration in the condensate being about 30 per cent. The highest temperature reached by the carbon is 110° C., which is reached when steaming out (Liddle, loc. cit.), and the drying can be readily effected with air at 100° C.

The operating costs of the plant as given by the British Carbo-Union, Ltd., are as follows :—

Power.—The power required for exhausting the solvent air mixture and for drying and cooling the carbon varies, according to local conditions, from 0·05 to 0·2 K.W.H. per Kg. of solvent recovered.

Steam.—In the smaller plants the steam consumption is 3·5–5 Kg. of saturated steam per Kg. of recovered product, while in the larger plants it is somewhat less, being from 3–4·5 Kg.

Water.—About 50–80 Kg. of cooling water are required per Kg. of recovered solvent. If the water is recooled, the consumption falls to about 2–5 Kg.

Attendance.—The operation of the plant is extremely simple and according to the Carbo-Union, even in the case of large plants, it may be attended by one man.

Repairs.—Owing to the absence of moving parts, the repair costs are negligible.

Depreciation of Carbon.—This is apparently very small, and according to Liddle[1] over 10,000 cycles have been obtained with one filling of carbon in several Carbo-Union plants.

In the same article Liddle states that a number of unexpected difficulties arose in the development of the process, but that these have been completely overcome as a result of practical experience. He instances the following points: The recovery plant must be designed to work at a temperature far below the oxidation limits of the solvent. The carbon must be capable of taking the highest

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[1] Liddle. *Chem. Age*, 30/1/32.

charge possible in proportion to its weight. It must not be too retentive, and should hold a low rest charge. The grains should be shaped so as to offer a minimum of resistance to the gas passing through. The spinning cabinets should also be so designed that dangerous pockets of high concentration do not form in the trunking.

The photograph (Fig. 63) shows the adsorbers of the plant constructed for the British Acetate Silk Corporation, Ltd., at Stowmarket. This plant has a capacity of 18 tons per 24 hours, and a recovery efficiency of over 98 per cent. This figure does not include factory losses and suction leakages, but Liddle (loc. cit.) reports that overall factory recoveries of about 80 per cent are frequently obtained.

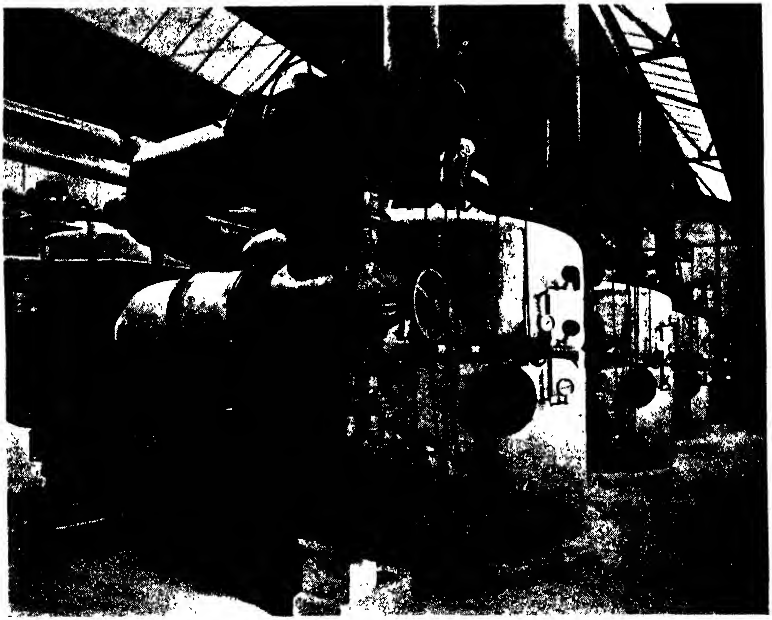
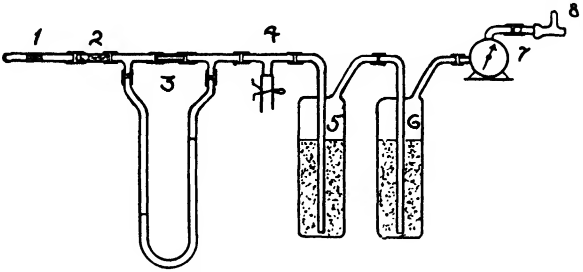


Fig. 63. Adsorbers—Acetone Recovery Plant. (British Carbo Union.)

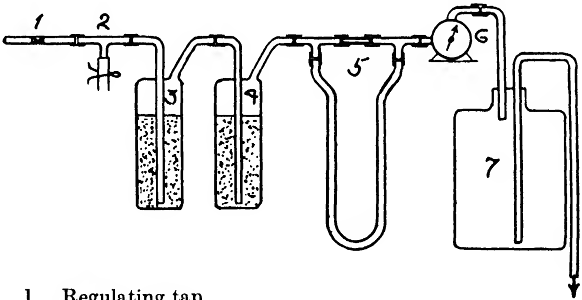
The British Carbo-Union plant is about the same in first cost as an absorption plant employing a liquid medium for the extraction of the solvent vapour. It has the advantages of being much more compact, thus requiring smaller foundations and buildings, and is much cleaner in operation since there are no liquid media to deal with. The company has supplied approximately 160 plants, and they state that in several cases where their plant has been installed insurance companies have reduced their fire-risk premiums.



1. Regulating tap.
2. Cotton filter.
3. Flow meter.
4. T-shaped tube with pinch cock.
5. Adsorption vessel.
6. Adsorption vessel.
7. Gas meter.
8. Equipment for testing break point.

FIG. 64. Gas Vapour-mixture under Pressure.

The company have devised a useful method of determining the solvent content of air or gas mixtures, depending on the adsorption of the vapour by means of active carbon. Two types of apparatus



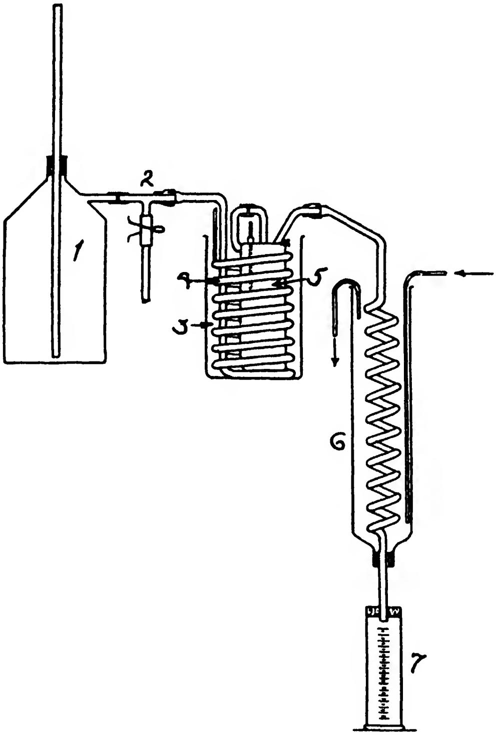
1. Regulating tap.
2. T-shaped tube with pinch cock (no cotton filter required).
3. Adsorption vessel.
4. Adsorption vessel.
5. Flow meter.
6. Gas meter.
7. Aspirator.

FIG. 65. Gas Vapour-mixture not under Pressure.

are in use depending on whether the solvent mixture is under pressure or has to be aspirated through the apparatus. Figs. 64 and 65 illustrate the two types. The pressure required is from

100–200 mm. of water. The adsorption vessels are filled with the adsorbent carbon to about two-thirds of their capacity (about 120 gm.). The air or gas stream is regulated to 3 litres per minute.

If the approximate concentration is not known it is advisable to carry out a preliminary test, when only one adsorption vessel is required. The air or gas mixture is passed through the apparatus for 30 minutes, which is usually sufficient to adsorb a measurable quantity of the solvent. The adsorber is then disconnected and steamed out with the aid of the apparatus shown in Fig. 66.



1. Steam boiler.
2. T-shaped tube with pinch cock and steam condensate outlet.
3. Heating bath.
4. Lead pipe coil.
5. Adsorption vessel.
6. Condenser.
7. Measuring cylinder.

FIG. 66. Arrangement of Apparatus for Steaming Out.

Having carried out the preliminary test the main test is carried out in a similar manner except that two adsorption vessels are employed, thereby ensuring that all the solvent has been stripped completely. Having adsorbed for 30 minutes or such time as will ensure complete stripping by the two adsorbers, the latter vessels are stoppered and steamed out. The adsorbers are placed in a heating bath (160–180° C.) containing mineral oil, glycerine or other liquid having a boiling point not less than 200° C. A spiral coil is also inserted in the heating bath with the object of superheating the steam to at least 120° C. A mixture of solvent and water is distilled off; in the case of acetone, it is, of course, in solution in the water, and appropriate tests must be made to determine the solvent content of the distillate. The two vessels are steamed out individually, and their solvent contents noted separately. The solvent content thus determined, with volume of air or gas gives the required concentration. The distillation having been carried out for 20 to 30 minutes at 160–180° C. leaves the carbon practically free from water. The carbon should then be cooled indirectly, after which it is again ready for use. The adsorption as well as distillation processes should be controlled by weighing.

Taking into consideration the high load and practically perfect adsorptive capacity of active carbon, this test is suitable even for the most dilute mixtures and its accuracy is within a few per cent of the concentration to be measured.

CHAPTER IX

ACETATE RAYON, ITS PROPERTIES AND PROCESSING

Acetate rayon possesses the advantage over other forms of rayon that it requires no further treatment after it is spun; viscose rayon, for example, must be desulphured and washed, while collodion rayon must be denitrated before it can be further manufactured. In the case of acetate rayon it may be dyed directly it is spun, unless very pale shades are required, in which case it will require a mild bleaching treatment before dyeing.

Acetate rayon prepared by the dry spinning process has a cream colour, but this is largely due to the oil used to lubricate during the drawing-off process; if it be degreased with ether or other volatile solvent, the threads appear almost white when dry, although in mass they still have a cream shade. The lustre and handle depend, of course, upon the conditions of the spinning process—the lustre may vary from the high glass-like appearance, which was the usual appearance in the early days of the industry, to a soft, subdued lustre closely resembling that of natural silk; the handle depends upon the number and thickness of the filaments in the individual threads—thus, the finer the filaments and, therefore, the greater the number for a given denier, the softer and more silk-like the handle.

With regard to its chemical properties, acetate rayon is practically identical with the cellulose acetate from which it has been spun; its physical properties are changed to some extent, thus, there is generally a fall in the viscosity determined in acetone solution, and the clarity is increased as a result of the extensive filtration which the acetate has undergone preparatory to the spinning process.

The regenerated cellulose rayons resemble cotton in their behaviour with water, that is to say they are readily wetted and imbibe water to a certain extent in consequence of the affinity of the hydroxyl groups they contain for water; acetate rayon contains a very small percentage of free hydroxyl groups, and is therefore only wetted by water with difficulty. It is the least hygroscopic of the rayons as is illustrated by the following figures due to K. Biltz[1]:—

% Rel. Humidity.	*% Increase in weight on dry weight of rayon.*			
	Viscose.	*Acetate.*	*Collodion.*	*Cuprammonium.*
31·0	5·3	1·9	7·0	5·8
53·9	9·3	3·5	13·3	10·4
62·1	10·2	4·4	14·7	11·5
90·9	20·8	9·3	30·2	26·3

The mean temperature at which the determinations were made was about 19° C.

Thanks to its water-resisting property, acetate materials are much less easily stained than are those of other rayons; and because it is less porous than regenerated cellulose it is less readily soiled, and more easily cleansed than many other textile materials.

The microscopical appearance of acetate rayon has been studied by numerous workers, notably A. Herzog.[2] There is much to be learnt from the inspection of acetate rayon with the microscope: longitudinal examination of the individual filaments reveals variations in thickness and thus assists in detecting faults in the spinning process; even more important is the cross-sectional examination, for a well-spun acetate rayon of good and even covering power possesses a regular and almost circular cross-section. The earlier types of acetate rayon were characterized by their bone-like  cross-section, which was due to irregularities in the spinning process due to poor and uneven filtration, variations in feed of spinning solution to the jets, and also in the drawing-off speeds, too rapid and irregular evaporation of solvent, etc. By maintaining rigorous spinning conditions, as has already been indicated in the chapter dealing with the spinning process, acetate rayon of uniform circular cross-section can be produced successfully.

Before considering the tensile strength and extensibility of acetate rayon, mention must be made of the "denier" system of expressing the relation between the weight and length of yarns. This system originated in the Italian silk industry, the denier being an obsolete Italian weight used as the unit of the system.

"Count" is defined as the weight in deniers of 400 ells (equal to 520 yards or 476 metres), the denier being 0·0532 gm. or 0·001875 oz.

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[1] K. Biltz. *Textile Forschung*, 1921, **3**, 91.

[2] A. Herzog. *Die mikroscopische Untersuchung der Seide und der Kunstseide*, 1924.

Owing to the unwieldiness of the figures used in this system, two other methods of expressing count have been developed, viz. the metric system and the Macclesfield system.

In the metric system the count is the weight of 9000 metres of yarn in gm., and is still expressed as deniers.

In the Macclesfield system the denier has a different value again, being equal to $\frac{1}{17}$ of a dram (avoirdupois). Here the count is defined as the weight in deniers of 1000 yards of yarn.

It is extremely confusing that there should be three systems of expressing the count of yarns, but although at first sight they seem very different, it will be found on comparison that a given yarn will have very nearly the same count whichever system is used. For example, if 9000 metres weigh 120 gm., the count on the metric system will be *120 deniers*. Since 9000 metres weigh 120 gm., 1000 yards will weigh 6·88 drams, or *117 deniers* on the Macclesfield system; and 520 yards will weigh 3·58 drams, or *119 deniers* on the Italian system. Although the variation is not very great, the system used should always be mentioned, since the best low denier yarns to-day should not vary more than 1–2 per cent either way.

Tensile Strength and Elongation.—The tenacity of acetate rayon is less than that of viscose when dry, but practically the same when wet. The dry tenacity is less than a quarter of that of natural silk. The following figures are adapted from those given by P. Krais [1] in 1924:—

Fibre.	*Fineness in deniers.*	*Tenacity (gm./denier).*		*Loss*
		Dry.	*Wet.*	%
Viscose	5·3	2·34	1·15	50·8
Acetate	5·0	1·58	1·32	16·4
Natural silk	1·27	6·14	5·75	6·4

More recently (1928) King and Johnson [2] have tested a large number of different rayons over a denier range of 45–300 under standard conditions of temperature and humidity, the yarns being conditioned for at least 30 hours before testing. Accuracy was ensured by testing 20 lengths of yarn taken indiscriminately. When determining the wet tenacity, it was found that immersion of the yarn for two minutes in water immediately before testing was sufficient in the case of regenerated cellulose rayons, but that not less than fifteen minutes' immersion was necessary in the case of

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[1] P. Krais. *Textilind.*, 1924, p. 43.

[2] P. E. King and E. N. Johnson. *J. Soc. Dyers and Col.*, 1928, **44**, 346–50.

acetate. The results were lower than those obtained by Krais (*supra*); at 66 per cent relative humidity almost all the yarns examined had a tenacity less than 1·5 gm. per denier. As before, it was found that the tenacity of cellulose acetate yarns was less than that of viscose in the dry condition, but the wet tenacities were about equal in the two cases. The average wet tenacity was about 0·5 gm. per denier.

As regards extensibility it was found that acetate gives a rather greater elongation than viscose both in the dry and wet condition, and both are considerably more extensible than collodion or cuprammonium rayons. The following are approximately the figures obtained :—

Fibre.	*Per cent Elongation.* *Dry.*	*Wet.*
Viscose	23	27
Cuprammonium . . .	11	11
Collodion	10	10
Acetate	25	30

Typical results for various counts of acetate rayon were as follows :—

Denier.	*No. of filaments.*	*Tenacity (gm./denier).*		*Elongation.*	
		Dry.	*Wet.*	*Dry.*	*Wet.*
45	13	1·14	0·74	19·7	—
60	20	1·14	0·68	20·9	24·7
75	—	1·42	0·97	20·6	21·6
90	30	1·17	0·73	22·2	30·0
100	17	1·14	0·66	23·5	29·7
140	26	1·16	0·66	25·0	33·8
150	26	1·15	0·68	24·6	33·9
170	34	1·17	0·68	24·9	33·5
250	52	1·19	0·69	27·0	36·1
300	52	1·18	0·67	26·1	35·3

The decrease in tenacity with increasing relative humidity is shown by the following figures :—

	Tenacity (gm. per denier) at Rel. Humidity.					
Denier.	56–58	67	69	71	75	91
45	1·23	—	1·14	—	1·03	0·84
100	1·18	1·09	1·06	—	1·02	—
150	1·27	1·20	—	1·15	1·11	0·90

H. Stadlinger[1] has examined a number of varieties of acetate rayon and obtained the following results :—

1. Setilose—Fabrique de Soie Artificielle de Tubize.
2. Celanese—British Celanese, Ltd.

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[1] H. Stadlinger. *Textilber.*, 1930, **11**, 450–8.

3. Rhodiaseta (F)—Soc. pour la Fabr. de la Soie Rhodiaseta, Rousillon.
4. Rhodiaseta (G)—Deutsche Acetat-Kunstseide A.-G., Rhodiaseta, Freiburg.
5. Aceta—Aceta G.m.b.H., Berlin Rummelsberg.
6. Apex—Apex Art. Silk Co., Ltd., Edmonton, London.
7. Drya—N.V. Nederlandsche Kunstzijdefabriek.

	1	2	3	4	5
Acetyl per cent .	53·2	53·8	54·4	54·3	54·9
Viscosity 2 per cent in acetone . .	5·70	5·80	5·55	5·75	8·85
Tenacity (dry) .	1·22	1·23	1·25	1·33	1·34
Tenacity (wet) .	0·64	0·64	0·76	0·78	0·90
Tenacity (dry)* .	1·08	1·08	1·12	1·22	1·36
Elongation (dry) .	28·2	26·0	27·7	24·7	26·4
Elongation (wet) .	31·7	32·2	38·5	32·8	36·4
Elongation (dry)* .	20·5	19·4	21·5	19·9	19·9

* Dry tensile strength after immersion for 0·5 hr. in boiling water. Tenacities are expressed in gm. per denier.

On boiling with water for half an hour, Celanese and French Rhodiaseta were much reduced in lustre and assumed a woolly appearance, but Aceta was practically unaffected under the same conditions.

With regard to dyestuffs it was found that the highest affinity for Cellit dyestuffs was possessed by Setilose, followed fairly closely by Celanese, while the other rayons had much smaller affinities.

The softest handle was possessed by Setilose and Aceta, while Rhodiaseta was the harshest.

The cross-sections of Setilose, Celanese, French and German Rhodiaseta and Aceta rayons were almost circular and slightly indented, while those of Apex and Enka-Drya were ribbon-like and free from indentations.

More recently F. Ohl[1] has published the results of an examination of four brands of cellulose acetates and of the rayons spun from them :—

1. Cellit L—I.G. Farbenind. A.-G.
2. —Verein für Chem. Ind.
3. —Wacker G.m.b.H.
4. —Soc. pour la Fabr. de la Soie Rhodiaseta.

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[1] F. Ohl. *Textilber.*, 1931, **12**, 647–51.

	1	2	3	4
Acetyl per cent	53·97	54·82	53·20	53·80
Sulphuric acid per cent	0·092	0·019	0·022	0·098
Temperature of yellowing	190° C.	210° C.	190° C.	210° C.
Temperature of carbonizing	200 C.	240° C.	200° C.	240° C.

The highest viscosity was possessed by No. 2, determined in acetone solution at 20° C. This acetate also had the greatest tensile strength when spun into rayon, both in the dry and wet condition and gave the most satisfactory cross-section. On boiling the rayons with water that from No. 2 suffered the least loss of lustre and only became slightly woolly; those from 1 and 4 lost most of their lustre and became slightly and very woolly respectively; while that from No. 3 was practically delustred and became very woolly. No. 2 evidently yielded the most satisfactory rayon, and Ohl concludes that cellulose acetate for the production of rayon should have a low sulphuric acid content and yield acetone solutions of high viscosity which decreases but little with rise of temperature and on storage. He also mentions a high acetyl content, presumably because No. 2 has the highest of the four; the variation in these four is negligible in practice, and in any case it is scarcely likely that he was able to determine the acetyl content with sufficient accuracy to be able to give a result to the second place of decimals.

The methods of testing acetate rayon are described in Chapter VII.

Treatment of Acetate Rayon.—The various processes to which acetate rayon is submitted, including weaving and knitting, before it appears on the market in the form of fabrics and garments, will now be considered in some detail. Dyeing processes are dealt with in a separate chapter (Chapter X).

Lustre.—One of the characteristics of natural silk which has given to that fibre so much importance in the textile world is its pleasing lustre. The cause of lustre in textile fibres has already been discussed in Chapter VIII (p. 192), where it is pointed out that lustre is a surface phenomenon depending upon the orientation of the micellæ in the skin of the fibres.

In the early days of the rayon industry, and especially in the case of acetate rayon, the lustre of the threads was too brilliant and harsh; gradually, however, improved conditions in the spinning process and various methods of treating the yarns and fabrics have made it possible to obtain almost any degree of lustre at will from a perfectly matt fibre to one possessing a very high gloss.

