5

Cuprammonium processes

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5.1 Short history

5.1.1 Who invented the cuprammonium process?

In 1857 a German chemist Matthias Eduard Schweizer (1818–1860; a chemistry lecturer at the Oberen Institute-Schule in Zürich who progressed in 1852 to professor) reported in his article[1] *Das Kupferoxyd-Ammoniak, ein Auflösungsmittel für die Pflanzenfaster*, that cotton, linen cellulose and silk dissolve at room (*gewöhnlicher*) temperature in cuprammonium solution (ammonial copper oxide solution). Schweizer previously observed that ammonia reacts with metal oxide to form a basic compound (*Kupferoxyd-Ammoniak*).[2] The colour of the solution is due to the complex cupric tetramine hydroxide $Cu(NH_3)_4(OH)_2$. Schweizer wrote that '*das Ammoniak mit gemmissen Metalloxyden Verbingen bilden Könne*'.

Schweizer is generally credited as the inventor of the solution. However, it is somewhat curious that Schweizer did not apply for a patent for his 'invention', although he described his new observation as '*eine höchst interessante Eigenschaft'*.[1] Note that in the article there was no description of the experimental conditions such as the composition of copper ammonium solution, the concentration of cellulose or silk, temperature, and so on.

There is a story that John Mercer, a famous calico printer in Lancashire, UK, who developed a process for improving the lustre and dyeability of calico cotton cloth by dipping it in sodium hydroxide solution under tension, made the actual discovery that cuprammonium solution was a suitable solvent for cellulose. However, he applied this solution to coating calico to make it waterproof. Wheeler wrote in his book,[3] citing Parnell's *Life of John Mercer*, that Mercer dissolved cellulose in cuprammonium solution, and then regenerated the cellulose with sulphuric acid some time before Schweizer's 'invention'.[4] This is the first mystery in the history of the cuprammonium process.

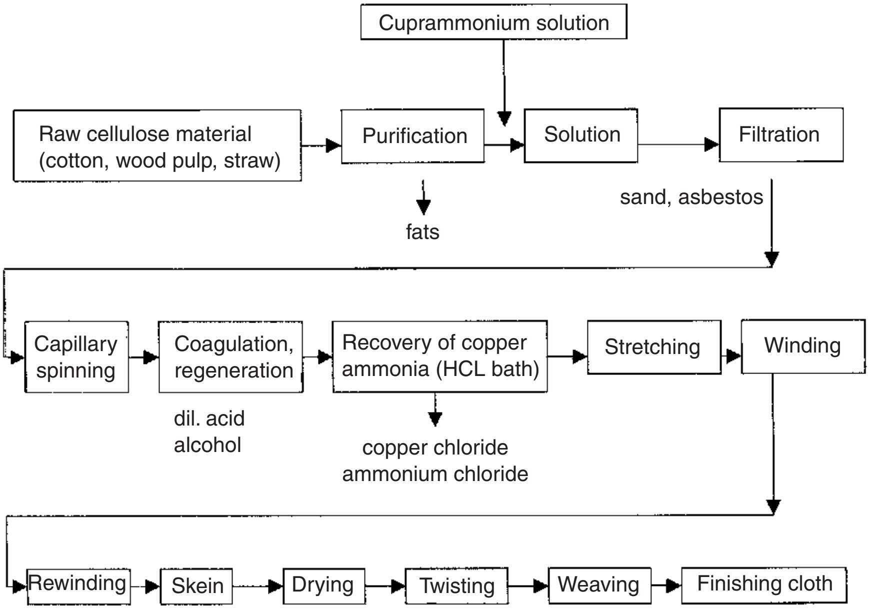
William Crooks (later, Sir William), who once cooperated with Joseph

Table 5.1 Prehistory of cuprammonium cellulose industry

Year	Inventor	Remarks
18??	John Mercer (UK)	Use of cuprammonium cellulose solution for treatment of cotton cloth
1857	M E Schweizer (Germany)	Dissolution of cotton cellulose into cuprammonium solution
1881	William Crooks (UK)	Fibres from cuprammonium cellulose solution for electric lamp, BP 2612 (1881)
1882	Edward Weston (USA)	Fibres from cuprammonium cellulose solution for electric lamp, BP 4458 (1882)