The lustre of acetate rayon may be wholly or partially destroyed by the action of boiling water or steam ; with prolonged treatment the fibres take on a woolly appearance. On examining such delustred fibres under the microscope, it is found that they have lost the smooth glassy appearance which they originally possessed and have become indented. As previously indicated the change is probably wholly a physical one, although there is a slight decrease in the acetyl content of rayon so treated. Similar loss of lustre occurs with hot ironing using a damp cloth over the surface of the rayon. Lustre is also destroyed by the action of aqueous solutions of acids and alkalies, especially hot solutions. Here, of course, there is a considerable loss of acetic acid, the amount depending on the concentration of acid or alkali, and on the time for which the treatment is continued ; and in such cases Greenhalgh attributes loss of lustre to the surface hydrolysis, rather than to physical causes.[1] " Blinding " or loss of lustre also occurs during dyeing with certain dyestuffs, and according to F. M. Rowe this is due to crystallization of the dyestuff within the fibre.[2]

Various methods of treatment have been patented for preventing delustring of acetate rayon in presence of boiling aqueous liquids, etc. Thus, A. J. Hall [3] prevents delustring in hot, aqueous liquids by adding to the liquor the minimum amount of a protective salt, the amount actually used depending on the nature of the salt employed. Suitable salts include the chlorides of the alkali and alkaline earth metals, and those of aluminium or magnesium, and the sulphates of the alkali metals and of copper magnesium and zinc, also sodium sulphite, alum, chrome alum, sodium chlorate, potassium oxalate, or sodium nitrate. He claims that the dyeing properties are unaltered by such treatment, and that the process is particularly applicable to the dyeing of acetate-wool union materials. The salts are usually employed in 10 to 30 per cent concentration.

British Celanese, Limited,[4] state that the addition of 0·1 to 3 per cent of ammonium, sodium, potassium, or calcium thiocyanate to the bath prevents or diminishes delustring by boiling liquids.

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[1] Greenhalgh. *Dyer and Calico Printer,* 1926, **55**, 27.

[2] F. M. Rowe. *J. Soc. Dyers and Col.*, 1926, **42**, 207–8.

[3] Silver Springs Bleaching and Dyeing Co., Ltd., and A. J. Hall. B.P. 246,879.

[4] British Celanese, Ltd. B.P. 282,722.

A. J. Hall[1] has also stated that if the filaments of acetate rayon in the fully set and finished condition are stretched beyond the elastic limit, i.e. from 15 to 20 per cent elongation, with or without previous treatment with a swelling agent for cellulose acetate (e.g. acetone, alcohol, formaldehyde or glycerol), the fibre can be boiled for one hour without curling, losing lustre, or becoming woolly.

Relustring.—Numerous methods have been suggested for restoring the lustre of delustred acetate rayon. British Celanese, Limited (and others)[2] treat the yarns or fabrics with aqueous solutions of one or more swelling agents for cellulose acetate such as acetic acid, phenol, benzyl alcohol, triacetin, cyclohexanone, and ammonium or other thiocyanate. The duration of the treatment depends on the agent used and the degree of lustre desired. In general the temperature should not exceed 30–40° C., and from one to five hours is a convenient time for the treatment to continue. The same firm[3] have covered another process in which the rayon is immersed in boiling or nearly boiling aqueous solutions of neutral salts or sugars. Suitable salts include ammonium, sodium, potassium, and aluminium chlorides or sulphates. In an example, the yarn is immersed in a boiling solution of 2–3 per cent ammonium sulphate and 5–10 per cent cane sugar for 10 to 40 minutes. The material may also be treated with a swelling agent such as ammonium thiocyanate previous to such immersion.

Clavel[4] submits acetate materials which have been purposely or accidentally delustred to the action of swelling agents, such as formic and acetic acids, acetone, thiocyanates, etc., followed by exposure to dry steam, preferably under slight pressure, and under conditions which preclude the deposition of moisture.

The Bleachers' Association, Limited, restore lustre to acetate rayon by the application of ethyl lactate or ethylene glycol monoethyl ether, followed by drying.[5]

Acetate materials may also be relustred by the application of steam of at least 20° of superheat at ordinary or preferably increased pressure, according to British Celanese, Limited.[6]

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[1] Silver Springs Bleaching and Dyeing Co., Ltd., and A. J. Hall. B.P. 277,089.

[2] British Celanese, Ltd., Briggs, Kidd, and Palmer. B.P. 259,265.

[3] British Celanese, Ltd., Palmer, and Fulton. B.P. 259,266.

[4] R. Clavel. B.P. 269,605.

[5] Bleachers' Association, Ltd. B.P. 301,567–8.

[6] British Celanese, Ltd., Ellis, and Olpin. B.P. 349,980.

Delustring and Modification of Lustre.—The lustre of acetate rayon may be wholly or partially destroyed by various methods. The rayon may be treated with hot aqueous liquids with or without swelling agents for cellulose acetate. Thus, in 1920 the British Cellulose and Chemical Manufacturing Co., Ltd., with Dreyfus,[1] Briggs, and Clotworthy described the treatment of acetate materials with hot water or steam, solutions of thiocyanates or acetic acid, followed by drying without tension. This renders them more or less crinkled in appearance, and softer to the touch than before treatment, as well as reducing the lustre. The patent recommends the use of water at 80° C. or at the boiling point, while solutions are used at ordinary temperatures. The same firm later prescribed treatment with hot or boiling aqueous liquids (with or without delustring agents) or with steam, and cane sugar is added as a protective agent.[2]

G. B. Ellis, for Rhodiaseta,[3] has covered regular delustring without loss of strength or elasticity by soaking for 2–24 hours in a 10–30 per cent solution of calcium, lithium, or magnesium chloride, and. after squeezing treating with boiling, dilute acid (0·1–0·01N) for 1–20 minutes. The same firm describe the treatment of acetate materials at 40–80° C. in aqueous emulsions of organic swelling agents or solvents for cellulose acetate.[4] Such substances include cyclohexanone, cyclohexanol, di- and triacetins, methyl phthalate, anisole, etc., in concentrations of less than 5 per cent.

The I.G. Farbenind. A.-G. have covered a delustring method,[5] which consists in impregnating the materials to be treated with urea solution, and after drying they are steamed for 20–30 minutes, followed by washing and drying. The delustring effect of urea can be increased by adding water soluble aliphatic, or hydroxycarboxylic acids or their salts to the solution.

British Celanese, Limited,[6] impregnate the materials with triethanolamine followed by steaming or treatment with a hot aqueous liquid. Di- or triethanolamine may also be used. In a later

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[1] British Cellulose and Chemical Mfg. Co., Ltd., Dreyfus, Briggs, and Clotworthy. B.P. 165,164.

[2] British Celanese, Ltd., Palmer, and Fulton. B.P. 260,312.

[3] G. B. Ellis (for Rhodiaseta). B.P. 301,335.

[4] Soc. pour la Fabr. de la Soie Rhodiaseta. B.P. 313,072.

[5] I.G. Farbenind. A.-G. B.P. 345,673.* Addn. to B.P. 309,194.*

[6] British Celanese, Ltd. B.P. 355,466.

patent,[1] the same firm with Ellis and Storey describe the use of hot aqueous solutions of phenols for delustring acetate rayon. For example, complete delustring may be achieved by immersing the material in 0·1N phenol at 75–95° C. A softer handle is secured by adding soap to the bath, and the specification states that delustring and dyeing may be effected simultaneously.

The deposition of white or opaque substances in a finely divided condition within the fibres also brings about modification of the lustre of acetate rayon. This is due to the scattering of the incident light which is caused by the added substance. Such deposition may be made during the spinning process by addition of finely divided substances to the spinning solution, or by the addition of a metallic compound to the spinning solution followed by an after treatment of the rayon with a suitable reagent to bring about precipitation of an insoluble compound within the fibres. It may also be achieved by treating the rayon in a swollen condition with colloidal dispersions of suitable substances. The following processes illustrate the available methods.

H. Dreyfus [2] covers the addition of finely divided substances to the spinning solution; substances mentioned include barium sulphate, zinc oxide, insoluble silicates, etc. The insoluble substance should be ground dry, graded, and finally ground wet in presence of a dispersing agent and a protective colloid to give particles of 0·0005 to 0·0025 mm. diameter. In a later patent [3] he adds to the spinning solution organic fibrous materials such as cotton, linen, straw, wheat husks, wool, or artificial fibrous materials, in a finely divided condition.

British Celanese, Limited, Riley, Parkinson, and Sims [4] have described the spinning of solutions of cellulose acetate containing 0·5 to 4 per cent of titanium dioxide having a particle size of 0·0001 to 0·00035 mm., for the production of rayon having a modified lustre. (The specification also mentions the use of zinc oxide and barium sulphate, and states that the opacity may be increased by the addition of 2–6 per cent of boric acid or a borate (calculated on the weight of titanium dioxide added)).

Gardner [5] impregnates with 4 per cent of its weight of a soluble

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[1] Br. Celanese Ltd., with Ellis and Storey. B.P. 358,574.*

[2] H. Dreyfus. B.P. 338,490.* [3] Ibid. B.P. 344,510.

[4] British Celanese, Ltd., Riley, Parkinson, and Sims. B.P. 341,897.*

[5] Gardner. B.P. 290,263.

titanium salt, which is hydrolysed within the fibre at 65–100° C., giving a matt deposit of an insoluble titanium compound.

British Celanese, Limited, and Parkinson[1] have described a delustring process which consists in treatment with colloidal solutions of inorganic substances, such as alumina, titanium dioxide, tin dioxide, silica, zinc oxide, etc. The use of a swelling agent at the same time facilitates absorption. The same firm[2] later covered a process in which the rayon is impregnated with a dispersion containing rubber latex and one or more insoluble substances such as zinc oxide, zinc sulphide, aluminium hydroxide, and preferably also containing a swelling agent such as a thiocyanate or acetone, followed by drying. Mineral pigments may also be introduced in the same manner.

Delustring by the deposition of organic substances within the fibres has been described by the Silver Springs Bleaching and Dyeing Co., Ltd., and A. J. Hall. In the first patent[3] anthraquinone, or a derivative thereof (which is colourless in the oxidized state), is deposited in the fibres in the reduced or leuco state. In a later patent[3] the material is treated with aqueous suspensions of aliphatic acids containing ethyl oxalate, followed by ammonia treatment, whereby oxamide is formed within the fibre giving reduced lustre and a "scroop" handle. The delustring is fast to soaping.

Some years ago the I.G. Farbenind. A.-G. proposed to delustre acetate rayon by mechanically roughening the surface by abrasion with powdered glass, pumice powder, emery powder, or silica.[4] The patent is no longer in force, but the British Celanese, Ltd., and Taylor have[5] covered a similar process using kieselguhr (120 mesh), pumice powder, powdered glass, carborundum, or emery. Other abrasives which are soluble in solvents and can therefore be removed completely when the process is complete include sodium sulphate, alum, and sodium chloride. Such a process must have a deleterious effect on the strength of the rayon.

Lustre Pattern Effects.—The sensitivity of cellulose acetate materials to various reagents and treatments renders it particularly

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[1] British Celanese, Ltd., and Parkinson. B.P. 343,121.

[2] British Celanese, Ltd. B.P. 346,511.

[3] Silver Springs Bleaching and Dyeing Co., Ltd., and A. J. Hall. B.P. 316,169. and 316,638.

[4] I.G. Farbenind. A.-G. B.P. 309,194.*

[5] British Celanese, Ltd., and Taylor. B.P. 328,247. Cf. 335,204.

suitable for the production of pattern effects. For example, British Celanese, Limited, and G. H. Ellis[1] print or stencil the fabric with one or more substances which prevent the delustring action of hot or boiling aqueous media or steam, followed by treatment with moist steam, which delustres the portions which are not protected. Other effects may be obtained by printing with substances which accelerate delustring. A similar process covered by the same firm[2] involves local treatment (e.g. by printing) of the fabric with an aliphatic carboxylic acid, followed by steaming. Succinic and citric acids accelerate delustring; acetic, chloracetic, and propionic acids retard delustring. Hydroxy acids are said to be particularly advantageous.

A simpler process of producing mottled or printed pattern effects due to the same firm[3] consists in damping the materials in the required design and then ironing them at 100° C. or higher. By suitably adjusting the moisture content and/or the temperature of ironing, it is claimed that any required degree of lustre may be obtained.

The process of restoring lustre due to the Bleachers' Association, Limited, and described above[4] may be applied to the production of pattern effects. For example, the material is first completely delustred by padding with soap solution and steaming; it is then printed with a thickened paste containing ethyl lactate or ethylene glycol monoethyl ether, followed by drying and washing. Suitable dyes may be added to the printing paste.

An interesting method of producing lustre pattern effects described by the British Celanese, Limited,[5] consists in weaving together two types of acetate yarns, one of which can be readily delustred with boiling water or soap solutions, the other being more resistant, and then subjecting the fabric to a suitable delustring process.

Weighting.—The weighting of acetate rayon yarns is usually accomplished by precipitating an insoluble metallic compound (usually of tin) within the fibres. British Celanese, Limited, have a number of patents relating to such methods. For example,[6] they impregnate the materials at 45–65° C. with an aqueous solution

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[1] British Celanese, Ltd., and G. H. Ellis. B.P. 266,777.

[2] Ibid. B.P. 277,414.

[3] British Celanese, Ltd. B.P. 295,043.*

[4] See n. 5, p. 219.

[5] Ibid. B.P. 310,845.

[6] Ibid. B.P. 258,874.

of a metallic salt which is also a swelling agent, and then treat them with a reagent which will precipitate an insoluble compound within the fibre; e.g. one part of acetate rayon is soaked in thirty parts of a stannic chloride solution of density 1·2, for half an hour at 40–50° C., and after rinsing it is transferred to a solution of disodium hydrogen phosphate of density 1·035. After further rinsing the material is treated with a solution of sodium silicate of density 1·035, and finally it is washed. It is claimed that material so treated has an increased resistance to heat. In an addition to this patent [1] it is claimed that weighting may be effected at lower temperatures in presence of zinc chloride, or other zinc salt. A modified process,[2] in which a precipitating agent is not used, consists in treatment with a solution of a metallic salt, e.g. stannic chloride of such concentration that it acts as a gelling agent to the cellulose acetate, or a more dilute solution may be used if the material is first treated with a swelling agent such as phenol, formic acid, or a thiocyanate. The metal is fixed by washing with water, or a dilute alkaline soap solution. A combined mordanting and loading process due to the same firm [3] consists in treating the materials with alkaline solutions of a tin salt, under such conditions as to bring about partial hydrolysis, with or without the addition of swelling agents. It is claimed that materials so treated can be dyed with direct, mordant, or vat dyes, as well as with basic and insoluble colours.

Dreyfus [4] states that increased quantities of loading agents can be introduced into acetate rayon if it be treated with an aqueous solution of a swelling agent such as glycollic acid, lactic acid, etc., before or during each stage of the process. Suitable swelling agents are 7–10 per cent acetone, 30 per cent alcohol, 15–20 per cent diacetone alcohol, or 10–20 per cent ammonium thiocyanate. In an addition to this patent [5] the use of thiocarbimides, cyanates, or carbimides (particularly those of the alkali metals and ammonium) urea, urethanes, thiourea, and thiourethanes, guanidine, or their alkyl, aryl, or aralkyl derivatives, as swelling agents is claimed. In a further addition [6] it is claimed that improved results are

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[1] Ibid., Ellis and Olpin. B.P. 309,876. Addn. to 258,874.
[2] British Celanese, Ltd. B.P. 279,502.†
[3] Br. Celanese Ltd. and Ellis. B.P. 302, 775.
[4] H. Dreyfus. B.P. 281,084.
[5] Ibid. B.P. 284,798. Addn. to 281,084.
[6] British Celanese, Ltd., Dreyfus and Ellis. B.P. 285,941. Addn. to 281,084.

obtained if the loading solutions contain a thiocyanate in a proportion which is less than that which is chemically equivalent to the loading metal present.

Clavel also has a number of patents relating to the loading of acetate rayon. For instance,[1] the material is passed through a bath containing 5 litres of a 10 per cent solution of albumen and 50 gm. of ammonium carbonate. After squeezing, the material is transferred to a second bath containing a 4 per cent solution of stannic chloride, acidified with 10 per cent of phosphoric acid. It is claimed that the dried fabric exhibits an increased affinity for sulphonated direct dyestuffs. In an addition to this patent [2] the materials are first given an acid reaction by immersion in an acid solution (solution of phosphoric or chloracetic acid or of aluminium sulphate) to which a protective colloid such as glue may be added, if desired. Alternatively the acid and colloid may be added to the impregnating bath. The acid may be removed by subsequent treatment with a cold alkaline bath. In a further specification,[3] Clavel proposes to weight acetate rayon by printing or padding with a metallic salt such as stannic chloride, in admixture with an acid or acid salt and a thickening agent, followed by suitable treatment (e.g. with an alkali phosphate) to convert the metallic salt into an insoluble derivative.

British Celanese, Limited,[4] have also patented a weighting process which consists in treating the materials with tannic acid solution of such concentration (e.g. 30 per cent) as to exert a swelling effect. The materials are immersed in the solution and maintained at 50–70° C. for one-half to two hours. The tannic acid is preferably, but not necessarily, fixed by treatment of the materials with a solution containing tartar emetic or stannic chloride. It is claimed that yarns and fabrics treated in this manner exhibit increased resistance to heat, slipping, and laddering.

Sizing.—The sizing of textile materials is necessary to protect the threads from damage in the various processes of a mechanical nature, such as weaving, to which they are submitted in the course of manufacture. The sizing process consists in the application of an adherent dressing which will strengthen the threads and fix loose and broken filaments in position, thus protecting them from

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[1] R. Clavel. B.P. 277,602.

[2] Ibid. B.P. 280,094. Addn. to 277,602.

[3] Ibid. B.P. 300,894.

[4] British Celanese, Ltd. B.P. 260,290.

further damage. Such treatment is particularly necessary in the case of acetate rayon, which is comparatively weak, and has a high elasticity.

A good sizing material should not affect the lustre of the rayon, nor should it decrease the elasticity to such an extent as to render the yarn brittle. It should be of a uniform nature, and after it has been applied and dried it should form an even coating, the threads being free from variations in " stretch ".

Starchy pastes as usually prepared are not suitable for the sizing of rayon, since they contract on drying. Commercial dextrin made up into a 10 per cent solution by mixing with a suitable amount of water, and boiling for a quarter of an hour forms a simple sizing material for woven fabrics. It should be applied in the cold. Gum arabic is also used, usually in admixture with other materials, since alone it tends to make the threads brittle. In this respect gum tragacanth is to be preferred. Gelatine gives an elastic coating, but has poor keeping properties.

There are also a number of patented preparations for the sizing of acetate rayon. For example, British Celanese, Riley, and Awcock[1] describe a sizing material suitable for Celanese, consisting of a water insoluble soap of resin or naphthenic acids and one or more lubricating agents such as non-volatile drying oils, fats, waxes, or liquid or solid fatty acids, and also one or more resins, e.g. dammar resin or gum mastic. Calcium, magnesium, zinc, and aluminium soaps are preferred. The composition is prepared by dissolving the constituents in an indifferent volatile solvent such as benzene, toluene, xylene, or oil of turpentine, and the solution is applied to the yarn by dipping or during winding, or it may be applied as the rayon is produced by the dry spinning process. The amount used is from 5–10 per cent on the weight of the rayon. It is not brittle, dusty, or sticky.

The I.G. Farbenindustrie A.-G.[2] make use of water soluble hydroxy alkyl ethers of carbohydrates such as starch or cellulose. These are obtained by treating the carbohydrate with alkylene oxides (e.g. propylene oxide) in presence of aqueous alkalies at the ordinary temperature, until the product is soluble in water. The product is neutralized with acid and used as a size. It can be

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[1] Br. Celanese Ltd., Riley, and Awcock. B.P. 244,947.

[2] I.G. Farbenind. A.-G. B.P. 341,516.

removed by washing the materials with water. Similar compounds have been claimed by British Celanese, Limited.[1]

British Celanese, Limited, Dreyfus, and Taylor[2] have covered the use as sizing materials of polymerized, or partly polymerized, vinyl acetate, etc., dissolved in alcohol or benzene, or the polymerization may be effected on the fibre.

Size may be applied to acetate materials in one of several ways; thus, it may be applied as the threads are leaving the spinning cabinet before they are wound; or the rayon yarn may be sized by immersion in a bath of size while in the form of hanks; again, it may be sized and dried during transference from one bobbin to another; or finally it may be sized on the warp beam.

Hank sizing is very simple and is largely used but is liable to give rise to difficulties due to unevenness, and adhesion of the individual threads, unless the operation is performed with great care.

Bobbin to bobbin sizing is perhaps the most satisfactory method, as the threads are certain to obtain an even and uniform coating. The machine for carrying out this process is of very simple construction.

Beam sizing was originally carried out on a machine similar to the one used for cotton warps, suitably modified to meet the requirements of the rayon industry. It is more usual now, to employ a machine in which the threads pass over a roller lightly furnished with size, followed by drying by passing over heated cells, either at a small distance from the surface of the cells or in direct contact. The threads are then rewound on the weaver's beam.

Special methods of sizing have been patented from time to time. Thus British Celanese, Limited,[3] impregnate the yarn in packages or on bobbins, with suitable sizing material, in an air-tight chamber. The sizing material is in the form of a solution in a volatile solvent, and to assist penetration the chamber is evacuated, or the pressure is increased, or both expedients may be adopted alternately. After removing from the chamber the yarn is unwound, dried by evaporation, and rewound.

Winding.—The winding of acetate rayon is carried out on machines similar to those used for the winding of natural silk. Owing to its extremely delicate nature, and the small amount of

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[1] British Celanese, Ltd., Dreyfus, Dickie, and Sowter. B.P. 344,528.
[2] British Celanese, Ltd., Dreyfus, and Taylor. B.P. 346,267.
[3] Br. Celanese, Ltd., Addy, Billing, and Halkyard. B.P. 264,382.

twist in the threads, it requires very careful manipulation if damage is to be avoided.

There are a number of methods of winding, according to the form in which the rayon is initially wound, and the purpose for which it is required. In the dry spinning process the rayon is usually received on cylindrical bobbins. If it is to be dyed before further treatment it must be rewound in hank form. This is achieved by winding it on to collapsible reels, which usually have a circumference of 44 inches. The thread is cross-wound on the reels and the machine is so constructed that it stops automatically in the event of a thread breaking, if the bobbin is empty, or if the required length has been wound. In the last case the hank is tied with coloured thread ("lease-band") and removed from the reel. It is then ready for dyeing and processing. The important point in this and all winding machines for acetate rayon is the absence of all rough or abrasive surfaces on parts which come into contact with the threads, and the avoidance of undue tension and sharp bends in the travel of the threads.

A machine for winding in the reverse direction, i.e. from hank to bobbin, is illustrated in Fig. 67. The principle is similar to that of the bobbin to hank machine.

Yarns may be wound either from the original bobbins or from hanks on to warping bobbins for the preparation of warp beams for weaving, in cheeses for the same purpose, on paper tubes for the loom shuttle, or on pirns (bottle bobbins) and as conical cheeses for knitting machines.

The precautions which must be observed in the winding of acetate rayon may be summarized as follows :—

(*a*) The yarn must not be subjected to friction or abrasion.

(*b*) It must not come into contact with a stationary surface ; if it is necessary to change the direction of travel, this must be achieved by passage over a smooth pulley of as large a diameter as possible.

(*c*) Tensioning must be a minimum, consistent with avoiding loose winding ; it must also be uniform, otherwise defects will be caused at a later stage.

(*d*) Winding speed should be constant and not too great. In winding cones, pirns, and similar forms, the machine should be fitted with an automatic tension varying device, to allow for the variation in speed due to the form of the cone.

(*e*) The winding rooms should be free from draughts, and maintained at a reasonably constant temperature and humidity. The latter is not so important with acetate rayon as with the regenerated celluloses, since the former does not readily absorb moisture from the atmosphere (or lose it in the case of dry atmospheres). A relative humidity of 60 per cent at 65° F. is suitable.

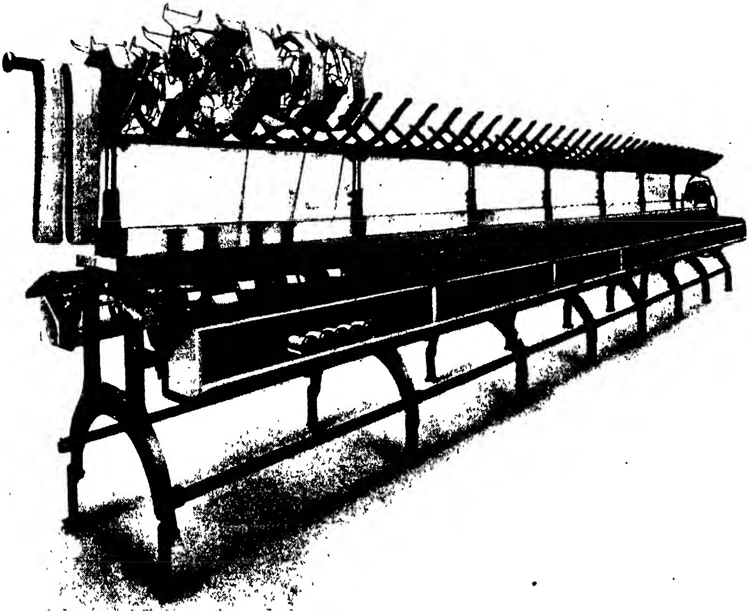

FIG. 67. Hank to Bobbin Winder. (Prince Smith & Stells, Ltd.)

Weaving.—The weaving of acetate rayon is, in principle, the same as that of any other textile material, but there are important differences in detail. It is essential, for example, that the weaving shed shall be clean and well-lighted. Individual drive is to be preferred, since it is more even than that obtained with the use of overhead shafting and belting; there is also the advantage that dirt is not dropped from belting, nor oil from bearings on to the yarns or fabrics. Other precautions will be mentioned during the description of the various operations.

All weaving processes comprise three stages, viz. preparation of the warp, preparation of the weft, and the weaving operation proper.

Preparation of the Warp.—The warp beam consists of a wooden or metal roller, with flanged ends, on which are wound " ends " or lengths of yarn, in sufficient number to make up the width of the fabric which is to be woven. It is essential that these ends shall be wound parallel with uniform tensions throughout. Yarns intended for warp ends are usually wound twice in order to secure even tensioning, i.e. they are wound on bobbins, from which they are rewound on the warp bobbins.

A typical warping mill is shown in Fig. 68. It consists of three principal parts: a " creel " or rack, shown at the back of the photograph, which holds the bobbins, these may number 400 or more according to the denier of the yarn and the width of the piece; the mill proper, which is a hollow cylinder, 40 to 60 inches in diameter, built up as shown; and the supports which hold the beam during the warping process.

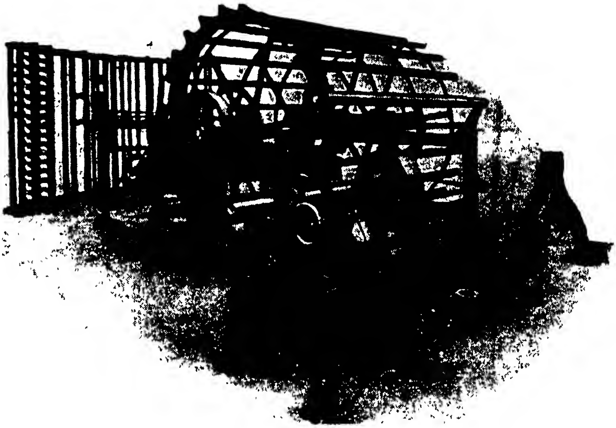

Fig. 68. Warping Mill. (Wm. Whiteley & Sons, Ltd.)

The ends pass from the bobbins on the creel through a " reed ", a comb-like arrangement, which serves to separate the ends and keep them parallel, and then through a second reed, which feeds them in the required width to the tensioning rollers of the mill. The warp is usually built up in sections of 6–8 inches. As the mill rotates, it draws the threads from the creel through the reeds, to which is imparted a slow lateral motion, and a layer of ends is thus laid on the mill at the left-hand side (looking at the figure) where the bars have an upward taper. In the photograph this first series of ends is shown in process of being laid on. When the first layer is complete, the reeds are moved and a second layer is wound on the mill, and so on until the whole width of the warp is built up.

The warp having been wound on the mill, a beam is placed in position in the bearings on the opposite side of the mill from the creel, and the ends of the warp threads are attached to it in a suitable manner, after which they are unwound from the mill by rotating the beam; a lateral motion is imparted to the beam in the opposite sense to that of the reeds in the first operation, so that the threads are wound evenly and parallel to each other on the beam.

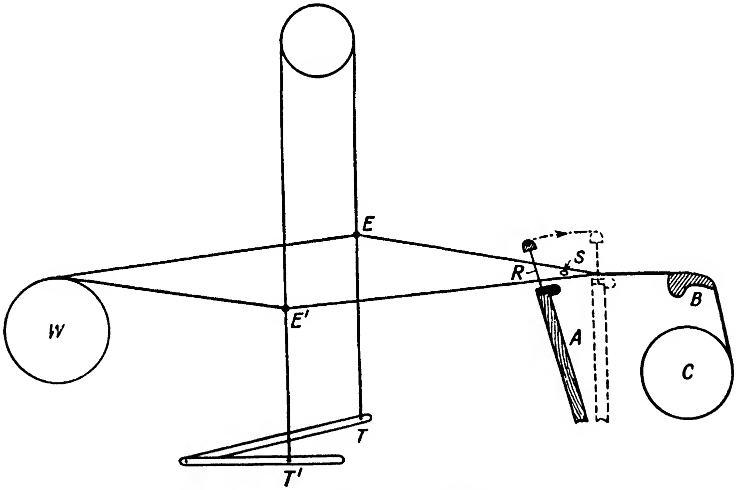

FIG. 69. Diagram of Loom Mechanism.

Preparation of the Weft.—This is a simple matter compared with the warping and beaming process, and consists in winding the yarn from hank to bobbin, and from bobbin to paper tubes or shuttle bobbins, which, when filled are fitted into the shuttle of the loom.

Weaving.—The warp beam having been prepared, it is placed in the bearings provided at the rear of the loom. The description of the weaving process will be best understood by reference to the diagrammatic representation in Fig. 69. From the warp beam W,

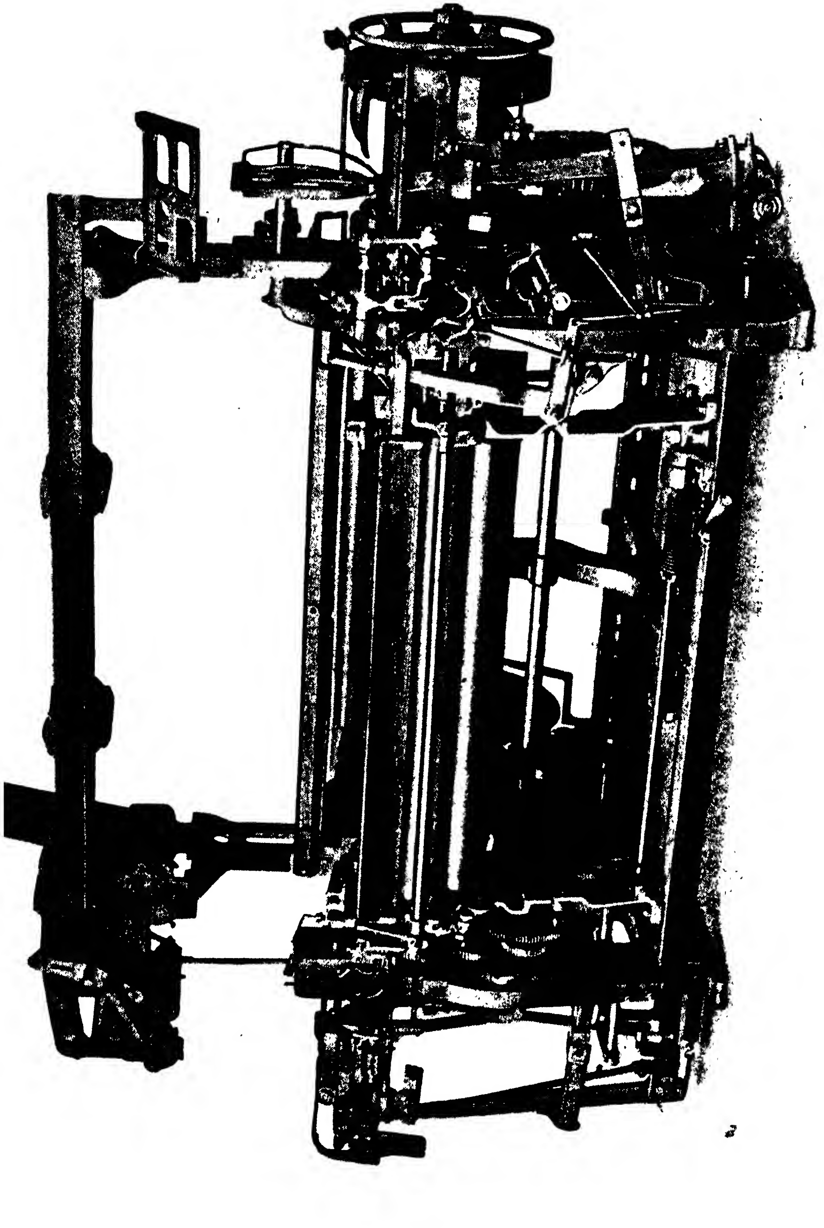

FIG. 70. Modern Rayon Loom. (The Northrop Loom Co., Ltd.)

the threads or ends are passed over the back bearer B, which is a wooden bar covered with velvet (in some looms this back-bearer is omitted, the warp passing directly to the " fell " of the cloth, in order to avoid change of direction in the ends, and contact with a stationary surface), and are then threaded through eyelets E, E′, in the " healds ", which are fixed in shafts, consisting of wires or cords, which can be moved in a vertical direction. The ends are passed through these eyelets in an order determined by the pattern of the weave. After leaving the healds the threads pass through a reed R, fixed on a horizontal bar called the " sley ", which is attached at either end to a member A, called the " sley sword ", these members being pivoted at the bottom so that a to and fro motion can be imparted to the sley, in the direction of the warp.

The action of the loom in weaving can be divided into three movements, " shedding," " picking," and " beating-up." Shedding consists in the division of the warp threads into two sections, as shown in the diagram, by the movement of the shafts of the healds; in this way a " V "-shaped opening or " shed " is formed at the take-off end of the loom. Picking consists in the insertion of a " pick " or thread of weft into this shed by the passage of the shuttle from one side of the loom to the other. As soon as such a pick has been inserted the sley sword moves forward, carrying with it the reed R, which " beats-up " the weft thread into its final position, in close proximity to its predecessor. At the same time the position of the healds is reversed by the action of the treadles T, T′, or some other mechanism, so that a new shed is formed with the threads reversed. The shuttle again passes through the shed, inserting a fresh pick, which is in its turn beaten up, and the cycle of operations is repeated in the above order until the piece is completed. The cloth passes over a smooth piece of wood B, and is wound on the cloth roller C.

The above description is necessarily simplified; in practice the action of the loom is complicated by the introduction of various types of weaves and patterns. The mechanical devices by which the various operations are performed are not described. Fuller information is available in various textbooks on weaving, such as *The Preparation and Weaving of Artificial Silk* (Pitman), by T. Woodhouse.

The illustration Fig. 70 shows a modern loom for silk and rayon goods. It is a special two shuttle model, and is fitted with a two-colour battery. The let-off motion is controlled by the special Automatic Roper let-off, and the back rest is highly polished to reduce friction on the warp yarn. The sley is specially prepared, with corduroy raceboard cover, and a glass rod behind the reed, also for the purpose of minimizing friction. The emery roller is covered with filleting, and the take-up roller is of large diameter and polished, so that the machine is well adapted to the weaving of acetate rayon goods.

Regarding the construction of a loom for weaving acetate rayon, this should be as rigid as possible. It is very important that the warp threads should be as free as possible from vibrations due to the action of the loom. It is quite common to mount the warp beam in supports which are separate from the main structure of the loom, and the warp should be kept stretched taut, without excessive tension, during weaving. The object of using two shuttles is to allow of the use of a mixed weft, thus blending the rayon threads which compose the weft and concealing irregularities. The shuttles should be so constructed that the thread runs freely without tensioning, such tensioning being frequently the cause of "bright picks", i.e. threads having an increased lustre. Barring in the direction of the warp is due to irregular tension in the warp ends. Other causes of barring are irregularities in the original yarn, due to non-uniform stretching in course of manufacture. A comprehensive article dealing with such defects was published in the *Silk Journal* in 1927 by Hegan and Shearer,[1] where an interesting test for over-stretching is given. The procedure is as follows: The yarn is wound in a single layer on a metal cylinder of 10 cm. circumference, and a mark is made across the threads parallel to the axis of the cylinder so that the yarn is divided into lengths of 10 cm. The yarn is then unwound, moistened, and dried without tension so that any stretched portions will partially contract. When dry the yarn is rewound on the cylinder. If the yarn has been partially over-stretched, the mark will no longer be straight, but will form a series of periodic curves corresponding to the periodic stretch which has been applied to the yarn.

Types of Weave.—There are ~~four~~ three main types of weave: known respectively as the plain, twill, and satin weaves. The plain weave as its name implies is the simplest form of weaving and is of great

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[1] Hegan and Shearer. *Silk Journal*, 1927, No. 32, p. 67.

antiquity. It is characterized by the fact that each weft thread passes alternately over and under the warp threads, giving close interlocking. In the twill weave, the weft threads pass over a number of warp threads, and then under the same number, the points of intersection shifting by the space of one warp thread at each pick, thus giving a diagonal effect. The satin weave has regular intersections, which are nowhere in contact, and the face of the material is composed entirely of warp or weft threads. In this type of weave, the concealed yarn is frequently of cheaper material than the facing yarn..

The plain weave is used for cheaper materials, such as crepe de chines, taffetas, shantungs, etc., since it is very simple to produce, and gives the maximum output for a given weight of yarn. The twill weave is found in duvetyn, charmeuse, and similar fabrics, while the satin weave, as its name implies, is used for all kinds of satin fabrics. Velvets are made by the satin weave, using a double warp or weft. The double yarn forms loops which are afterwards cut to produce the pile.

Fabrics less than about 40 cm. wide are classed as ribbons. These are usually made with satin weave on a special loom, which produces up to 100 at a time.

Knitting.—Knitted materials, especially those which are made wholly from acetate rayon, are not so durable as woven fabrics. The operation of knitting machines is very clearly described in *Artificial Silk* by T. Woodhouse (p. 166 et seq.). The principles are the same as those which govern machine knitting with other yarns, but many difficulties have had to be dealt with when adapting them to knitting with rayon. It is necessary, for example, to lubricate acetate threads, preferably with an emulsion of olive oil in soap solution, as otherwise, the threads are of too rigid a nature and will not loop properly. Knitting machines work at high speeds, and it is therefore necessary to adopt some device which will prevent excess thread unwound from the bobbins from being caught. Draughts in the workrooms are particularly deleterious, as the threads in passing from the bobbins to the needles are easily blown about and may become entangled in moving parts of the machine, causing breakages, with consequent loss and slowing down of production.

Production of Effects.—It has already been indicated that acetate rayon is particularly suitable for the production of all kinds of ornamental effects. Those depending upon local intensification or reduction of lustre have already been described above. Other processes include the production of woolly effects on acetate yarns and fabrics, production of brocade effects, ornamentation with metallic powders, and also by removal of parts of the fabric by means of solvents, production of pile, cockled, crepe, and other effects, etc.

Clavel [1] produces woolly effects by treatment with dilute acetic or formic acids at the boiling point, the effect being restrained by the addition of a protective colloid.

The Calico Printers' Association and Roberts [2] treat acetate fabrics with a mercerizing agent other than caustic soda in selected areas only. In this way brocade effects are produced, and in some cases, on dyeing, the fabric exhibits peculiar coloured pattern effects, the dyeing properties of the treated portions having undergone modification.

Embossed effects are produced by impregnating acetate fabrics with a volatile swelling agent such as water, aqueous solutions of thiocyanates, alcohol, acetone, etc., and then subjecting to heat and pressure.[3] Similar effects can be produced on circular knitted fabrics by spraying with a softening agent diluted with a non-solvent for cellulose acetate, e.g. aqueous acetone, followed by an embossing process.[4] Embossed materials may receive further treatment by the application of effect materials to the raised portions; thus, local saponification effects may be produced followed by cross dyeing.[5]

Ornamental effects can be obtained by printing acetate fabrics with a paste containing one or more solvents for cellulose acetate and an inert powder such as barium sulphate or calcium carbonate, and a thickening agent such as starch, dextrin, or casein. The material is then maintained at 50–125° C. for some time, followed by washing with water, whereby the printed portions are completely removed.[6] Velvets having an acetate pile may be printed with mineral acids or their acid salts, which destroys the pile locally, and it may then be removed by brushing, giving pile pattern effects.[7]

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[1] R. Clavel. B.P. 206,818.

[2] Calico Printers' Association, Ltd., and Roberts. B.P. 215,860.*

[3] British Celanese, Ltd., Dickie, and Halkyard. B.P. 273,406.

[4] British Celanese, Ltd. B.P. 291,445*.

[5] Ibid. and Felgate. B.P. 323,210.

[6] British Celanese, Ltd. B.P. 263,555.*

[7] Ibid. and G. Rivat. B.P. 302,592.

Effect materials such as metallic, luminous, phosphorescent, or delustring powders can be applied to acetate rayon while the filaments are still sticky, by means of an air blast directed across the path of the filaments.[1]

A cockled appearance may be produced in acetate fabrics containing cotton yarns suitably distributed, by treating with nitric acid of density 1·14–1·30 for 1–5 minutes, followed by washing and drying. The acetate threads shrink more than the cotton, thus producing a cockled or pebbled appearance.[2] Caustic soda solution may be used for a similar purpose.[3]

Ribbons or tapes may be made from acetate yarns by the application of heat or pressure continuously or intermittently.[4] Embossed, ornamental, and other effects may be produced at the same time.

Several processes have been devised to raise the safe ironing temperature of acetate fabrics. They may be treated, for example, with dilute caustic soda solution to produce a regular and partial hydrolysis, not exceeding 6 per cent [5]; or a similar effect may be produced by the action of the vapour of ammonia or volatile organic bases.[6] Alternatively the caustic soda may be applied in the form of a paste containing thickeners, followed by drying, steaming, and washing.[7] An entirely different method due to Courtaulds [8] consists in adding a solution of an organic ester of silicic acid to the spinning solution, or treating the yarns or fabrics with such a solution.

The slipping, laddering, or splitting of woven and knitted fabrics, due to lack of cohesion between the threads, may be minimized or prevented by [9] impregnation at 80° C. with aqueous dispersions or solutions containing at least 8 per cent of one or more of the following substances: higher fatty acids or sulphonated fatty acids or their soluble salts, sulphoaromatic fatty acids or their soluble salts, or resin soaps. Alternatively [10] the materials may be treated at 80° C. with organic solvents for cellulose acetate such as toluene or methylated spirit, or with

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[1] British Celanese, Ltd., and Taylor. B.P. 341,057.

[2] British Celanese, Ltd. B.P. 342,075.

[3] Ibid. B.P. 345,022.

[4] H. Dreyfus. B.P. 341,034.

[5] British Celanese, Ltd. B.P. 304,596.

[6] Ibid. B.P. 313,971.

[7] Ibid. B.P. 316,521, and Addn. Pat. 318,468.

[8] Courtaulds and Diamond. B.P. 317,936.

[9] British Celanese, Ltd., and Ellis. B.P. 280,989.

[10] Ibid. B.P. 280,990.

5 per cent solutions or dispersions of such solvents in water. In both cases the materials are matured before scouring and finishing.