Wilson Swan (1828–1914) to develop an electric light bulb through his knowledge of vacuum technology, obtained a patent[5] on the carbonization of filaments of paper, cotton or linen treated with a solution of ammoniacal copper oxide to obtain a denser carbon filament. Edward Weston, a pioneer of artificial silk by the cellulose nitrate method, took out a similar patent[6] on carbon conductors for electric lamps. In 1885 Spiller also produced regenerated filaments from a cellulose–cuprammonium solution system. Table 5.1 summarizes the prehistory of the cuprammonium cellulose industry. In 1890 Louis Henri Despeissis, a French chemist, successfully produced (although on a laboratory scale) artificial fibre from cellulose dissolved in cuprammonium solution.[7] This was the most significant technological contribution to the regenerated cellulose industry, although his patent lost validity in 1892, because of non-payment of the patent maintenance fee. More sadly, soon afterwards he died. Despeissis was the first to attempt to produce pure cellulose fibre for clothing directly from cellulose, not from cellulose derivative fibres such as cellulose nitrate fibres (the collodion process, nitrate process, or Chardonnet process).

The principal process of the Despeissis patent is illustrated in Fig. 5.1.[8] In this process, cellulose (cotton or wood fibre) dissolved in aqueous cuprammonium hydroxide solution was extruded through a capillary to form fibres with a given cross-section area. Fatty and resinous materials attached to cellulose were removed in advance by washing in order to accelerate dissolution, and the solution was filtered through sand and asbestos to remove any undissolved matter. The solution was extruded into a bath of dilute acid (for example hydrochloric acid, formic acid, succinic acid, tartaric acid, or citric acid), alcohol and concentrated cresol solution. When cellulose in cuprammonium solution comes into contact with the above solution,[5] it precipitates immediately to give hard solid filaments, copper and ammonium being removed in the spinning bath. The filaments were



5.1 Production of artificial silk by the cuprammonium method (L H Despeissis, 1890).[7]

stretched in dilute hydrochloric acid using a winder, spool and drum. The remaining copper and ammonia in the filaments were reacted chemically to form the easily dissolved copper chloride and ammonium chloride. Dilute hydrochloride solution could be replaced with other solutions, which can precipitate cellulose. Washed filaments were dried and reeled. It was difficult to make a concentrated cellulose solution that could be employed on an industrial scale. The process described in Despeissis's patent was not commercialized in the original form.

In summary, the technology of cuprammonium solution was making progress as early as the 1850s–1880s in the following way:

1 Cuprammonium solution was found to be an adequate solution for cellulose.
2 Cellulose dissolved solution was first utilized as a coating reagent for cotton cloth and paper. (In the case of viscose, it was used to give waterproofing and rotproofing properties.)
3 Coarse short monofilaments were then produced for production of filament for electric light bulbs.
4 Endless thin filaments were finally produced on a laboratory scale as artificial silk for clothing.

In 1892, two years after Despeissis's invention, Rheinische Glühlampenfabrik, Dr. Max Fremery & Co. Kommerzial Gesellschaft at Aachen established a process of producing lamp filaments from cellulose in cuprammonium solution, based on their own unpatented 'invention'. The process was operated with economic success for several years and was the first commercial application of the cellulose-cuprammonium solution system. For example, in 1895 the company produced 2500 bulbs per day and eventually reacted production of over 4000.[6–9] Within five years, the company had developed a stretching process using rotating cylinders to make much finer filaments suitable for clothing.

Max Fremery (German chemist) (1859–1932) and John Urban (Austrian engineer) (1863–1940) applied for a patent in 1897 under the name of a German chemist Hermann Pauly,[10] who was a director of the Textilschule in Münchengladbach,[9] and was a Professor of chemistry at Wurzburg in 1924. It should be noted that Hermann Pauly was not the true inventor. The Pauly patent was applied for seven years after the Despeissis patent. The characteristics of the 'Pauly' (in fact, Fremery and Urban's) process is the dissolution of cellulose in aqueous cuprammonium solution at low temperature. For example, the specification of German Patent (Kaiserliches Patent) 98 642 (1897) indicates 'below 30°C' and the British Patent 28 631 (1897) claims 'as cool as possible'. Pauly insisted in the latter patent that 'The solubility of the cellulose in the ammoniacal solution of cupric oxide decreases as the temperature increases and on the other hand, the decomposition of the cellulose in the above solution increases as the temperature increases' and 'it is advantageous to keep the vessel, . . . , as cool as possible'. Pauly pointed out that the competitive cellulose nitrate fibre is 'extremely easily combustible' and that 'no (cellulose nitrate) process has, up to the present, been carried into practice'.* Pauly did not refer to the preceding technology and patents of the cuprammonium process in 'his' patent specification, although Fremery and Urban had already been engaged at least for six years in the business.