Various processes of producing fabrics which contain acetate rayon and possess a crepe appearance have been patented. For instance, mixed cotton-acetate fabrics treated with dilute nitric acid of 30–50° Tw., at temperatures of 0–50° C., assume the appearance of crepe de chine.[1] Fabrics woven from acetate yarns, some of which have been shrunk by the action of dilute nitric acid (density 1·1–1·22) at 0–60° C.—are again subjected to this treatment in the woven condition; this gives rise to irregular shrinkage, producing crepe-like effects.[2] Another method consists in treating fabrics which contain twisted threads of acetate rayon with swelling agents such as alcohol or benzene.[3] Crepe effects may also be produced by weaving a fabric with highly twisted yarn and then impregnating it with a swelling agent which becomes effective on dilution with water,[4] or the twisted yarn may be so treated before weaving.[5] The fabric is eventually scoured with an aqueous liquid. Suitable swelling agents include acetone, alcohol, or alcohol-benzene. Other methods based on the use of tightly twisted yarns are as follows: Highly twisted yarns of degummed natural silk are woven into a mixed fabric with acetate rayon, and the product is treated with hot aqueous liquids.[6] Or acetate yarns sized with a polymerized vinyl derivative or an artificial resin containing a softening agent such as olive oil, are highly twisted and incorporated in a fabric. This is afterwards scoured in an aqueous soap solution, or with an agent which will swell the threads or the sizing material without causing the latter to become soft. A suitable agent is xylene dispersed in water by means of a sulphonated oil.[7] Finally a process of creping may be mentioned in which highly twisted yarns are impregnated with an emulsion of a swelling or gelatinizing agent and dried. These yarns are incorporated in a fabric which is treated in such a manner (scouring or steaming) as to promote the swelling action.[8]

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[1] Bleachers' Association, Ltd., and others. B.P. 274,584.
[2] British Celanese, Ltd., Dickie, and Moncrieff. B.P. 335,180.
[3] G. B. Ellis (for Rhodiaseta). B.P. 335,020.
[4] British Celanese, Ltd., and Dickie. B.P. 351,999.
[5] Ibid. B.P. 352,000.
[6] British Celanese, Ltd. B.P. 352,113.
[7] H. Dreyfus. B.P. 352,451.
[8] British Celanese, Ltd., Dickie, and Moncrieff. B.P. 356,233.*

There are a number of specifications dealing with the subject of fireproofing acetate fabrics. Cellulose acetate is not readily inflammable, but when it is submitted to the action of a flame it melts and eventually burns. If it be treated with an aqueous solution containing 15–16 per cent of arsenic, stibinic, or phosphoric acid, followed by rinsing and drying, it will melt but does not ignite in a flame.[1] Another method of rendering films, fabrics, etc., of cellulose acetate less inflammable is to incorporate in them, at some convenient stage of the manufacturing process, one or more aliphatic acyl derivatives of nuclear chlorinated arylamines of the benzene series, such as o-chloroacetanilide[2]; alternatively one or more aromatic compounds containing bromo-substituted aliphatic side-chains such as benzyl bromide, in the proportion of 2–40 parts per 100 of cellulose acetate, may be used for the same purpose.[3] Other halogenated compounds which have been proposed as fireproofing agents for acetate materials include mono- or diacetylated tribromaniline in the proportion of 7–10 per cent,[4] and from 2–25 per cent of a bromo derivative of a lower fatty acid, e.g. tribromophenyl acetate.[5] It is claimed that acetate materials treated with this last compound do not discolour on prolonged exposure to ultra-violet light.

Waterproofing methods resemble those applied to other textile materials, but special methods of application have been devised. For example, insoluble metal soaps are introduced into fabrics by treating them simultaneously or successively with a swelling agent and a soluble metallic salt, followed by immersion in an aqueous solution of soluble soaps of fatty acids[6]; or the fabric may be treated with an emulsion of wax in soap solution after being swelled with a suitable agent.[7] The soap is also precipitated in the fabric by the action of a metallic compound applied before or after the emulsion.

Among other processes of treating acetate rayon may be mentioned those for producing "scroop". Scroop is a special quality of handle possessed by natural silk, which is difficult to describe, but familiar to most people, and which can be imparted to acetate rayon by treating it with an oil emulsion, e.g. olive

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[1] British Celanese, Ltd. B.P. 296,344.*

[2] Ibid. B.P. 312,609.

[3] Ibid. B.P. 313,134.

[4] Ibid. and Daly. B.P. 319,073.

[5] British Celanese, Ltd. B.P. 357,667.

[6] British Celanese, Ltd., and Ellis. B.P. 323,501.

[7] Ibid. B.P. 323,785.

oil-soap emulsion, usually immediately after the dyeing process. A method due to British Celanese, Ltd.,[1] consists in treatment with a solution or suspension of a salt of tartaric, citric, oxalic, or other polybasic aliphatic acid. Such treatment may be combined with an oil emulsion process, and the material is afterwards dried in a stretched condition, without washing.

Acetate fabrics may also be submitted to other finishing processes common to textile materials in general, such as pressing, stretching, calendaring, etc., due regard being paid to the special requirements of this material. In particular, acetate rayon is very liable to crease, and the greatest care is therefore necessary in operations such as dyeing to avoid the formation of permanent crease marks. If such occur, they can be removed by rewetting the fabric, followed by drying in a stretched condition on a stentering frame. Over-stretching must, of course, be avoided, since it weakens the material. The drying of acetate fabrics should be as rapid as possible, in order to avoid loss of lustre, but at the same time the use of too high a temperature should be avoided, since it would soften the yarn, leading to stiffness and brittleness in the finished materials.

Uses of Acetate Rayon.—The earlier uses of acetate rayon were as a substitute for a part of the natural silk in certain fabrics, i.e. the fabrics were woven with an acetate weft and a silk warp, or vice versa, thus cheapening the materials produced. With the development of new methods and machinery, and with a growing realization and appreciation of its special qualities, the use of acetate rayon has gradually extended and it is to be found to-day in almost every variety of textile work. It would be impossible to enumerate all the different types of goods in which it is to be found, but mention may be made of a few of the more important ones, which include woven and knitted fabrics of all kinds for dresses and underwear; hosiery, especially in admixture with other yarns; all classes of embroidery and knitting yarns; neckties; coat linings; and brocades and upholstery materials.

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[1] Br. Celanese, Ltd., and Ellis. B.P. 354,200.

CHAPTER X

DYEING AND PRINTING

A very clear exposition of the theories concerning the dyeing of acetate silk, and a comprehensive review of the patents relating to this subject have been given by C. E. Mullin in his book *Acetate Silk and its Dyes*. Since, however, a work which deals with the manufacture of cellulose acetate and its various applications could scarcely be considered complete without some reference to the dyeing and printing of acetate rayon, it has been thought advisable to include a chapter dealing with this very important subject.

Perhaps the most difficult problem which faced the chemists of the cellulose acetate industry in its early days was that of dyeing. Indeed, so great were the difficulties encountered that they considerably retarded the commercial development of the infant industry, and it is hard to realize nowadays, when we are familiar with a wide range of beautifully coloured acetate fabrics of all descriptions, the existence of these difficulties. It is gratifying to know that the majority of the developments which have been made in this sphere during the past ten or twelve years are the result of the work of British chemists.

Unlike the other forms of rayon which are regenerated cellulose, and therefore possess similar dyeing properties to cotton or other cellulose fibres, cellulose acetate rayon still remains an ester in which the hydroxyl groups which confer upon cellulose and regenerated cellulose their affinity for direct dyestuffs are bound to acetyl residues, and are therefore not available to exercise this affinity. This absence of free hydroxyl groups also accounts for the low wetting power of acetate rayon in aqueous liquids, a property which presents a further obstacle to ready and even dyeing. The earliest attempts to dye acetate rayon were made with known classes of dyestuffs, and it is not surprising therefore that they were attended with so little success; it was not until 1922 with the discovery of the Ionamines by Green and Saunders of the British Dyestuffs Corporation that special classes of dyestuffs for acetate rayon were introduced, but from that time steady progress has been made in the production of new dyestuffs, and in the evolution of new methods of application.

It was early realized that if the surface of the cellulose acetate fibre could be deprived of its acetyl groups by saponification, the rayon would then possess an outer skin of regenerated cellulose having much the same affinity for dyestuffs as viscose, cuprammonium and other regenerated cellulose rayons. The earliest patent relating to such a process was granted to H. S. Mork of the Lustron Company[1] in 1910, covering the use of caustic soda, ammonia, or sodium carbonate as saponifying agents. C. F. Cross and C. Dreyfus[2] described the saponification of cellulose acetate fibres with an ethyl or methyl alcoholic solution of an alkali or base, the latter being present in an amount less than the equivalent of the acetic acid in the cellulose acetate.

A number of patents have also been granted in which it is sought to minimize the somewhat violent action of caustic alkalies by various means. Thus the Société Chimique des Usines du Rhône[3] have covered the use of salts which set free a little alkali, and a patent of addition[4] covers the use of a salt having an alkaline reaction together with the neutral salt of an alkali metal. The British Cellulose and Chemical Manufacturing Co., Ltd., and J. F. Briggs describe a saponification process in which a very dilute solution of caustic soda (not more than 1 per cent), in quantity sufficient to produce a diminution in weight in the rayon of 10 per cent or less, is the reagent used.[5] In a later patent the same firm mention the addition to the saponification bath of sodium chloride, sulphate, or other salt in concentrations up to 5 per cent[6] for the purpose, no doubt, of repressing the ionization. Similar patents cover the use of aluminates, borates, or silicates, either alone or with alkali,[7] and sodium acetate in concentrations up to 5 per cent.[8]

The saponification process is now practically obsolete; it had a number of serious objections, for example, the saponification was

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[1] H. S. Mork. B.P. 20,672/1910.*

[2] C. F. Cross and C. Dreyfus. B.P. 125,153.*

[3] Soc. Chim. des Usines du Rhône. B.P. 150,989.*

[4] Ibid. Addition to 3. B.P. 192,994.*

[5] British Cellulose and Chemical Manufacturing Co., Ltd., and J. F. Briggs. B.P. 169,741.

[6] British Cellulose and Chemical Manufacturing Co., Ltd., and L. G. Richardson. B.P. 175,485.

[7] Ibid. B.P. 175,486.

[8] Ibid. B.P. 176,034.

only superficial, and the core of the threads consequently remained undyed; the treatment caused loss of weight; it was difficult to obtain even dyeing on rayon so treated; and there was a diminution in lustre and strength. In connection with this process, other methods of conferring affinity for direct and other dyestuffs may also be mentioned. Thus, the Society of Chemical Industry in Basle[1] spin a cellulose acetate solution containing from 5 to 20 per cent of nitrocellulose, the resulting fibre being denitrated with 10–20 per cent alkali or alkaline earth hyposulphite solution at 65° C. The resulting rayon is claimed to have good affinity for acid, basic, and vat dyestuffs. A similar principle is involved in a patent due to H. Dreyfus,[2] who proposes to diminish the water repellent properties, and to increase the affinity of acetate rayon for direct or mordant dyestuffs, by impregnating the materials with cellulose by treating with viscose, cuprammonium, zinc chloride, etc., solutions of cellulose and precipitating in the usual manner, or by treating with a solution of nitrocellulose in a non-solvent for cellulose acetate, followed by denitration with a dilute ammoniacal solution of a sulphydrate.

Abortive attempts were also made to colour the fibres *ab initio*, i.e. by the acetylation of previously dyed cellulosic materials,[3] or by the addition of dyestuffs to the spinning solutions.[4]

The dyeing of acetate rayon with the aid of solvents or swelling agents is also obsolete, although the principle is still of considerable importance in connection with dyeing "assistants". The theory underlying their use depends upon the micellar conception, the swelling process separating the micellæ, and facilitating the entry of the dyestuff particles. One of the earliest patents for the dyeing of acetate fibres (concerned with the triacetate) was granted to the A.-G. für Anilin Fabrikation[5] in 1905, and covered the addition of alcohol, acetone or glacial acetic acid to the dyebath. The swelling action of thiocyanates was patented by the British Cellulose and Chemical Manufacturing Company, Limited (with Briggs and Palmer),[6] in 1919, and covers the use of ammonium thiocyanate

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[1] S.C.I. in Basle. B.P. 268,363.

[2] H. Dreyfus. B.P. 323,521.

[3] Farbenfabr. vorm. Fr. Bayer & Co. D.R.P. 237,210.

[4] L. A. Levy. B.P. 226,309*; 227,146.*

[5] A.-G. für Anilin Fabrikation. D.R.P. 193,135/1905.

[6] Briggs, Palmer, and the British Cellulose & Chemical Manufacturing Co., Ltd. B.P. 158,340.

either before, during or after dyeing. It is claimed that such treatment increases the affinity of the fibre for basic, acid, direct, vat, and other dyestuffs. The solution is applied in concentrations of 5–25 per cent, and the length of treatment varies from 2–30 minutes according to the temperature of the bath. The process is also obsolete as far as dyeing is concerned, although it is still of considerable importance from the point of view of printing. It has certain drawbacks, for example, the use of too much thiocyanate exercises a delustring effect. Briggs states that the action of the thiocyanate is to increase the surface of the fibre.

The swelling action of mineral acids upon cellulose acetate has also received attention in this connection. Knoevenagel[1] mentions the use of hydrochloric, hydrobromic, nitric, and sulphuric acids. Here there is probably some surface hydrolysis of the fibres in addition to the swelling action, and similar results are obtained by the employment of ethyl hydrogen sulphate and similar compounds.[2]

The use of strong salt solutions as swelling agents in the dyeing process has also been suggested. The Bayer Company[3] have described the employment of nitrates of ammonium, sodium, etc., or of organic bases such as aniline, pyridine, and so on, to obtain deeper shades without the use of protective colloids. Mullin[4] suggests that this patent probably covers the use of such products as Celloxan and Acetane, which are dyeing assistants for acetate dyeing.

Special Dyestuffs for Cellulose Acetate.—The earliest special class of dyestuffs for use with acetate rayon was the Ionamines, which were discovered by Green and Saunders of the British Dyestuffs Corporation, Limited, about 1922. Originally Green and Saunders considered that dyestuffs containing hydroxyalkyl radicals attached to a nitrogen atom possess affinity for cellulose acetate on account of the carbinol groups which they contain. They prepared a number of azo compounds of this type, but without great success; the simpler bases soluble in water had an affinity for cellulose acetate, but this affinity decreased with an increasing number of carbinol groups. They then decided that the dyeing of acetate rayon was mainly a problem of solution, and that it was determined by the following factors: Amino, substituted amino

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[1] E. Knoevenagel. U.S.P. 981,574/1911.

[2] J. Y. Johnson (for Badische Anilin u. Soda Fabr.). B.P. 240,514.

[3] Bayer Co. B.P. 216,838.

[4] Mullin. *Acetate Silk and its Dyes*, p. 148.

or hydroxyl groups should be present in the dyestuff molecule, but strongly acid groups such as the sulphonic should be absent, since such groups inhibit, or at all events, reduce the dyeing properties of the compounds in which they are present. Basic compounds used in the form of an aqueous solution of the hydrochloride should be readily hydrolysed when dissolved in water yielding the free base, since it is this, and not the salt, which is taken up by the fibre. The free base should be soluble in water, even though it be only sparingly. The molecules should not be too large, since molecular complexity tends to diminish the solubility of the dyestuff in the fibre. These views are in fairly close agreement with Clavel's theory, which will be considered later in connection with theories of dyeing. As a result of lengthy researches based upon these conclusions, compounds were prepared which were found to possess the desired characteristics. These compounds have the general formula $X.NR^1.CHR^2.SO_3H$, that is to say, they are ω sulphonic acids, in which X is a hydrocarbon nucleus and R^1 and R^2 are alkyl groups or sulphonic acids of amino alkyl groups.

Such compounds, while stable in neutral solutions, are readily hydrolysed by heating with dilute acids or alkalies, changes which may be represented by the following :—

$$C_6H_5.N:N.C_6H_4.NH.CH_2SO_3Na + HCl + H_2O \rightarrow$$
$$C_6H_5.N:N.C_6H_4.NH_2 + HCHO + SO_2 + NaCl + H_2O$$
$$C_6H_5.N:N.C_6H_4.NH.CH_2.SO_3Na + NaOH + H_2O \rightarrow$$
$$C_6H_5.N:N.C_6H_4.NH_2 + HCHO + Na_2SO_3 + H_2O$$

The free bases are almost insoluble in water, but are soluble in acetate fibres, for which they possess the usual high affinity characteristic of amino compounds. The ease with which these compounds are hydrolysed is accounted for by the fact that the sulphonic group is situated outside the nucleus of the dyestuff molecule.

The first patent relating to the Ionamines[1] states that although compounds of the type $X.N_2.Y.NH.CH_2.SO_3H$ and $X.N_2.Y.N_2.Z.NH.CH_2.SO_3H$ are unstable in presence of alkalies, if the group X contains a para nitro group, on reduction with

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[1] A. G. Green, K. H. Saunders, and the British Dyestuffs Corporation, Ltd. B.P. 197,809.

sodium sulphide, the N methyl ω snlphonic groups remain intact, and a second ω sulphonic residue can then be introduced into the molecule by treatment with formaldehyde-bisulphite. Examples are given of the reduction in the cold of monoazo dyestuffs derived from p-nitraniline and the sodium N-methyl ω sulphonates of aniline, 2-amido-4-cresolmethylether, and naphthylamine; and of the secondary disazo dye from p-nitraniline, 2-amino-4-cresolmethylether and aniline N-methyl ω sulphonate of sodium; the last-named compound may be diazotized on the fibre and developed. The specification indicates that the compounds which contain no sulphonic group in the nucleus are of special value in dyeing acetate rayon.

There are a number of other patents relating to the Ionamines which need not be considered in detail. References to these are given below.[1]

The Ionamines are readily soluble in water and can be mixed with direct dyestuffs. They produce very level shades in a dyebath of about 20 to 100 times the weight of material to be dyed, provided the temperature is not raised too rapidly. They possess a certain degree of affinity for cotton, those having the greatest affinity for acetate having the smallest for cotton and vice versa—the same also applies to regenerated cellulose. Woollen goods are dyed by the unhydrolysed dyestuff in an acid bath, but are not affected by the free base. The chief disadvantages of these dyestuffs are the uneven penetration experienced in the dyeing of corded materials, and the occurrence of phototropic effects, i.e. a darkening on exposure to light. Green and Saunders state that nearly all yellow aminoazo bases exhibit this phenomenon on acetate rayon, the effect being most pronounced with the greener shades. The cause has never been clearly explained, but Greenhalgh[2] compares it with the desmotropism of p-nitrosophenol, which is white under certain conditions, and yellow under others. The white compound is p-nitrosophenol $OH<\overline{\underline{\qquad}}>NO$ and the yellow is quinoneoxime $O=<\overline{\underline{\qquad}}>=N.OH$. He suggests that the position or connections of the azo coupling in certain azo dyes may be altered by the action of light, thus producing the phenomenon of phototropism.

Dispersol Type of Dyestuffs.—Shortly after the discovery of the

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[1] Ibid. and G. H. Frank. B.P. 212,029, 212,030. British Dyestuffs Corporation, Ltd., W. H. Perkin, A. W. Fyfe, and M. Mendoza. B.P. 252,922.

[2] Greenhalgh. *Dyer and Calico Printer*, 1926, **55**, 146.

Ionamines, a second class of special dyestuffs made their appearance, together with new methods of application. The development of these dispersion dyes and processes was initiated by G. H. Ellis and the British Celanese, Limited. In a paper in the *Journal of the Society of Dyers and Colourists*[1] in 1924, Ellis indicates the lines on which this development took place. It was realized that the affinity of a dyestuff for cellulose acetate depends upon its basicity, and decreases if sulphonic acid groups are introduced into the molecule (and to a less extent if other acid groups are introduced). These acid groups can, however, be present depending upon their orientation in the molecule. The affinity is also dependent upon the molecular complexity or degree of aggregation of the dyestuff—the larger the particles the less the speed of diffusion into the fibre. Furthermore, the dyes most suitable for acetate rayon are those having a limited solubility in water. It was found that many dyestuffs which are insoluble or very sparingly soluble in water, can be dissolved in sulphoricinoleic acid, as well as in some of the higher fatty acids or their sulpho derivatives. If a solution of a dyestuff obtained in this manner is diluted with water, the dye remains dispersed, and the resulting dispersion is well adapted to the dyeing of acetate rayon. In this way the SRA dyestuffs of British Celanese, Ltd., originated, and according to the earliest patent relating to this type of dyestuff,[2] azo dyes which are free from sulphonic groups, dyes of the indophenol, di- or tri-phenyl methane, azine, oxazine, thiazine, or indigoid series, basic anthraquinone derivatives, the indophenols and indigoid dyes in unreduced form, and basic dyes in the form of free bases, can all be applied to acetate rayon in this manner.

A later patent[3] substitutes for sulphoricinoleic acid, carbocyclic compounds containing salt forming groups. Naphthenic acids, naphthalene sulphonic acids, or other carboxylic or sulphonic acids of the cycloparaffins, phenolsulphonic acids, etc., may all be used for the dispersion of dyestuffs. For example, m-nitrobenzene azodiphenylamine is heated and stirred with naphthenic acid; water or soap solution is added, and the mixture is made slightly alkaline with caustic soda and boiled; the resulting solution dyes acetate rayon yellow.

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[1] G. H. Ellis. *J. Soc. Dyers and Col.*, 1924, **40**, 285–90.

[2] British Celanese, Ltd., and G. H. Ellis. B.P. 219,349.

[3] Ibid. B.P. 224,925.

A large number of patents have been granted in connection with dispersol methods of dyeing acetate during the past seven or eight years, and references to these will be found in the footnote below.[1]

The use of the SRA dyestuffs is, of course, limited to users of Celanese yarns and materials. The procedure recommended by British Celanese, Limited, is as follows :—

The yarn is first scoured, for example with a solution containing about 1·5 gm. of olive oil soap per litre, and 1 c.c. per litre of ammonia (0·880) at 75° C. for half to one hour. An addition of "Celascour", another proprietary article of British Celanese, Limited, is also recommended. After well rinsing and bleaching, if necessary (in the case of pale shades) the yarn is immersed in a solution of the dyestuff preparation in soft water or soap solution, and dyeing occupies one to one and a half hours at 75° C. Certain SRA dyestuffs are suitable for diazotization and development on the fibre.

The SRA dyestuffs are obtainable in a considerable variety of shades, and are generally very satisfactory, giving level dyeings, which are fast to light, acids and alkalies, and soaping. They are dealt with in considerable detail by Mullin in *Acetate Silk and its Dyes.*[2]

Two classes of dyestuffs of the dispersol type are available for general use on acetate yarns and fabrics ; these are the Duranol colours of British Dyestuffs Corporation, Limited, and the Celatene colours of Scottish Dyes, Limited. Mullin [2] considers that the original patents concerned with the Duranol dyestuffs are B.P. 201,610, 225,678, 227,923. The first of these describes the manufacture of dyestuffs by condensing the p-sulphonic chloride of salicylic acid with diaminoanthraquinones, or by condensing halogen anthraquinones with anthranilic acid ; the second covers the condensation of aminoanthraquinones with other o-carboxylic acids ; and the third relates to acid dyestuffs obtained by condensing 4 : 8-dihalogenanthraquinone with two molecules of an aminobenzoic acid and reducing the nitro group of the product. There is no reference in the specifications to dispersion methods

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[1] **British Celanese, Ltd., and G. H. Ellis. B.P. 237,943, 242,393, (with Goldthorpe) 242,711, (with Goldthorpe) 253,978, (with Goldthorpe) 269,960 ; British Celanese, Ltd., and Ellis. B.P. 273,819, 273,820, 284,376 * (with Olpin) 305,556,† (with Olpin and Kirk) 321,401.**

[2] **Mullin. *Acetate Silk and Its Dyes*, p. 313.**

of dyeing, but the products are only very sparingly soluble in water, and are therefore capable of application in that manner. The first reference to dispersion methods by the British Dyestuffs Corporation [1] refers to the dyeing of acetate rayon in yellow to blue shades by means of aqueous dispersions of aminoanthraquinone dyestuffs, especially in presence of Turkey red oil. Other patents which probably refer to Duranol dyestuffs are referred to in the footnote below.[2]

The method of application of the Duranol dyestuffs is very simple, the paste colour being added to the dyebath (at 45° C.) after stirring with a little water. The temperature of the dyebath is gradually raised to 80° C., and maintained at that temperature for about half an hour. The yarns or fabrics require no after-treatment.

The Duranol dyestuffs are of excellent fastness to light, washing, alkalies, acids, etc. They differ from the SRA dyestuffs in being solubilized by a medium which is not of a soapy nature.

The Celatene colours are mostly anthraquinone derivatives, solubilized by substances of a soapy nature. They include such compounds as triaminoanthraquinone, hexaminodianthraquinonylthioether, amino-2-substituted anthraquinones, etc. References are given below.[3]

Although these dispersion dyestuffs are triumphs of British chemical research, the methods have naturally not failed to receive attention on the Continent. Thus the Cibacet and Celliton dyestuffs of the Society of Chemical Industry in Basle and the Celliton dyestuffs of the I.G. Farbenindustrie A.-G. are dispersed anthraquinone derivatives. The former firm cover the use of sulphite cellulose pitch (lignosulphonic acids) for the dispersion of non-sulphonated dyestuffs [4] The dye is ground with the pitch and evaporated if necessary. The product disperses readily in water, especially in presence of soap or sulphonated soaps. They have also described the use as dispersing agents of sulphite cellulose lye,[5] and of saponin or a condensation product of formaldehyde and a naphthalenesulphonic acid.[6] The I.G. have described the use of

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[1] British Dyestuffs Corporation, Ltd., Baddiley, and Shepherdson. B.P. 221,720.*

[2] British Dyestuffs Corporation, Ltd., and others. B.P. 224,077, 227,923,† 246,984, 257,353, 268,933, 270,428.

[3] Scottish Dyes, Ltd., and others. B.P. 214,765, 230,116, 231,206, 238,936, 243,505.

[4] Soc. Chem. Ind. in Basle. B.P. 249,549.

[5] Ibid. B.P. 263,579.

[6] Ibid. B.P. 300,399.

molasses for dispersing insoluble or sparingly soluble compounds excluding vat dyestuffs, e.g. a preparation of three parts of aminoazobenzene and three parts of molasses forms a suitable dyebath on mere dilution with water.[1]

Other dyestuffs of the dispersion type include the Direct Azonines of the Cassella Company, which, as the name implies, are various azo derivatives ; the Extra Pastes of the Badische Company, which Mullin suggests are composed as follows: Yellow 3G Paste, a nitraniline derivative ; Yellow R Paste, an aminoazo derivative ; Orange Extra Paste, Rose R Paste, Red-Violet Extra Paste, and Blue Extra Paste, aminoanthraquinone derivatives ; the Cibacete dyestuffs of the Ciba Company which are sold in powder form and require emulsification with a salt of ricinoleic acid or soap solution ; and in the United States the Newport Chemical Works also market a series of dispersed anthraquinone derivatives in paste form.

The chief difficulty experienced in the early development of dispersion dyestuffs for acetate rayon was the trouble due to the phenomenon of phototropism, which has already been discussed, in connection with the Ionamines.

Basic Dyestuffs.—The use of basic dyestuffs for acetate rayon was mentioned by Briggs in a survey of dyeing methods in 1921. He stated that dyeing proceeds without mordanting, but that the exhaustion of the bath is not good. A remarkable feature in the case of basic dyestuffs which have an affinity for acetate rayon, is the unexpected fastness which they display. A large number of patents have been granted for processes of applying basic dyestuffs to acetate rayon. Thus the Bayer Company [2] have covered the addition of a solvent or dispersing agent for cellulose acetate to the aqueous dispersion of the dyestuff. Suitable compounds are glycol, chlorhydrin, pyridine, and piperidine. A later patent to the same firm [3] is thought by Mullin to cover " assistants " such as Celloxan and Acetane, the compounds mentioned being salts of an oxyacid of nitrogen or chlorine.

Many of the dyestuffs of the Setacyl series (J. A. Geigy) belong, apparently, to the basic group. These colours are applied by dissolving in acetic acid, and adding the solution to the dyebath.

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[1] J. Y. Johnson (for I.G. Farbenind. A.-G.). B.P. 271,550.

[2] Bayer Co. B.P. 214,246,* 215,373,* 215,783.*

[3] Ibid. B.P. 216,838 ; cf. Mullin, *Acetate Silk and its Dyes*, p. 148.

The goods are dyed for a short time at 55–70° C. according to the depth of shade required. They are then removed from the dyebath, and an " assistant " Setacyl Salt A is added to the bath, after which the goods are returned and after 15 minutes a further portion of Setacyl Salt A is added, and after a further two minutes a final addition of assistant is made, if necessary. According to Mullin, the following process probably related to the application of the Setacyl dyestuffs[1]: The rayon is immersed in an aqueous solution containing a dyestuff having little or no affinity for acetate rayon, but which is precipitated by the addition of suitable aromatic compounds, preferably in presence of a protective colloid. Suitable precipitants include sulphonic acids of benzene, naphthalene, and anthraquinone, the salts of these acids, and their hydroxy, alkyl, chloro, and nitro derivatives. Glue or gelatine is a suitable colloid.

Mordanting.—Acetate rayon cannot be mordanted by any of the usual methods using tannin, aluminium salts, etc. Certain mordant dyestuffs, such as alizarin, will dye acetate rayon directly on account of phenolic and ketonic properties, but the shades obtained are, of course, quite different from those obtaining in the usual mordanting methods.

Many special methods of mordanting acetate rayon have been devised. Thus the British Dyestuffs Corporation, Limited, have covered mordanting with iron, aluminium, or chromium salts of thiocyanic, benzoic, or salicylic acids[2]; British Celanese, Limited, treat with a 40–50 per cent solution of a ferric salt, followed by dyeing with logwood[3]; while H. Dreyfus[4] covers mordanting with salts other than ferric chloride in concentrations of 15 per cent upwards. If the temperature at which the goods are treated is greater than 75–80° C., Dreyfus recommends the addition of a protective colloid to prevent delustring. In a later patent,[5] the same inventor states that the mordant metals are best applied to acetate rayon in the form of salts of aliphatic acids, especially hydroxy acids such as lactates, glycollates, citrates, or acetates, in concentrations of 5 per cent or higher. The specification also mentions the use of mixed salts such as aluminium sulphate-acetate, nitrate-acetate, etc., and also of basic salts. British

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[1] J. R. Geigy. B.P. 213,593.*

[2] British Dyestuffs Corporation, Limited. B.P. 240,293.*

[3] British Celanese, Ltd. B.P. 273,692.

[4] H. Dreyfus. B.P. 286,761.

[5] Ibid. B.P. 287,204.†

Celanese, with Rivat and Cadgène, have also covered mordanting with a metallic salt in presence of a swelling agent for cellulose acetate, such as formic or acetic acid, furfural, phenol, pyridine, and especially a mixture of furfural and formic or acetic acid.[1] In a similar specification, H. Dreyfus [2] describes the dyeing of cellulose acetate by treating with a swelling agent such as formic, acetic, or lactic acid, alcohol, acetone, diacetone alcohol, diacetin, mono and polyhydric phenols, thiocyanates, cyanates, thiocarbimides, carbimides, carbamides, urethanes, thiocarbamides, thiourethanes, guanidine, etc., followed by mordanting and dyeing with a mordant dyestuff. There are numerous other patents covering the mordanting of acetate rayon, based on the known properties of cellulose acetate.

Acid Dyestuffs.—Acetate rayon has very little affinity for the older acid dyestuffs, unless they are unsulphonated, or, in certain cases, contain only one sulphonic group. A large number of such compounds have been described, and also special methods for the application of acid dyestuffs to acetate rayon. It is noteworthy that most of these compounds are derivatives of azo compounds or of anthraquinone. Thus the Society of Chemical Industry in Basle have described the preparation of acid azo dyestuffs which give yellow to bluish-red shades on acetate rayon,[3] by coupling unsulphonated nitrodiazo compounds of the benzene series (except those having a hydroxy group in the ortho position to the diazo group) with monosulphonated monoamines of the benzene series not derived from metanilic or m-toluidine sulphonics acids and substituted at the nitrogen atom by a residue containing a benzene nucleus. They have the general formula NR : NXYZ, where R is a non-hydroxylated benzene nucleus carrying at least one nitro group; X is a benzene nucleus not having a sulphonic group in the ortho position to the azo group; Y is a residue containing a benzene nucleus; and Z is a hydrogen atom or alkyl group; and only one of the groups R, X, and Y contains a sulphonic group. British Dyestuffs Corporation, Limited, with Baddiley and Tatum [4] have covered compounds obtained by condensing a glycidic acid with aminoanthraquinone, in glacial acetic acid, with or without a copper catalyst. Thus 1 : 4 diaminoanthraquinone and methyl-

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[1] British Celanese, Ltd., Rivat, and Cadgène. B.P. 273,695.*

[2] H. Dreyfus. B.P. 285,948.

[3] Soc. Chem. Ind. in Basle. B.P. 220,203.

[4] British Dyestuffs Corporation, Ltd., Baddiley, and Tatum. B.P. 224,363.†

glycidic acid yield a blue dye, while 1 : aminoanthraquinone and phenylglycidic acid yield a red dye. British Cellulose and Chemical Manufacturing Company[1] state that acetate rayon, treated with a solution of ammonium thiocyanate before or during the dyeing operation, may be dyed with such acid dyestuffs as Methyl Violet, Dianol Fast Red K, etc. Other references relating to acid dyestuffs are given in the footnote below.[2]

Sulphato Dyes.—This interesting class of dyestuffs was originated by the British Dyestuffs Corporation, Limited, and applied to the dyeing of acetate rayon in 1924. The first patent relating to acetate rayon[3] states that certain of the sulphato dyestuffs described in B.P. 181,750 may be applied to cellulose acetate, These compounds are obtained by introducing into the amino group (primary or secondary) of dyestuffs or intermediates of the benzene and naphthalene series, the alcoholic sulphuric acid group $\text{-R-SO}_4\text{H}$ (R alkylene), the group $\text{-SO}_4\text{H}$ being termed the sulphato group. Methods for their preparation are given in the specification mentioned (B.P. 181,750). Compounds suitable for use with acetate rayon are the sulphato derivatives of monoazo dyestuffs, e.g. p-nitraniline coupled with ethyl sulphatoethylaniline, and the product reduced with sodium sulphide ; and m-nitraniline coupled with sulphatoethylaniline. Dyestuffs of this class are soluble in water and possess an acid character ; they are applied in the same way as acid dyestuffs, and give more level dyeings than the corresponding sulphonic compounds.

H. Dreyfus and H. C. Olpin[4] have also a patent dealing with sulphato dyestuffs, covering the dyeing of acetate rayon with sulphatoethyl derivatives of aminoanthraquinones, e.g. 1--sulphatoethylaminoanthraquinone gives a scarlet colour, 1--sulphatoethyl-1-amino-4-hydroxyanthraquinone - violet. Other examples giving blue, bluish-red, and violet shades are described.

Sulphur and Vat Dyestuffs.—Certain dyestuffs of these classes can be applied to cellulose acetate rayon provided means are adopted

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[1] British Cellulose and Chemical Manufacturing Co., Ltd., Briggs, and Palmer. B.P. 158,340.

[2] British Dyestuffs Corporation, Ltd., and others. B.P. 202,157,* 226,948,† 227,923,† 257,654.* Bayer Co., 225,862. Meister, Lucius, and Bruning. B.P 228,557, 232,599.* I.G. Farbenind. A.-G. B.P. 245,790, 258,611,* 267,695, 269,934, 275,230.* C. M. Barnard and British Alizarine Co., Ltd. B.P. 252,240, 252,646. J. W. Leitch & Co., Ltd. B.P. 261,822.*

[3] British Dyestuffs Corporation, Ltd., Perkin, and Bate. B.P. 237,739.

[4] H. Dreyfus and H. C. Olpin. B.P. 285,641.

to prevent saponification of the fibre. This is achieved by adding substances such as ammonium salts, and by using ammonia in place of caustic alkali in the vat, and also by keeping the temperature as low as possible. Thus, Clavel[1] reduces the dye by hydrosulphite in an ammoniacal bath containing sufficient caustic alkali to combine with the leuco base. To assist exhaustion salts are added such as the chlorides of calcium, barium, or magnesium, and to prevent precipitation colloids such as glue, gelatine, etc., may be added to the vat.

The Ciba dyestuffs are vat dyes and are applied to acetate rayon by making into a paste with caustic soda solution and Monopole soap. The paste is added to hot water followed by concentrated hydrosulphite, and this forms a stock solution. For the preparation of the vat, the stock solution is added to a bath containing hydrosulphite and glue. References to other patents relating to the dyeing of acetate rayon with sulphur and vat dyestuffs are given below.[2]

Developed or Azo Dyestuffs.—Owing to the affinity of cellulose acetate for organic bases, the rayon lends itself readily to dyeing by development methods. The method of application requires very careful attention if level dyeings are to be secured. A number of special acetate dyestuffs belong to this class; for example, the SRA Blacks of British Celanese, Limited, certain Ionamines, and the Azonines of the Cassella Company. The colours may in many cases be applied either in substance, or by applying one component to the fibre followed by diazotization and coupling with the second component.

The earliest British patent relating to the dyeing of acetate rayon with developed dyestuffs is due to Knoll and Company, and was granted in 1907. The dyeing takes place in presence of swelling agents or solvents for cellulose acetate such as dilute alcohol or acetic acid.[3]

In a series of patents R. Clavel[4] has covered various methods and

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[1] R. Clavel. B.P. 191,553.

[2] R. Clavel. B.P. 187,964. W. Kilby and Morton Sundour Fabrics, Ltd. B.P. 214,112.* British Celanese, Ltd. B.P. 220,505, (with Ellis) 262,506, 263,260,* 263,473, 295,579, 347,682. Durand et Huguenin. B.P. 274,094. J. Y. Johnson (for I.G. Farbenind. A.-G.). B.P. 320,027. Wilson, Thomas, and Scottish Dyes, Ltd., B.P. 320,216, and 330,253, probably refer to dyeing with Soledon and Indigosol dyestuffs.

[3] Knoll & Co. B.P. 24,284/1907.*

[4] R. Clavel. B.P. 187,964, 199,754, 204,179.

conditions for the application of azo colours to acetate rayon. He recommends, for example, the addition of soluble salts to the primary bath such as ammonium, sodium, potassium, calcium, barium, magnesium, tin, or zinc chlorides, and states that protective colloids may also be added. He describes the application of base and developer in one bath followed by diazotization in a second bath, or application of the base and diazotization in one bath followed by development in a second bath; or finally, application of the base in one bath followed by diazotization and development in a second bath in presence of protective colloids. He claims the use of temperatures of 60–100° C. for development and also for the application of the base.

There are a very large number of patents relating to developed dyeing methods[1] and also to the dyeing of acetate rayon with azo dyestuffs in substance.[2]

Black Dyeings on Acetate Rayon.—Very considerable difficulty has been experienced in producing a satisfactory direct black dyestuff for acetate rayon, and most of the methods are therefore indirect.

R. Clavel[3] treats the fibre with p-amino-diphenylamine in presence of an acid, followed by oxidation on the fibre.

British Celanese, Limited, with G. H. Ellis and others have developed several oxidation methods for producing black shades. For example, they treat with an amino compound such as aniline, p-aminophenol, benzidine, α naphthylamine, etc., followed by oxidation on the fibre with suitable reagents such as bichromates or chlorates in conjunction with an oxidation catalyst, e.g. salts of vanadium, copper, or iron. After drying without rinsing, the materials are aged by exposure to moist air or steam.[4] Or a suitable

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[1] Burgess, Ledward & Co., and W. Harrison. B.P. 193,646.* S.C.I. in Basle. B.P. 231,455.* British Celanese, Ltd., Ellis, and others. B.P. 253,978, 300,929, 310,779, 319,390. I.G. Farbenind. A.-G. B.P. 262,830,* 275,307.

[2] W. Harrison and Burgess, Ledward & Co. B.P. 190,313.* Badische Anilin u. Soda Fabr. B.P. 204,280.* Farbenfabr. vorm. F. Bayer & Co. B.P. 225,862, 253,457. British Dyestuffs Corporation, Ltd. B.P. 226,948.† Ibid., Horsfall, Lawrie, and Hill. B.P. 275,373. Meister, Lucius, and Bruning. B.P. 243,737. Chem Fabr. vorm. Sandoz. B.P. 245,758.* I.G. Farbenind. A.-G. B.P. 245,790, 258,611,* 269,934, 275,230,* 290,720, 301,564, 327,394, 348,269. S.C.I. in Basle. B.P. 281,704, 343,006, 343,016. H. Dreyfus. B.P. 292,180, 292,453. British Celanese, Ltd., and others. B.P. 298,993, 299,343, 306,981, 310,827, 316,526, 319,308, 343,502, 350,577. B.P. 349,683 to British Celanese, Ltd., describes the application of azo dyestuffs in vapour form, e.g. in steam or by means of transfers, or they can be removed locally to give pattern effects.

[3] R. Clavel. B.P. 194,840.

[4] British Celanese, Ltd., and Ellis. B.P. 255,962.

arylamine is oxidized on the fibre with p-toluenesulphonchloramide or its sodium salt in presence of acid and/or an oxidation catalyst such as vanadium chloride.[1] Mixed cotton-acetate materials are dyed black by treatment with an aqueous suspension of p-aminodiphenylamine or 2 : 4 diaminodiphenylamine which is absorbed by the acetate but not by the cotton. The material is then padded with an aniline black liquor containing aniline hydrochloride, potassium chlorate, and copper sulphate, and is dried and aged at 40–50° C. A black colour develops on both fibres, and finally the material is after-chromed with aqueous sodium dichromate of density 1·005.[2]

A considerable amount of attention to this question has been paid by A. J. Hall on behalf of the Silver Springs Bleaching and Dyeing Co., Ltd., with very successful results judging from the patent specifications. Thus he obtains fast black shades on acetate rayon by applying 2 : 4-diaminodiphenylamine from aqueous solutions or suspensions, followed by immersion in hot or boiling solutions of oxidizing agents; or by impregnation with a paste of an oxidizing agent, a catalyst, an acid and 2 : 4-diaminodiphenylamine followed by exposure to warm, moist atmospheres.[3] In a later patent [4] the compound used is α naphthylamine, and it is oxidized on the fibre by means of nitrous acid. In an addition to the first patent he dyes with 2 : 4-dinitrodiphenylamine, reduces to the diamine on the fibre, and then oxidizes to black as described in the chief patent.[5] He also obtains black shades on acetate rayon by treating with aqueous solutions or suspensions of aniline containing a small proportion of p-aminodiphenylamine (10 per cent) or of p-phenylenediamine, and the resulting fibre is treated with hot acid dichromate solution, saturated, or nearly so, with sodium chloride.[6] He states that it is advisable to add small amounts of copper sulphate and sodium chlorate.

Methods of producing black dyeings on acetate rayon, other than oxidation methods, have also been described. Lawrie, Blackshaw, and the British Dyestuffs Corporation, Limited, apply amines such as α naphthylamine, benzidine, tolidine, and

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[1] Ibid. and Olpin. B.P. 298,699.

[2] British Celanese, Ltd., Mellor, and McLellan. B.P. 351,557.

[3] Silver Springs Bleaching and Dyeing Co., Ltd., and A. J. Hall. B.P. 258,699.

[4] Ibid. B.P. 321,034.

[5] Ibid. B.P. 322,893. Addn. to 258,699.

[6] Ibid. B.P. 337,746.

pp′ diaminodiphenylamine, to the material, followed by diazotization and development with β hydroxynaphthol.[1] The I.G. Farbenindustrie A.-G.[2] dye the rayon with picramic acid coupled with 1 : 8 aminonaphthol. Improved fastness is said to be obtained if the dyeing is diazotized on the fibre and developed with β naphthol or m-tolylenediamine.

British Celanese, Limited, G. H. Ellis, and Miller[3] state that acetate rayon can be dyed with aniline black by using considerably larger quantities of acid in the padding liquor than usual.

The I.G. Farbenindustrie A.-G.[4] claim the production of black shades giving clear white discharges when treated with zinc formaldehyde sulphoxylate, by treating the material with a dyestuff of the type $(4)H_2N.R.N:N.R'.NX_2(4')$, where R and R′ are phenylene residues which may contain halogen or alkyl substituents and X_2 is an aliphatic residue such as methyl-ethyl, $(CH_2.CH_2.OH)_2$, followed by diazotization on the fibre, coupling with β naphthol-3-carboxylic acid. If both components are applied simultaneously and developed with nitrous acid, the discharge obtained with the above-mentioned reagent is yellowish.