Figure 5.2 is a flow sheet of the manufacturing process of cuprammonium rayon by Hermann Pauly's method.[12] The figure is based on German Patent 98 642 (1897). Comparison of the two patents is made in detail in Table 5.2.[13] It is clear that the 'Pauly' patent lies within the range of the Despeissis patent. The former claims are much narrower and more restrictive than the latter. For example, Pauly referred to acetic acid as a coagulating liquid,

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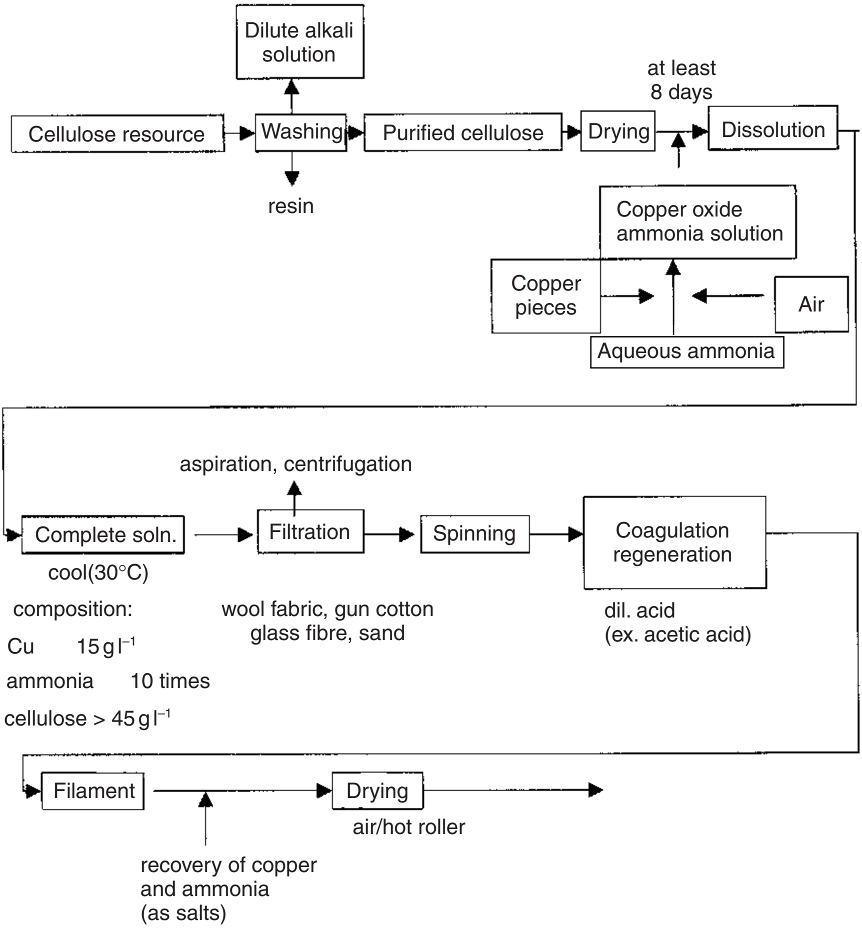
*It is noteworthy that at the time Pauly applied for 'his' patent, Chardonnet's company ('Société Anonyme Pour la Fabrication de la Soie de Chardonnet') was already producing (1894–1898) cellulose nitrate artificial silk, at the Besançon with a production capacity of between 100–1000 kg day^{-1} at a price of 21.75–30.0 francs kg^{-1}. The company made a profit of 20 200 French francs and paid a dividend of 6.25% in 1898.[11]



5.2 Herman Pauly's (actually, Fremery and Urban's) procedure for the production of cuprammonium artificial silk (1897).[10]

although this was omitted in the Despeissis patent. This fact strongly suggests that Fremery and Urban tried to ignore the existence of the preceding French patent, but as a matter of fact, were in contravention of that patent, which was already invalid and in effect only the published technical literature.