Dyeing of Mixed Goods.—On account of the special dyeing properties of cellulose acetate rayon, many varied and beautiful effects are obtainable by the use of mixtures with cotton, other rayons, wool, and silk.

Acetate Rayon-Cotton Mixtures.—(With cotton is included regenerated cellulose rayons such as viscose, cuprammonium, and collodion yarns.) Since direct cotton colours have practically no effect on acetate rayon, the production of resist effects in these mixtures is a very simple matter. Also, on the other hand, cotton and regenerated cellulose rayons are not affected by many of the special acetate dyestuffs, especially the dispersion colours (SRA, Duranol, and Celatene). When using direct, sulphur, or vat dyestuffs for the production of resists in acetate-cotton mixtures, the dyestuff must be chosen with some care, since a number of them stain the acetate to a slight extent. Colours which are very suitable for obtaining resist effects with acetate-cotton mixtures are the CR Chlorazol dyestuffs of the British Dyestuffs Corporation, Limited.

[1] Lawrie, Blackshaw, and British Dyestuffs Corporation, Ltd. B.P. 224,359.†
[2] I.G. Farbenind. A.-G. B.P. 290,720.
[3] British Celanese, Ltd., Ellis & Miller. B.P. 332,624.
[4] I.G. Farbenind. A.-G. B.P. 353,592.

After scouring in a weakly ammoniacal soap bath the material is immersed in a dyebath of 20 to 30 times its weight, and maintained at a temperature of 80–90° C.—higher temperatures delustre the acetate—for thirty minutes to one hour. After dyeing and rinsing the material is given another soaping to clear the white rayon.

Black and other shades on the cotton of mixed fabrics may be obtained by a process of the British Dyestuffs Corporation, Limited,[1] using sulphur dyestuffs. The material is padded in a bath containing 3 parts of the dyestuff dissolved in a solution of 6 parts of sodium sulphide in 160 parts of water, to which has been added a solution of 3 parts of ammonium sulphate in 40 parts of water, the whole being adjusted to 80° C. The material is then rinsed and dried. The thionol colours of B.D.C. are suitable for use in this process, e.g. Thionol Black GSX conc., Thionol Brown B, Thionol Green B, etc. By using this process the acetate rayon is not saponified by the alkaline bath.

Vat dyestuffs such as Duranthrene Blue GCD, Duranthrene Green 2 B, Duranthrene Yellow G extra, Duranthrene Golden Orange Y, Duranthrene Red BN, etc., may be applied to the cotton of mixed fabrics without affecting the acetate, by the use of β-naphthol, and by dyeing at lower temperatures (50–55° C.). Under these conditions the lustre of the acetate is not affected.

Solid shades may be obtained on such mixtures either by one or two bath methods. For example, a bath is made up containing a suitable acetate dyestuff such as a Duranol or Ionamine together with a direct colour. Alkali should not be used in the dyebath. The material is immersed in the bath, and the temperature is slowly raised to 85° C. and maintained from half to one hour. The two-bath method is useful in the case of colours which would precipitate each other if used in one bath ; the method is specially useful where a high degree of fastness is required, such as can only be attained by the use of a vat dyestuff for the cotton component.

Two-colour effects are, of course, obtainable by either the single or double bath method ; for the former care must be taken to select pairs of dyestuffs which do not mutually precipitate, and for the latter the colours used must, of course, withstand cross-dyeing.

By the choice of suitable dyestuffs and their use under stated conditions, similar effects may be obtained on other mixtures, such

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[1] British Dyestuffs Corporation, Ltd. B.P. 238,721.*

as acetate rayon-wool, acetate rayon-natural silk, acetate rayon-cotton-wool, etc.

Printing of Acetate Rayon.—The printing of acetate rayon can be carried out by methods similar to those in use for dyeing, i.e. saponification processes may be used together with, or followed by, application of direct dyestuffs, or special acetate colours may be used. Otherwise the methods do not differ from those generally employed in textile printing. The usual thickeners such as dextrin, gum arabic, tragacanth, etc., are used, and some alkali is included in the direct pastes. Various organic liquids are frequently included in the pastes to improve the penetration.[1]

All kinds of ornamental effects can be obtained by printing acetate rayon with pastes containing various reagents, followed by suitable treatment. For instance, the fabric may be printed with a paste containing one or more solvents for cellulose acetate, an inert powder such as barium sulphate or calcium carbonate, and a thickener such as dextrin, starch, or casein, and after maintaining at 50–125° C. for some time it is washed in water, whereby the printed portions are completely removed.[2] Clavel[3] produces metallic or other effects by coating or printing with a paste containing a thickener, finely divided metal, pigment, or other powder, and a solvent or swelling agent for cellulose acetate. The fabric is dried rapidly, and is then dyed at 80–100° C., washed and stretched. The stretching process fractures some of the treated threads to give a metallic or other effect on a white or dyed background. British Celanese, Limited, have a series of patents relating to the production of effects by carbonization processes. The original patent[4] was directed to the removal of vegetable fibres including regenerated cellulose from fabrics in which such fibres are associated with cellulose acetate rayon, by treating in a carbonizing bath, containing sulphuric acid. To prevent delustring of the acetate rayon, sodium sulphate is added to the bath. The specification states that the dyeing and dye resisting properties of the acetate are unaffected. This process is applied to fabrics consisting wholly of acetate rayon[5] by printing locally with a paste containing alkali. After steaming and washing the regenerated cellulose on

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[1] British Celanese, Ltd. B.P. 297,848. I.G. B.P. 330,652.

[2] British Celanese, Ltd. B.P. 263,355.

[3] R. Clavel. B.P. 269,128.

[4] British Celanese, Ltd. B.P. 274,074.

[5] Ibid. B.P. 302,363. Addn. to 274,074.

the surface of the fabric can be removed by treatment with an acid or acid salt solution.

Coloured pattern effects can be produced on acetate rayon in various ways. Thus the Calico Printers' Association [1] first print with a resist such as starch or dextrin, and then immerse in a mercerizing solution containing an agent other than caustic soda, e.g. mineral acids, zinc chloride, or calcium thiocyanate. The time of treatment varies with the concentration and temperature of the solution. If the fabric is dyed with direct dyestuffs, only the portion mercerized is affected, and alternatively special acetate dyestuffs do not colour the mercerized parts.

Zinc formaldehydesulphoxylate is used by the Society of Chemical Industry in Basle [2] alone or in conjunction with an acid (tartaric) or an alkali (potassium carbonate), together with the usual thickeners for printing white discharges on acetate rayon dyed with azo dyestuffs. Coloured discharges can be obtained by the addition of suitable dyestuffs to the printing paste.

Dyes other than developed or ice colours may be discharged, according to the Société pour la Fabrication de la Soie Rhodiaseta, by the application of adsorbent substances such as animal charcoal, kaolin, Fullers' earth, or infusorial earth in aqueous suspension, but more particularly when applied as a printing paste.[3] The action is enhanced by the addition of swelling agents and by heat, e.g. by steaming after printing.

R. Clavel states that clear white or coloured discharge effects can be obtained on acetate fabrics weighted with tin or zinc salts and dyed with direct dyes, by the application of pastes containing sodium hydrosulphite.[4]

The British Celanese, Limited, dye with suitable colours such as magenta, violet PDH, aniline diazotized and coupled with phenylmethylpyrazolone, 1 : 4 diaminoanthraquinone, 1 : 4 aminohydroxyanthraquinone, and then print with a preparation of a chlorate with a ferricyanide or vanadate as catalyst, with or without the addition of resistant colours such as methylene blue, rhodamine G extra, mineral pigments, etc.[5] The same firm state that discharge printing by means of reducing metallic salts such

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[1] Calico Printers' Association and Roberts. B.P. 215,860.*

[2] S.C.I. in Basle. B.P. 285,973.*

[3] G. B. Ellis (for Rhodiaseta). B.P. 297,186.

[4] R. Clavel. B.P. 308,757.

[5] British Celanese, Ltd., and Ellis. B.P. 312,655.

as tin and titanium chlorides ('ous) is facilitated by the addition of a thiocyanate to the paste. In this way complete discharges may be obtained even with very deep shades such as navy blue, black, and brown. Basic dyes may be used at the same time for obtaining coloured discharges.[1] They also prefer a discharge paste containing a finely divided metallic formaldehydesulphoxylate instead of a dissolved one, and state that such pastes are more stable.[2]

As aids to penetration, especially in discharge printing, British Celanese, Limited, and G. H. Ellis[3] recommend the addition of p-dihydroxy compounds such as quinol, toluquinol, or their monoethers and halogen derivatives.

The Calico Printers' Association, Limited, and J. R. Whinfield have patented a method for obtaining white resist or discharge effects by overall printing of acetate materials before or after printing with zinc acetate, zinc oxide, or other metallic compound, with dyestuffs having an affinity for cellulose acetate, and capable of forming insoluble complexes with such metallic compounds. The materials are then steamed and heated with dilute acid to remove the insoluble complex. Coloured discharge effects are obtained by adding to the zinc acetate paste dyestuffs having an affinity for cellulose acetate but which do not form metallic complexes.[4]

For coloured discharge printing the British Celanese, Limited, have covered the use of pyrazolone dyestuffs such as aniline or o- and p-anisidine diazotized and coupled with 1-phenyl-3-methyl-5-pyrazolone, which are added to reducing discharge pastes.[5] The same firm obtain coloured discharges on acetate fabrics dyed with azo dyestuffs by using discharge pastes containing stannous chloride or stannous thiocyanate, an anthraquinone derivative, and a swelling agent such as phenol, quinol, or alcohol. Anthraquinone dyestuffs sensitive to hyposulphites are usually unaffected by stannous salts.[6]

Établissments Petitdidier[7] print fabrics containing cotton or viscose and acetate rayon with a colour having an affinity for the acetate, followed by steaming and rinsing. The whites are cleared by treatment with a 0·1 per cent solution of sodium hyposulphite.

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[1] Ibid. and Miller. B.P. 342,333.

[2] British Celanese, Ltd., and Ellis. B.P. 341,909.

[3] Ibid. B.P. 346,694.

[4] Calico Printers' Association, Ltd., and J. R. Whinfield. B.P. 348,715.

[5] British Celanese, Ltd., and Ellis. B.P. 346,751.

[6] Ibid. B.P. 351,457.

[7] Établissements Petitdidier. B.P. 256,238.

In an addition to this patent[1] the whites are cleared by passing through a bath containing 20–25 gm. of potassium permanganate per litre, and then through a solution of sodium bisulphite of density 1·116. This method is claimed to be more effective than the use of hyposulphite described in the prior patent.

Certain dyestuffs exercise a delustring effect during the printing process. According to British Celanese, Limited,[2] this can be prevented by adding various solvents to the paste, e.g. methyl or ethyl ether of ethylene glycol or benzyl alcohol.

An interesting discovery was made in 1929 by the French firm Scheurer, Lauth & Cie, with L. Diserens.[3] They state that the difficulty of obtaining clear white discharges on acetate rayon is due to the poor penetration of the rayon by the sodium hyposulphite used. This difficulty may be overcome by adding resorcinol to the discharge paste. Although resorcinol is a solvent for cellulose acetate, the improved penetration cannot be due to this property alone, since other solvents such as phenol and acetone are not effective. If cellulose acetate be heated with a 50 per cent solution of resorcinol, addition of ferric chloride solution to the acetate does not give the characteristic violet coloration due to resorcinol, indicating that a reaction has taken place between the cellulose acetate and the resorcinol, probably similar to the reaction between acetic anhydride and phenol. Resorcinol is effective with a larger range of dyestuffs than the thiocyanates under similar conditions, and gives whiter discharges. Wolff[4] gives a favourable report on the use of resorcinol, but states that its utility is restricted as in the case of thiocyanates. Its use in this connection was also mentioned by Schneevoigt in 1926.[5]

Before leaving the subject of dyeing and printing, mention must be made of an interesting process discovered by G. H. Ellis of British Celanese, Limited,[6] who found that if an acetate fabric be impregnated with a primary amine which is diazotized on the fibre, dried, and then exposed to light, e.g. under a photographic negative, upon development with a suitable coupling component, an image is produced on the fabric. Suitable amines for this

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[1] Ibid. B.P. 270,657.

[2] British Celanese, Ltd. B.P. 306,534.

[3] Scheurer, Lauth & Cie, and L. Diserens. Sealed Note No. 2,662, 23/6/26, Bull. Soc. Ind. Mulhouse, **95**, 349–52, 1929.

[4] Wolff. Rept. by A. Wolff. *Idem*, 352–4.

[5] A. Schneevoigt. *Textilber.*, 1926, **7**, 354.

[6] British Celanese, Ltd., and Ellis. B.P. 310,773.

purpose are p-nitroaniline, nitro-o-anisidines, *a* naphthylamine, benzidine, etc.

An interesting paper discussing the identification of dyes on cellulose acetate fibres by C. M. Keyworth must also be mentioned.[1] The author examined 220 dyestuffs, most of which are in the colour index, and describes their reactions on the fibre with the following reagents: Alcohol, dilute hydrochloric acid, 5 per cent acetic acid, 1 per cent ammonia, saline caustic soda, hydrosulphites B, BX, and RS (the latter being prepared from 100 gm. of hydrosulphite NF, 50 gm. Rochelle salt, 50 c.c. of caustic soda solution of density 1·40, and 800 c.c. water), titanous thiocyanate, hydrogen peroxide, " Chemic ", concentrated acid, and caustic soda solution of density 1·25. He found that basic dyestuffs are stripped more or less completely by alcohol or 5 per cent acetic acid, and less readily by dilute hydrochloric acid. Hydrosulphite RS and titanous thiocyanate also effect the decolorization, but the action of hydrogen peroxide restores the colour. This is not the case with azo or anthraquinone dyestuffs. The colour of dyestuffs of the triphenylmethane series is destroyed by saline caustic soda, but restored by the action of acids. Basic and anthraquinone dyestuffs become lighter in shade when the fibre is treated with concentrated acids, and conversely in the case of azo dyestuffs. In the case of developed azo colours, many are stripped by the action of alcohol, but the direct azo dyes are little affected. Five per cent acetic acid has little action upon azo dyestuffs. Alcohol will usually strip completely the anthraquinone dyestuffs, but the other reagents, viz. dilute hydrochloric acid, 5 per cent acetic acid, and 1 per cent ammonia have no appreciable action.

As a result of the tests made, the author concludes that the following dyestuffs are identical or very similar to each other, and correspond to the indexed colour indicated.

Index Colour.	Special Colour.
Auramine . . .	Setacyl Yellow AO.
Alizarine Yellow WS .	Cellutyl Fast Yellow AY.
Anthracene Brown WLP	Cellutyl Fast Yellow AB.
Metanil Yellow Y .	Cellutyl Fast Golden Yellow.
Citronine Y (conc.) .	Cellutyl Yellow C.
Chlorazol Orange G .	Cellutyl Fast Orange G.
———	Duranol Orange G, Celatene Orange, Celliton Orange R.

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[1] C. M. Keyworth. *J. Soc. Dyers and Col.*, 1927, **43**, 343–61.

Index Colour.	Special Colour.
Orange II	Cellutyl Fast Orange 2 R.
Magenta	Setacyl Red FC, Cellutyl Fast Bright Red.
———	Duranol Red G, Celliton Pink R.
———	Duranol Red 2 B, Celliton Fast Pink B.
———	Celatene Red Violet, Celliton Fast Red Violet R.
Methyl Violet	Setacyl Violet MB.
Fast Violet B	Celatene Brilliant Violet B.
Modern Violet	Setacyl Violet BR.
Anthracene Blue BDG.	Cellutyl Fast Lilac.
Turquoise Blue G	Setacyl Turquoise Blue S, Cellutyl Sky Blue.
Aeronal Brilliant Blue	Setacyl Sky Blue S.
Prune Blue	Cellutyl Fast Blue.
Brilliant Green Crystals	Cellutyl Fast Green Y, Setacyl Green B.
Malachite Green	Setacyl Green M, Cellutyl Fast Green B.
Methylene Green	Setacyl Blue Green M.

Setacyl Scarlet G, R, and B were found to be mixtures of Setacyl Brilliant Pink G and Setacyl Orange CR ; Setacyl Black G, B, and R are mixtures of Setacyl colours, and Setacyl Direct Black G, B, and R are mixtures of Setacyl Direct Blue with Setacyl Reds and Yellows.

To the anthraquinone class belong the Celatene, Duranol, Celliton, and Celliton Fast Colours. The Setacyl Direct, Cibacet, and Cellit dyestuffs belong to the azo group, and the Setacyl colours are basic in character. Among the SRA colours are representatives of both the anthraquinone and azo series. The Cellutyl dyestuffs include basic, azo, and mordant dyestuffs, and the Cellitazols are organic bases which are diazotized on the fibre and developed.

Theories relating to the Dyeing of Acetate Rayon.—The earliest theory advanced to explain the dyeing of acetate rayon was the solution theory of E. Knoevenagel,[1] which was first stated in 1921. It was known that cellulose acetate readily takes up phenols and amines from their aqueous solutions, and Knoevenagel regarded this process as being analogous to the removal of these compounds from solution in water by an organic solvent such as benzene. The theory received support from experiments made by Green and Saunders in 1923 in connection with the Ionamines.[2] They found that when an aqueous solution of Ionamine A (which contains two salt-forming groups) is shaken with cold benzene, the benzene remains colourless. If, however, the solutions are warmed and again shaken, the benzene becomes yellow and the aqueous layer almost

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[1] E. Knoevenagel. *Kolloidchem. Beih.*, 1921, **13**, 233.

[2] Green and Saunders. *J. Soc. Dyers and Col.*, 1923, **39**, 10.

colourless. This is explained by the slight decomposition which occurs on warming liberating a small amount of free base which dissolves in the benzene. The equilibrium is thereby disturbed, and a further amount of Ionamine decomposes setting free more base, which again dissolves in the benzene. The interface water-benzene acts as a semi-permeable layer allowing free passage to the base, but preventing that of the aldehyde bisulphite residue. In the same way the surface of the acetate fibres is regarded as a semi-permeable membrane which allows the base to enter, and having entered it is firmly held. Mullin, however, suggests that it is held chemically.

Meyer and his co-workers also support the solution theory. Meyer found that cellulose acetate absorbs o-nitroaniline and is coloured uniformly throughout.[1] He also showed that all substances which can be extracted from aqueous solution by ethyl acetate are also absorbed by cellulose acetate. Meyer and Schuster [2] found that undenitrated nitrocellulose behaves similarly to cellulose acetate and absorbs o-nitroaniline from aqueous solution in accordance with Henry's Law.

V. Kartaschov [3] regards cellulose acetate as a solid colloid having a negative charge, which, however, plays no part in the dyeing process since the absorption of the dye is not accelerated by the use of an electric current. He also regards dyeing as a solution phenomenon, and has established the fact that dry cellulose acetate will absorb dry anthraquinone when it is kept in contact with it for several days at 60° C. The same worker later, in conjunction with G. Farine,[4] made a detailed study of the dyeing of acetate rayon (Celanese) by 15 water insoluble anthraquinone derivatives. They found that the derivatives which are most soluble in absolute alcohol contain either a nuclear methyl group or a methylamino group. The diaminoanthraquinones were found to be more soluble than either the mono- or tetra-amino derivatives, whilst the introduction of a hydroxy group causes a slight diminution in the solubility. The Celanese was treated with an aqueous suspension of the dyestuff at 60° C.; the superficial dyestuff was then washed out, and the dyed rayon was dissolved in acetone, the amount of

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[1] K. H. Meyer, *Textilber.*, 1926, **7**, 737.
[2] K. H. Meyer and C. Schuster. Idem.
[3] V. Kartaschov. *Helv. Chim. Acta*, 1925, **8**, 928.
[4] Ibid. and G. Farine. *Idem*, 1928, **11**, 813–36.

colouring matter taken up being determined. It was found that superficial crystallization of the dyestuff on the fibre first takes place, followed by dissolution, and that the solubilities were independent of the concentration of the suspension and of the particle size, and were analogous to those in alcohol. A study of the partition ratios of the dyestuffs between water-rayon and water-alcohol, indicated that for varying amounts of rayon the values were identical for each dyestuff. These results indicate that the association or polymerization of the dyestuffs is the same in each solvent and that adsorption does not occur.

These results have been further supported, more especially in regard to anthraquinone dyestuffs, by the work of A. P. Sachs and H. Brandenburger,[1] who concluded that dyeing of acetate rayon is a process of solid solution preceded by deposition of crystals of the colouring matter on the surface of the fibre. Brandenburger [2] has also discussed the solution theory in its bearing on the fastness to water and washing of dyestuffs on acetate rayon. He states that in general water soluble dyes are inferior to dispersed dyes as regards fastness to water at 40° C., but that dispersed dyestuffs are inferior in fastness to soap solutions to water soluble and developed dyestuffs.

Recently E. Clayton [3] in a paper to the *Journal of the Society of Dyers and Colourists*, describes dyeing experiments with picramic and picric acids and with 2-aminoanthraquinone. From their behaviour towards acetate rayon he concludes that the dyeing process is one of absorption (in which adsorption may play a small part), followed almost immediately by the dissolution of the dyestuff particles in the substance of the fibre. A true solution (in alcohol) of 2-aminoanthraquinone gives a shade on the rayon four to five times as deep as that obtained with a suspension or equivalent concentration in the usual Turkey-red oil solution, but the dye may be removed by repeated extraction with alcohol or benzene in which the cellulose acetate is insoluble. If a hot solution of cellulose actate in acetone is coloured with 2-aminoanthraquinone and is then poured into excess of water, the dyestuff remains in the acetate; if, however, the acetate is precipitated by pouring

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[1] A. P. Sachs and H. Brandenburger. *Textilber.*, 1929, **10**, 215. Sachs, *Textile Col.*, 1929, **51**, 2.

[2] Brandenburger. *Textilber.*, 1929, **10**, 227.

[3] E. Clayton. *J. Soc. Dyers and Col.*, 1930, **46**, 367.

into benzene a considerable proportion of the dyestuff is removed by the benzene. From this the author concludes that dyed cellulose acetate is not an adsorption complex. He concludes that any advances in dyeing methods for acetate rayon will probably be made in the production of dyestuffs which are not only soluble in cellulose acetate but are either soluble in water or capable of forming extremely fine dispersions in aqueous media.

The fact that an increase in the number of sulphonic groups in a dyestuff molecule decreases the affinity for cellulose acetate is further indirect evidence for the solution theory, since it is analogous to the decrease in solubility of organic compounds in organic solvents brought about by the introduction of sulphonic groups into the molecule. On the other hand, the presence of carboxyl groups in an organic compound increases its solubility in water without lessening that in organic solvents, and similarly it has been found that dyestuffs containing carboxyl groups will dye acetate rayon quite readily.

Clavel is more inclined to a chemical theory to explain the dyeing of cellulose acetate. Together with Stanisz,[1] he investigated the action of a large number of dyestuffs on acetate rayon and noted that, contrary to the general opinion then prevailing (1923), this fibre can be dyed with a considerable number of compounds by suitably modifying the conditions. They concluded that the dyestuff molecule must contain certain groups which are active or positive to the acetate molecule, while it should not contain negative groups, or, at all events, such groups should not predominate. Among the active groups mentioned are the hydroxyl, nitro and amino groups, while the sulphonic group is typical of the negative grouping. The affinity of acetate rayon for basic substances is remarkable; thus it will even take up to some extent acid and direct dyestuffs, this being due, according to Greenhalgh,[2] to selective absorption of the dye base. This author states that the affinity is so great that acetate rayon can even bring about decomposition of the dyestuff complex. The diminution in the dyeing caused by the addition of acetic acid or of sodium chloride to the dyebath is a natural consequence of the reduction in the amount of free colour base present and supports the theory of Greenhalgh. According to Clavel (loc. cit.), the dyeing

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[1] Clavel and Stanisz. *Rev. Gen. Mat. Col.*, 1923, **28**, 145, 167.
[2] Greenhalgh. *Dyer and Calico Printer*, 1926, **55**, 106.

capacity is influenced by two factors, viz. the degree of basicity of the dyestuff, and the size of its molecules. The greater the degree of basicity the greater the affinity. The presence of carboxyl groups in the molecule tends to diminish the affinity ; this is seen to a much greater extent in the effect of sulphonic groups ; in both cases there is a reduction in the degree of basicity. The presence of amino groups compensates to some extent for the repressing action of the sulphonic group, but it can be stated that, in general, the presence of two or more sulphonic groups per amino group will entirely prevent dyeing. The effect of the sulphonic group is less, however, if it is not directly attached to the nucleus of the dyestuff molecule. As previously mentioned, this lessening of affinity by the introduction of sulphonic groups has been used as evidence in support of the solution theory of dyeing.

As regards the size of the dyestuff molecule, Clavel and Stanisz state that the pore size of acetate rayon is small compared with that of other rayons, and as a dyestuff can only dye when it can enter the pores, the affinity will decrease as the molecule increases in magnitude. They instance Auramine O, Fuchsin, and Victoria Blue B, which are closely related compounds. In the case of Auramine O the dyeing on acetate rayon is almost as deep as on cotton ; Fuchsin dyes the fibre only slightly ; and Victoria Blue B merely stains it, the stain being removed by treatment with cold soap solution. This certainly supports the contention that affinity decreases as the size of the molecule increases. It has been shown more recently by Kartaschov[1] that it is the particle size which is of importance, rather than the actual size of the molecules. Thus fast shades can be obtained by the dispersol method using dyestuffs with a heavy complex molecule. In the case of basic dyestuffs dissolved in water, there is considerable hydrolysis with liberation of free base. As hydrolysis proceeds the particles of free base grow larger by aggregation of the molecules so that the degree of dispersion is diminished, and with it the affinity for acetate rayon. This explains the action of salts such as sodium or magnesium chlorides which assist dyeing by repressing hydrolysis. In the case of acid dyestuffs the assistance of salt is probably due to its swelling effect together with flocculation of the dyestuff on the fibre.

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[1] Kartaschov. *Helv. Chim. Acta*, 1926, **9**, 152–73.

Similar considerations apply to the dyeing of acetate rayon with dyestuffs of which the hydroxy group is characteristic. Here again the presence of sulphonic groups in the dyestuff molecule lessen or even present dyeing.

Caille's explanation of the affinity of acetate fibres for basic dyestuffs,[1] viz. that it is due to the combined sulphuric acid present in the cellulose, is not very satisfactory in view of the stabilizing process which cellulose acetate undergoes before it is used for the production of rayon, and which leaves only traces of combined sulphuric acid in the product. The explanation may have been nearer the truth in the earlier days of the acetate industry, when methods of manufacture were not so highly developed as they are to-day.

In summing up, it would seem that the weight of evidence favours the solution theory of dyeing ; at the same time one cannot entirely rule out the other explanations which have been advanced. In view of the complex molecular nature of cellulose acetate, and the micellar structure possessed by acetate rayon, it is quite possible that any or all of the other mechanisms may come into play, depending upon the dyestuff used, and the conditions under which dyeing is carried out ; that is to say, while the dyeing process may be regarded primarily as one of solid solution, adsorption, and the chemical forces resulting from the secondary valencies of the cellulose acetate molecule may also take part in the process.

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[1] Caille. *Chim. et Ind.*, 1926, **15**, 61–4 T.

CHAPTER XI

OTHER USES OF CELLULOSE ACETATE

Besides being used for the manufacture of rayon, cellulose acetate has found a variety of other uses. In fact, as indicated in Chapter I, the production of rayon is one of the later developments of the acetate industry, its earliest applications being in the lacquer industry, and particularly in the " doping " of aeroplane fabrics. It has also been employed in the manufacture of non-inflammable films, although owing to its high cost compared with nitrocellulose, and to certain technical difficulties, it has not yet supplanted the earlier nitro films. Similar remarks apply to its use in the manufacture of lacquers. Cellulose acetate moulded goods are now made in large quantities, notably by the British Celanese, Limited, who also make all kinds of acetate materials in the form of sheets, tubes, etc., under the name of Cellastoid. Transparent wrapping materials made of cellulose acetate do not appear to have made much headway ; they are more expensive to produce than similar products derived from viscose (Cellophane, etc.). Some headway has been made, however, in the application of cellulose acetate to the manufacture of splinterless glasses.

A variety of solvents have been described from time to time for use in the acetate lacquer industry, and all kinds of claims, justifiable and unjustifiable, have been made in their regard, both in patent specifications and elsewhere, and it is only possible to mention a few of them. The addition of an unusually large quantity of water to acetate lacquers is said to be possible if cyclic acetals derived from polyhydroxy alcohols, used alone or with other solvents, form the medium of the lacquer.[1] In an example 10 parts of cellulose acetate are dissolved in a mixture of 60 parts of monoformaldehyde glycerol and 30 parts of water. The I.G. Farbenind. A.-G. have also covered the use as solvent of 1 : 4 dioxan, alone or with other solvents [2] ; the Celluloid Corporation have described

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[1] Carpmael (for I.G. Farbenind. A.-G.). B.P. 286,789.

[2] I.G. Farbenind. A.-G. B.P. 275,653.

special mixtures containing a lower alkyl acetate in preponderating proportions, e.g. 82·5 parts of ethyl acetate, 8·5 parts of ethyl alcohol, and 9 parts of water[1]; and quite recently Imperial Chemical Industries, Ltd., have covered the pentaerithrityl ethers as solvents and plasticizers.[2] Other solvents include all kinds of esters—methyl and ethyl formates, acetates, etc., epichlorhydrin, diacetone alcohol, benzyl alcohol, and mixtures of such solvents with non-solvents like benzene, petroleum hydrocarbons, etc.

In connection with the production of films and celluloid like masses, great difficulties were at first experienced in finding plasticizers which would render the products flexible. Camphor, which is used for this purpose with nitrocellulose in the manufacture of ordinary celluloid, is a non-solvent for cellulose acetate, and is therefore useless for this purpose. A great variety of substances have been suggested many of them having been made the subject of patent specifications. Among the commoner plasticizers may be mentioned diacetin, triacetin, triphenyl, and tricresyl phosphates. It will be observed that they are high-boiling liquids or low-melting solids, with low vapour pressures. The properties desirable in a cellulose acetate plasticizer have recently been outlined by H. Messer in a paper contributed to the *Journal of the Society of Chemical Industry*.[3] He points out that a satisfactory softener must be colourless, odourless, insoluble in water, not easily hydrolysed, a liquid, or, if a solid, of low melting point, of high boiling point with a low vapour pressure, light and heat proof. If the softener were soluble in water, trouble would be caused by absorption of water from the atmosphere, resulting in the ultimate precipitation of the cellulose acetate, with production of turbidity and brittleness. Hydrolysis might liberate compounds having a deleterious influence on the product. If a high melting solid were used as a plasticizer, it would crystallize, again with the production of turbidity and brittleness; and the use of a compound having a low boiling point or high vapour pressure would result in gradual evaporation, leaving the product brittle. Resistance to heat is necessary to allow the softener to withstand the temperatures used in the mixing and moulding processes; and light proof qualities are necessary to prevent colour changes in the finished materials.

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[1] Celluloid Corporation. B.P. 314,087.

[2] Imperial Chemical Industries, Ltd. B.P. 358,393.

[3] H. Messer. *J.S.C.I.*, 1931, **50**, 386 T.

Messer further makes the interesting suggestion that the choice of a plasticizer should be governed by structural considerations. He points out that acetone and methyl and ethyl acetates are the best solvents for cellulose acetate, and that a suitable softener should possess similar solvent properties to these compounds, but should, at the same time, be without their high volatility. Arguing from these considerations, he concludes that the ideal softener should contain the keto grouping of acetone or the ester grouping of the acetates, together with a high boiling nucleus, which is itself a good softener for the acetate. The synthesis of a number of such compounds is outlined: for example, sodium salicylate is combined with chloracetone, and the free hydroxy group is acetylated giving the compound $OAc.C_6H_4.COOCH_2Ac$, i.e. a compound which contains two ester groups and an acetone radical.

It is impossible to mention all the different types of compounds which have been suggested as plasticizers for cellulose acetate; among recent patents may be mentioned two due to Hands and Spicers, Ltd. The first[1] describes the use of chlorpropanes having more than three carbon atoms per molecule; it is claimed that when used in small proportion (2–3 per cent) in association with other plasticizers, they reduce the inflammability of the product. The second[2] covers the use of mixtures of diphenyl monocresyl phosphate and phenyl dicresyl phosphate as plasticizers, the relative proportions being so chosen that the final mixture corresponds to a mixture containing 45–65 per cent of triphenyl phosphate and 55–35 per cent of tricresyl phosphate. In this manner the reduction of inflammability due to the triphenyl phosphate and the pliability imparted by the tricresyl phosphate are obtained without the disadvantages resulting from the tendency of the former to crystallize out and for the latter to impart a greasy character to the film.

The use of cellulose acetate for the manufacture of photographic films has been referred to above. The manufacture of such films and also of transparent wrappings is carried out to a large extent by processes which have not been made public. The general principle of such methods is to apply a solution of cellulose acetate in a volatile solvent containing suitable softening agents to a travelling belt having a perfectly smooth surface, and made of a material which is

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[1] Hands and Spicers, Ltd. B.P. 279,139.

[2] Ibid. B.P. 294,008.

insoluble in the solvents and softeners used. The film is solidified by evaporation, the solvent vapours being drawn off to a recovery plant, and when dry the film is stripped from the belt. Various ornamental effects can be produced by the inclusion of pigments, metallic powders, etc., in the solution, or their application to the film while still sticky.

A great disadvantage attaching to the early types of transparent wrapping materials was their permeability to water vapour. While they could be correctly described as waterproof, inasmuch as they would not allow the passage of liquid water, if hygroscopic substances were completely sealed within such wrappings, and then exposed to a damp atmosphere (90 per cent relative humidity for example), the absorption of water by the contents of the package was only slightly retarded, and they would become as damp finally as though completely unprotected, thus rendering the wrapping unsuitable for packing goods such as boiled sweets, unless some further protection in the form of waxed parchment were used. The Du Pont Cellophane Co., Inc.,[1] have overcome the difficulty by producing a compound material consisting of a basis of regenerated cellulose (cellophane) coated with a composition containing 30–70 per cent of a cellulose ester or ether; 30–60 per cent of a gum or resin; 2–6 per cent of wax, e.g. paraffin wax; and 5–30 per cent of a plasticizer such as an aryl or alkyl phosphate or phthalate, the whole being applied in solution in a solvent containing alcohol, toluene, butyl acetate and ether or ethyl acetate. It is probable that nitrocellulose is the ester used in this process, although it is possible that cellulose acetate would serve equally well.

There are a number of patents covering the application of cellulose acetate in the manufacture of splinterless glass, which is in great demand at the present time, owing to the enormous development of the motor industry. The earliest work on this subject was done by J. C. Wood as long ago as 1905, who sought to secure a sheet of celluloid between two sheets of glass, but without commercial success. The first successful safety glass was that produced in France by Benedictus in 1910, and a British company was formed in 1912 to manufacture according to his process, the product being the well-known Triplex. The process is largely a secret one, but the

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[1] Du Pont Cellophane Co., Inc. B.P. 283,109

principle consists in applying a thin film of gelatine to the sheets of glass so as to bind them to the intermediate layer of celluloid.

One of the greatest difficulties which has been encountered in the safety glass industry where celluloid is used as the intermediate layer, is the discoloration which takes place with age. Cellulose acetate forms a very satisfactory substitute for celluloid from this point of view, although it is much more difficult to secure adhesion with the acetate than with the nitrate. Mallabar[1] fastens the acetate sheet between the layers of glass by means of gelatine. The acetate is either partially hydrolysed or treated with a solvent to render it more adhesive, and the sheets are united by the application of pressure. British Celanese, Limited,[2] dispense with an adhesive, and produce a safety glass permeable to ultra-violet light by uniting two sheets of high quartz glass by means of cellulose acetate powder mixed with sufficient plasticizer to form the sheet in situ, the whole being subjected to a pressure of 300 to 800 lb. per sq. in. at 50–80° C.

There has been an extraordinary development in the production of moulded goods of all descriptions during recent years, largely as a result of the invention of synthetic resins. Increasing attention is now being paid to the use of cellulose acetate as a moulding compound, especially for the production of small and delicate articles, for which the resins are unsuitable on account of brittleness or difficulty in moulding, and for fancy moulded goods, where brilliant decorative effects are desired. Cellulose acetate is not, of course, resistant to heat, but its high dielectric constant, great mechanical strength, easy moulding properties, and the variety of effects obtainable render it a very attractive material to the moulder. Of its manifold applications mention may be made of all kinds of electrical apparatus; fountain pens and parts for same, knobs and handles, cigar and cigarette cases, imitation tortoise-shell articles, combs, knife handles, etc., etc.

In addition to cellulose acetate, mouldings also usually contain a filler, which is added either to impart colour, or to cheapen the composition. The strength of the mouldings depends entirely on the cellulose acetate, and the addition of fillers such as mineral powders tends to weaken them. A plasticizer is also necessary, and volatile solvents may also be used.

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[1] Mallabar and Non-Flam Film Co., Ltd. B.P. 288,782.

[2] British Celanese, Ltd. B.P. 306,397.

There are three methods in common use for moulding cellulose acetate plastics, viz. thermo-plastic moulding, in which the composition is moulded hot in a hydraulic press ; seasoning moulding in which the articles are rolled, stamped, or pressed from the composition, rendered soft by the addition of volatile solvents, after which they are seasoned over long periods ; and injection moulding, a patented process due to A. Eichengrün, which has been developed in this country by F. A. Hughes, Ltd.

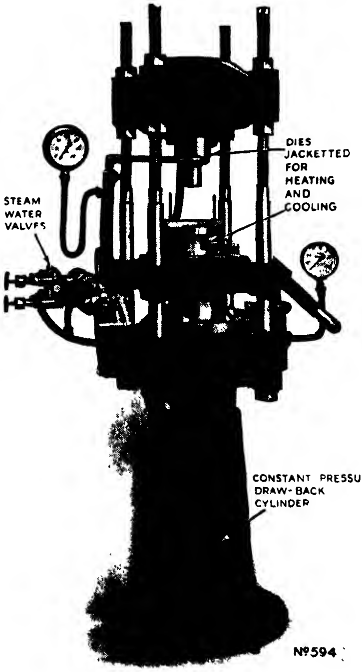

Fig. 71. Auto-Cellulose Press. (Francis Shaw & Co., Ltd.)

Thermo-plastic Moulding.—The dry ingredients, cellulose acetate in the form of powder, fillers, and colouring materials, are first mixed thoroughly in a dry mixer, followed by incorporation with the aid of steam heated rolls. The material is then " blanked-off " into rectangular sheets by means of water-cooled rolls, which, unlike the mixing rolls, run at the same speed. The sheet stock so obtained is preheated on a heated table, and is cut and rolled by hand into pieces of suitable size for the moulds. Alternatively it may be powdered and used in that form, or after conversion into pellets. The moulding press used for cellulose acetate articles is shown in Fig. 71 ; it is provided with a constant pressure draw-back cylinder to facilitate rapid opening of the press. The steam and water supplied to the mould casing is operated by a special double-acting valve ; and with suitably constructed moulds these presses have a very high rate of output.

Seasoning Moulding.—The procedure in this case closely resembles that used in the manufacture of ordinary celluloid, the products appearing on the market as sheet, rod, or tube. The Cellastoid products of British Celanese, Ltd., probably belong to this class.

Injection Moulding.—A special cellulose acetate composition for use in this (or other processes) is now sold under the name of Cellomold (by Cellomold, Ltd.). The properties of this material are stated to be as follows :—

Specific Gravity	1·2–1·3.
Water Absorption	0·84 per cent.
Bending Strength	550 Kg./sq. cm.
Tensile Strength	260 do.
Impact Bending Strength	30 cm. Kg./sq. cm.
Heat Resistance	70–100° C.
Internal Resistance	5×10^6 megohms/cm.^{3}
Surface Resistance	3×10^6 megohms/sq. cm.
Dielectric Constant	6.
Breakdown Voltage	45 kv. per mm.

The product is only slightly affected by sulphuric acid up to 25 per cent strength, but is decomposed by the strong acid and by caustic soda ; it is not affected by fats or oils, but dissolves in such solvents as acetone, alcohol, ether, benzene, etc.

In the ordinary hot and cold moulding process the mould is heated to the required temperature (130–150° C.), the preheated material, in the form of loose powder, pellets, or solid stock, is introduced, and after closing the mould, it is cooled under pressure. When cold, the mould is opened and the moulding extracted. For hollow-ware, powder or pellets are preferred, but for thick articles such as knife handles it is better to use stock cut approximately to the shape required. When using solid stock, scrap and " flash " produced during moulding can be remoulded ; or if powder is being used, the scrap can be ground up and used again, so that there is no loss as in the case of synthetic resins.

The injection process of moulding cellulose esters and ethers was patented by Dr. A. Eichengrün in 1920 (B.P. 171,432). It is specially useful for small and intricate mouldings, with or without inserts, and in cases where press moulding is impossible on account of the shape of the article required. The principle of the process is to squirt the thermoplastic Cellomold through a narrow channel and orifice into a cold or moderately warm mould. The pressure normally used for this purpose is about 8 tons per sq. in., and the finish of the moulded articles is therefore highly polished. The forcing of the composition through the narrow channel also affects the physical character of the finished moulding, giving increased strength and elasticity. The channel orifice of the mould has unequal cross-section and a zig-zag shape, which also helps to improve the strength of the moulded goods, and can be used to produce unique colour effects by adding mixed pigments to the stock.

The principal methods of injection moulding are four in number, viz.: (*a*) by hand-operated machines; (*b*) by hydraulically-operated machines; (*c*) by compressed air machines; and (*d*) by power-operated crank-machines.

Hand-operated Machines. — Fig. 72 shows a hand machine for injection moulding (made by Messrs. Francis Shaw, Ltd., of Manchester), which is designed for making small articles up to ¼ oz. on a 30 second cycle. It consists of two parallel rods, supported by two end frames and carrying three sliding members. One half of the mould is bolted to the end-frame, and the other half is carried on the first sliding member. The second sliding member carries the injection cylinder and the self-measuring funnel, and the third sliding member carries the piston and is attached through a link motion to the other end frame. There are two sets of springs between the sliding members, the first pair serving to release the cylinder

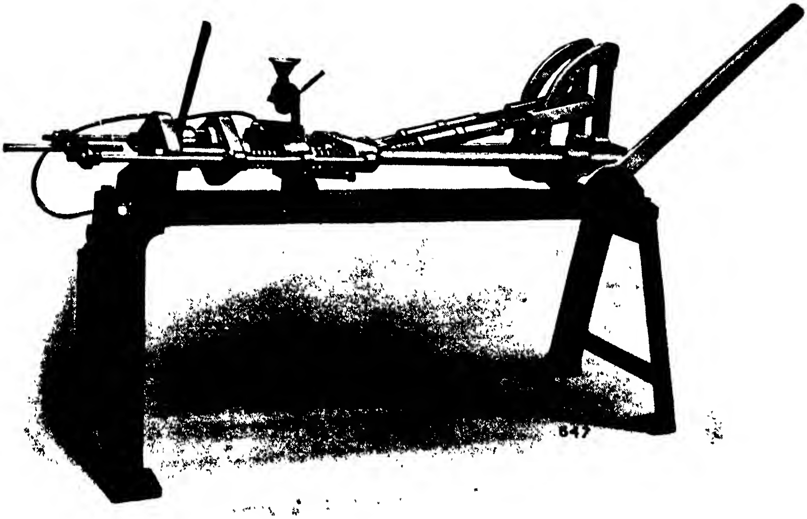

FIG. 72. Hand Injection Machine. (Francis Shaw & Co., Ltd.)

nozzle from the mould face, and the second pair to transmit the movement of the piston member to the cylinder member until the latter is in contact with the face of the mould. The two light rods attached to the extreme end of the piston member carry the ejector bar, and two collars that can be adjusted to open the die to the required amount. The procedure is as follows: The moulding powder is introduced into the injection cylinder, which is heated electrically to 160–200° C. When the material is sufficiently plastic, the operating handle (which is at an angle of 90° to the machine bed in the starting position) is pulled to the left, thus closing the mould; on further depression, the cylinder member is pushed forwards against the pressure of the first and weaker set of springs, until the nozzle of the cylinder is in contact with the face of the mould. The operating handle is now at an angle of about 20° to the bed of the machine, and further depression forces the piston about 1 inch into the injection cylinder. During the last operation the mechanical advantage is such that the plastic material is forced into the mould with high velocity.

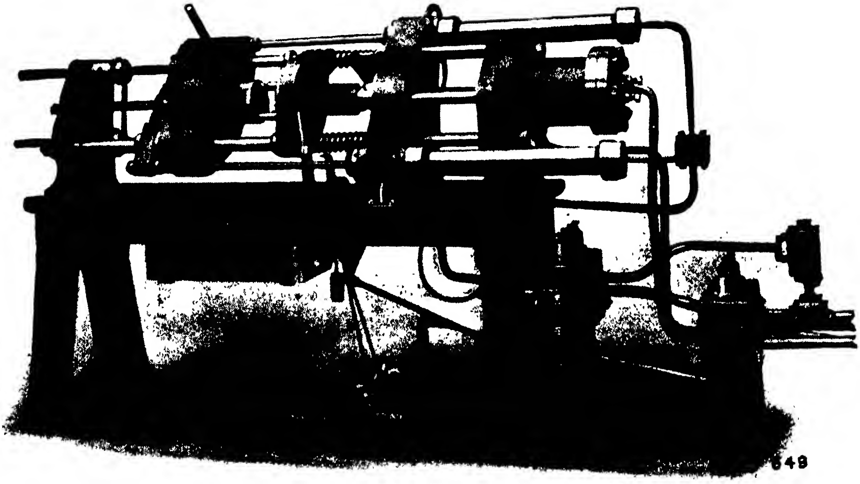

Fig. 73. Hydraulic Injection Machine. (Francis Shaw & Co., Ltd.)

Hydraulically-operated Machines.—Fig. 73 shows a hydraulic injection machine made by the same firm. It has ten times the capacity of the hand machine, and for small articles has a very high output: thus with a sixteen impression mould, between 3,000 and 4,000 articles can be made per hour. The principle of the machine is similar to that of the foregoing, but the mechanism is actuated by hydraulic rams. The normal working cycle is 15 seconds including a short period for cooling.

Compressed-air Machines.—These are useful where high pressure water is not available. The machine is similar in construction to the hydraulic machine, and operates with a normal air pressure of 300 to 500 lb. per sq. in., giving a ram pressure of about 7 tons. (See Fig. 74.)

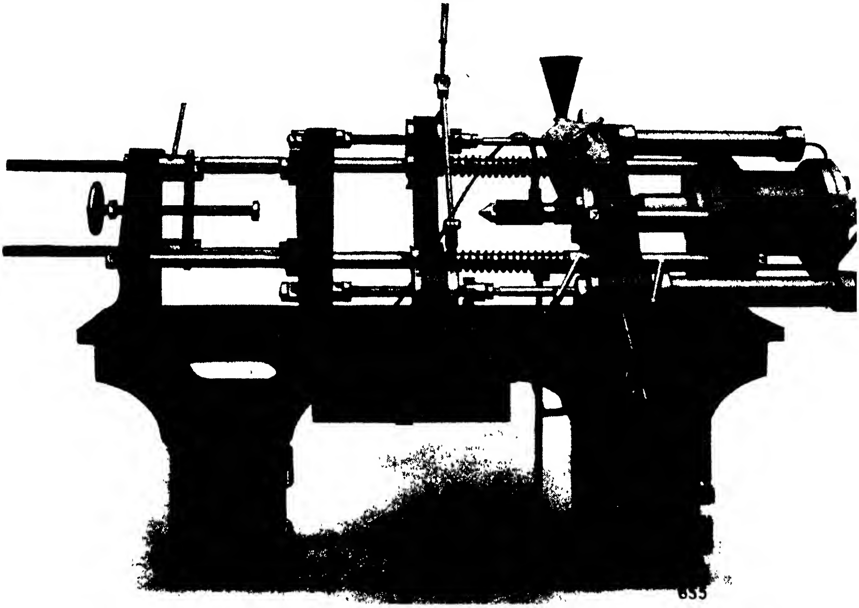

FIG. 74. Compressed Air Injection Machine. (Francis Shaw & Co., Ltd.)

Power-operated Crank Machines.—These are a new development, whose merits have to be proved. The principle is similar to that of the other machines, the injection piston being operated by a crank or cam on a shaft carrying a heavy flywheel. Its main advantage is small power consumption, a 2 h.p. motor being sufficient to operate it.

Other Esters of Cellulose.—Apart from the nitrates of cellulose, the acetate is the only ester of that substance which is manufactured and used commercially. Other esters have been prepared, however, many of which possess interesting possibilities, and doubtless some of them will eventually find commercial applications.

Cellulose Formates.—Cellulose readily forms derivatives with concentrated formic acid in presence of condensing agents such as sulphuric acid. Berl and Smith[1] prepared a mixture of cellulose mono- and diformates by treating 6·5 gm. of hydrocellulose with 100 gm. of anhydrous formic acid and 5 gm. of sulphuric acid at room temperature. The cellulose was converted to a gelatinous mass after four days' treatment in this manner, and after removal of excess formic acid and sulphuric acid with water, the product was found to have a formic acid content of 20–23 per cent. It was soluble in chloroform and acetone and partially soluble in pyridine.

Knecht[2] states that when a solution of oxalic acid is dried on cotton, it decomposes into carbonic and formic acids, the latter forming an ester with the cellulose.

E. Elöd[3] has patented a method for formylating cellulose by the action of 98–100 per cent formic acid at 5–20° C. in presence of an esterifying catalyst such as gaseous hydrochloric acid or phosphoric anhydride, and at least 40 per cent (calculated on the weight of the cellulose) of a swelling agent such as zinc chloride or calcium bromide.

Quite recently G. Tocco[4] has described the dry spinning of formic acid solutions of cellulose diformate and states that films produced in this manner consist of pure cellulose, having excellent mechanical properties. The extrusion is carried out in vacuo on account of the relatively high boiling point of formic acid. The addition of casein to the solutions improves the plasticity of the films, and also diminishes the inflammability. Tocco claims that the pure cellulose films obtained from cellulose formate are stronger than those from viscose, and they can be made much thinner. Considerable trouble is, however, experienced with corrosion in the plant materials.

Cellulose Butyrates.—A number of patents were granted to Little Inc. (Assignees of Esselen and Mork) about 1920, for the production

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[1] Berl and Smith. *Ber.*, 1907, **40**, 903.

[2] Knecht. *J. Soc. Dyers and Col.*, 1907, **23**, 231.

[3] E. Elöd. B.P. 275,641.

[4] G. Tocco. *Giorn. Chim. Ind. Appl.*, 1931, **13**, 414–18.

of cellulose butyrates, but none of these are in force.[1] The method consisted in pretreatment with the catalyst (1–5 per cent sulphuric acid) mixed with 90 per cent acetic acid. After thorough impregnation, excess pretreating agent was removed, and the cellulose was heated with a mixture of about equal parts of butyric acid and butyric anhydride. The product was soluble in chloroform, acetylene tetrachloride, acetone, ethyl acetate, phenol, hot alcohol, hot benzol, and solvent naphtha, alcohol-benzol, and alcohol-carbon tetrachloride. More recently the Soc. Chim. des Usines du Rhône-Poulenc [2] have covered the production of cellulose butyrate by pretreating cellulose with butyric acid, followed by esterification with butyric anhydride in presence of a sulphonic acid of an aliphatic hydrocarbon, and other suitable catalysts if desired, and preferably in presence of a diluent such as benzene, which is a solvent for the ester.

Cellulose Esters of Higher Fatty Acids.—Judging from the patent literature, a considerable amount of research has been devoted to the production of higher fatty acid esters of cellulose. The Soc. de Stearinerie et Savonnerie de Lyon [3] have described the production of esters of acids containing more than five atoms of carbon, by condensation of cellulose with the acid chloride of the acid in question in presence of such substances as pyridine or quinoline. The esters are soluble in many organic solvents, particularly aromatic hydrocarbons, and yield on evaporation of the solutions, colourless and transparent films, without the addition of plasticizing agents. The production of cellulose dipalmitate is described in an example. The preparation of the distearate and dilaurate by similar methods without alteration of the fibrous structure of the cellulose has been described by Grün and Wittka [4]; and the preparation of such esters from hydrocellulose by heating with the acid chloride and pyridine by Gault and Ehrmann.[5]

Cellulose esters of higher unsaturated fatty acids have been described by the Farbenfabr. vorm. F. Bayer & Co., [6] being obtained by treating the carbohydrate with the chloride of the fatty acid.

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[1] A. D. Little Inc. (Assignees of Esselen and Mork). B.P. 161,564*; 167,143,* 182,820.*

[2] Soc. Chim. des Usines du Rhône-Poulenc. B.P. 323,869.

[3] Soc. de Stearinerie et Savonnerie de Lyon. B.P. 201,510.

[4] Grün and Wittka. *Z. angew. Chem.*, 1921, **34**, 645.

[5] Gault and Ehrmann. *Compt. rend.*, 1923, **177**, 124.

[6] Carpmael (for Farbenfabr. vorm. F. Bayer & Co.). B.P. 239,726.†

In this way esters of oleic, linoleic, linolenic acids and of the unsaturated acids of train oils have been prepared. The products are viscous or limpid oils, soluble in hydrocarbons, turpentine, etc., and were claimed to be suitable as substitutes for drying oils, and in the manufacture of varnishes, artificial filaments, plastic compositions, etc. They are oxidized by exposure to the atmosphere or on heating, being rendered insoluble by such treatment. Clark and Malm (Kodak)[1] treat cellulose in presence of chloracetic anhydride and magnesium perchlorate at 60–65° C. with an unsaturated monocarboxylic acid such as crotonic acid, cinnamic acid, etc., thus obtaining the cellulose esters of these acids. Mixed esters may be produced by this method.

Cellulose Esters of Aromatic Acids.—Benzoic esters of cellulose have been prepared by the action of benzoyl chloride on cellulose or hydrocellulose, and have been described by Cross, Bevan, and Briggs.[2] The I.G. Farbenind. A.-G.[3] have covered the preparation of esters of naphthenic and phenylacetic acids by treating cellulose, which has been swollen with 30 per cent caustic soda, with a halide of the fatty acid, the cellulose being preferably suspended in benzene, chlorbenzene, etc.

Mixed Esters.—There are a number of patents relating to the preparation of mixed esters of cellulose, such as acetoformates, nitroacetates, acetate-butyrates, acetate-crotonates, etc. Thus, the Soc. Lyonnaise de Soie Artificielle and P. Chevalet[4] treat cellulose at a low temperature with formic acid mixed with less than 50 per cent by weight of sulphuric acid (d. 1·842) and then with a mixture of acetic acid with more than twice its weight of sulphuric acid. When the esterification has proceeded sufficiently far, the product is precipitated with water or alcohol. The ester so obtained, an acetoformate, is soluble in formic acid down to 40 per cent dilution, in formaldehyde and its derivatives, in pyridine, ureas, cyanates, thiocyanates, solutions of calcium chloride, etc. It is said to possess all the plastic qualities of cellulose acetate, and the strength of filaments made from it can be increased considerably by immersing in a bath containing 11 per cent of ammonium carbonate.

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[1] Clark and Malm (Kodak, Ltd.). B.P. 289,853.
[2] Cross, Bevan, and Briggs. *Z. angew. Chem.*, 1913, **26**, 255.
[3] I.G. Farbenind. A.-G. B.P. 305,661.
[4] Soc. Lyonnaise de Soie Artificielle and P. Chevalet. B.P. 266,300.

The I.G. Farbenind. A.-G.[1] prepare nitrocetates of cellulose by treating cellulose at 50–100° C. with acetic acid, acetic anhydride, and ammonia or urea nitrate in presence of 0·3–1·0 per cent sulphuric acid.

Mixed esters of acetic and butyric acids are prepared by treating cellulose according tó the method of B.P. 237,567 (partial acetylation) with butyric or isobutyric anhydride. These esters are soluble in benzene at ordinary temperatures.[2]

Cellulose Esters of Inorganic Acids.—It is over half a century since Girard investigated the action of various mineral acids on cotton cellulose. As long ago as 1895, Stern[3] stated that when cellulose is dissolved in cold concentrated sulphuric acid a disulphuric ester of cellulose is formed. It is doubtful whether such esters have been isolated. Nitric acid esters of cellulose are, of course, well known and need not be described here. The I.G. Farbenindustrie A.-G.[4] have an interesting patent which covers the preparation of cellulose esters of inorganic acids in general. The method consists in treating alkali cellulose, in the preparation of which more than 1 molecule of caustic alkali per $C_6H_{10}O_5$ molecule has been used, with an excess of an inorganic acid chloride. The specification states that the best results are obtained by impregnating 100 parts of cotton with 40 per cent caustic soda solution at — 10° C. After four hours, the impregnated cotton is pressed to 200–300 parts by weight. In an example, 100 parts of cotton are treated in the above manner, and after pressing to 300 parts, are slowly introduced into an ice-cold solution of 160 parts of phosphorus oxychloride in 900 parts of benzene. The heat evolved raises the solution to the boiling point, but the reaction afterwards proceeds smoothly and after 12 hours the product is separated, washed with alcohol and ether, dried in a vacuum, and purified by dialysis of an aqueous solution. The yield is about 80 per cent of the theoretical, and the product contains 16 per cent of PO_4.

The I.G. Farbenind. A.-G.[5] have also described the production of chlorinated esters of saturated organic acids by treatment, for example, with phosphorus pentachloride, while suspended in an inert medium such as tetrachlorethane. The products are said to be soluble in organic solvents, and to be stable to acids.

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[1] I.G. Farbenind. A.-G. B.P. 319,825.

[2] G. B. Ellis (for Rhône-Poulenc). B.P. 321,575.

[3] Stern. *J.C.S.*, 1895, **67**, 74.

[4] I.G. Farbenind. A.-G. B.P. 279,796.

[5] I.G. Farbenind. A.-G. B.P. 306,132.

Surface Treatment of Cellulose—Immunized Cotton.—It is almost thirty years since Meister, Lucius, and Bruning proposed to modify the dyeing properties of cotton by treating it with glacial acetic acid. Since then, a number of patents have been granted for various treatments calculated to modify the surface of the cotton fibre, and thereby to render it resistant to direct dyestuffs, or to confer upon it affinity for other classes of dyestuffs. The so-called "Reserve Cotton" is made by surface benzoylation, according to the patent of Cassella and Co.[1] The method which is general consists in treating the cotton with an acid chloride in presence of an inert solvent such as benzene. Alternatively the cotton may be treated with caustic soda in presence of soap or Turkey red oil.

The Textilwerk-Horn A.-G.[2] prepare an immunized cotton by treatment with caustic soda, followed by partial esterification with an aromatic sulphonchloride, particularly p-toluene sulphonic chloride. The product is resistant to substantive dyestuffs.

The Chem. Fabr. vorm. Sandoz [3] have described the production of effect threads resistant to substantive dyestuffs by acetylating the cotton with an acetylation mixture, of which the activity has been so modified by adjusting the quantity of catalyst and the temperature that the cellulose is converted into mono and diacetates, while retaining its fibrous form, strength, and elasticity. A suitable bath consists of 3 kg. of acetic anhydride, 5 kg. of acetic acid, and 2·5 gm. of sulphuric acid. The reaction is allowed to proceed at 15° C., and after 48 hours a dyeing test is made to ascertain if the esterification has proceeded to the desired extent. In a later patent [4] the same firm claimed that the resistance of these partly acetylated products to direct dyestuffs is further increased by steaming under pressure, even the monoacetate being rendered completely resistant by such treatment. The acetylation process of the first patent was later modified, so that it could be carried out in a shorter time by using less catalyst, or a less active catalyst, and allowing the reaction to take place at a higher temperature (greater than 25° C.). For example, 100 parts of bleached cotton yarn are treated with a bath containing 30 parts of zinc chloride, 250 parts of acetic anhydride, and 720 parts of acetic acid at 80° C. for half to three-quarters of an hour.[5] A second addition to the

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[1] Cassella & Co. Ges. B.P. 224,502.

[2] Textilwerk Horn A.-G. B.P. 195, 619.

[3] Chem. Fabr. vorm. Sandoz. B.P. 280,493.

[4] Ibid. B.P. 318,366.

[5] Ibid. B.P. 323,500.

original patent[1] claimed that a product of softer feel could be obtained by carrying out the process with the theoretical amount, or with slight excess of acetic anhydride; and a third addition covered pretreatment of the cotton with one of the constituents of the acetylation bath.[2]

According to P. Karrer[3] cotton may be given an affinity for acid dyestuffs, by first partially esterifying with a sulphonic acid of benzene, toluene, or naphthalene, and heating the product with ammonia, aliphatic, or aromatic primary, secondary, or tertiary amines, or with hydrazine or its derivatives. For example, 10 parts of cotton partially esterified with p-toluene sulphonchloride is heated for six hours with 50 parts of 25 per cent aqueous ammonia in an autoclave at 100° C. In this way it acquires an affinity for such acid dyestuffs as tartrazine, Orange II, sulphorhodamine, etc. In an addition patent[4] the process was modified to cover treatment of partially esterified fibres in the wet state with ammonia gas, or with the vapours of suitable amines. It was also stated that amidation could be effected by means of pyridine, piperidine, quinoline, or other heterocyclic bases. The process can be applied to viscose or other regenerated celluloses. According to a specification of the Chem. Fabr. vorm. Sandoz,[5] the so-called "animalized" cotton may be prepared in one operation by treating cotton, mercerized cotton, viscose, or other regenerated cellulose rayon, at 110° C. with benzene or toluene sulphonic chloride and a tertiary base such as pyridine in presence or absence of a solvent such as nitrobenzene. The treated material has an affinity for acid dyestuffs.

The Society of Chemical Industry in Basle immunize cotton to direct dyeing by esterification with maleic anhydride with or without a catalyst[6]; or by impregnating the cotton with crude copper sulphate solution, followed by drying and acetylation with acetic anhydride at 100° C.[7] The immunization is complete in less than one hour.

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[1] Ibid. B.P. 323,515.

[2] Ibid. B.P. 323,548.

[3] P. Karrer. B.P. 249,842.*

[4] Ibid. B.P. 263,169.*

[5] Chem. Fabr. vorm. Sandoz. B.P. 284,358.*

[6] S. C. I. in Basle. B.P. 315,434.

[7] Ibid. B.P. 315,435.

APPENDIX I

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APPENDIX II

Abridgment Classes of British Patent Specifications of interest to the manufacturer of cellulose acetate products.

Series (A)—List of Classes 1855–1908.	Corresponding Classes Series (B). 1909–30.	Corresponding Group Volume Series (C) 1931 onwards.
1. Acids, alkalies, oxides, and salts inorganic.	1. (i) Chemical processes and apparatus.	III
2. Acids and salts, organic and other carbon compounds (including dyes).	2. (ii) Cellulose, non-fibrous and cellulose derivatives (including artificial filaments, sheets, and the like containing same. 2. (iii) Dyes and hydrocarbons and heterocyclic compounds and their substitution derivatives.	IV
15. Bleaching, dyeing, and washing textile materials, yarns, fabrics and the like (excepting dyes).	15. (i) Dyeing and otherwise treating textile materials and the like with liquids and gases, Apparatus for (including Bleaching and washing, Processes and materials for). 15. (ii) Dyeing, Processes and materials for.	IV
32. Distilling, concentrating, evaporating, and condensing liquids.	32. Distilling and evaporating liquids (including condensing vapours and crystallizing).	III
42. Fabrics, dressing, and finishing woven, and manufacturing felted (including folding, winding, measuring, and packing).	42. (i) Fabrics, finishing, and dressing. 42. (ii) Fabrics, treating otherwise than by finishing and dressing.	VIII
74. Lace-making, knitting, netting, braiding, and plaiting.	74. (i) Braid and braiding machines, crochet, lace, and lace-making, and net-making machines. 74. (ii) Knitting and knitted fabrics.	VIII
87. Moulding plastic and powdered substances.	87. (ii) Ibid.	V

Series (A)—List of Classes 1855–1908.	Corresponding Classes Series (B). 1909–30.	Corresponding Group Volume Series (C) 1931 onwards.
120. Spinning (including the preparation of fibrous materials and the doubling of yarns and threads.	120 (i) Spinning, Preparation of fibrous materials for (including obtaining, opening, carding, and like treatment of fibres in general).	IX
	120. (ii) Spinning, twisting, and winding yarns and threads.	
	120. (iii) Yarns and threads and miscellaneous spinning accessories and processes and treatment of fibres.	
121. Starch, gum, size, glue, and other stiffening and adhesive materials.	121. Ibid.	V
142. Weaving and woven fabrics.	142. (i) Looms, driving, reversing, stopping, and starting, and loom shedding mechanism and pattern cards, chains, surfaces, and the like.	IX
	142 (ii) Looms, kinds or types of, and details not otherwise provided for.	
	142 (iii) Looms, weft supplying, inserting, beating-up, cutting, doubling, and twisting in.	
	142. (iv) Woven fabrics and articles, and warping, leasing, bailing, and beaming yarns.	

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PATENT INDEX

* Patent no longer in force on 31st December, 1931.
† Renewal Fees due at 31st December, 1931.

BRITISH PATENTS

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