Why did Fremery and Urban apply for their patent under another person's name? VGF, which was established by them later stated in the book[14] 'from tactile economic considerations'. Why was the 'Pauly' patent finally accepted at Kaiserlichen Patentamt? The following remark in Wicht's 'Glanzstoff'[15] may help to gain some understanding. 'While

Table 5.2 Comparison of the Despeissis method and the 'Pauly' method

Items	Despeissis patent (1890) (FP203741)	'Pauly' patent (1897) (DP98642)
Cellulose resource	Cotton,woodpulp, straw	(Any cellulose)
Purification of cellulose	Washing	Treatment with dil.alkali soln.
Cuprammonium solution (preparation)	No description (based on Schweizer method)	Several methods
(composition)	No description	Cu; $15\,\mathrm{g\,l^{-1}}$ ammonia; $>150\,\mathrm{g\,l^{-1}}$
Spinning solution		
(purification)	Filtration	Filtration
(filtering materials)	Sand, asbestos	Woollen cloth,gun cotton, glass fibre, sand
(cellulose concentration)	No description	$>45\,\mathrm{g\,l^{-1}}$
(stock)	No description	Low temperature desirable (30°C)
Spinning method	Capillary	No description
(coagulation bath)		
	Dilute acid (hydrochloric acid, sulphuric acid, formic acid, tartaric acid, citric acid), alcohol, conc. phenol	Dilute acid (acetic acid)
Recovery of copper and ammonia	Dip into hydrochloric acid (in the form of salt)	As salt
Scope	Production of filaments from cuprammonium soln	Production of filaments from cuprammonium solution, prepared at low temperature

processing your patent application at the Kaiserliches Patentamt (German patent bureau) it has, for example, become evident that there has already been a French patent (F.P. 203 740-1890) which had expired already. In addition, this patent did not include a useable process for a consistent production of marketable threads.' This remains a mystery even today (i.e. the second mystery) in the history of the cuprammonium rayon industry.

An Alsatian textile engineer Joseph Foltzer, who published the first book[16] on regenerated cellulose technology (in France in 1903), called cupro rayon by the name 'Despeissis silk'. He had worked in Germany and Switzerland, and later took out some patents (for example, French Patent 345 687, German Patent 165 577 (1905), Swiss Patent 37 584 (with E. Weliss), German Patent 209 923 (1908) and German Patent 229 677 (1908)). After his book was published, Foltzer returned to Alsace and was arrested on suspicion of unlawful disclosure of German secrets. Arnold Hard wrote in his book[17] 'Germany considered Foltzer had committed a grave offence in publishing details of what they claimed was their own secret process'. Perhaps Foltzer was arrested for political reasons because he had revealed the 'secret' that there was no secret in German cuprammonium technology.

In 1899 an eminent Alsatian textile chemist Emil Bronnert (1868–1924), with Fremery and Urban, applied for a series of patents,[*] separately and jointly, before establishing their company (VGF): Vereinigte[†] Glanzstoff-Fabriken A G (VGF) started with capital of 2 million marks on September 19, 1899 financed by the Bergisch–Märkischen Bank.

After VGF was established they applied for two patents in the names Fremery, Urban and Bronnert (German Patent 115 989, date of application, Jan. 11, 1900: German Patent 119 230, Dec, 10, 1900). After that, all patents were obtained under the name of VGF until the end of World War II. The above patents, including, of course, the 'Pauly' patent, can be regarded as the fundamental VGF patents. The rights to these patents, owned by Fremery, Urban and Bronnert were estimated to be worth a million marks to VGF.

The first textile fibre factory using the cuprammonium process was opened at Oberbruch near Aachen, by expanding the experimental 1897 Rheinische Glühlampen factory to a capacity of 1.2 tonnes-filament/day.[18] Thereafter, a second factory was founded at Niedermorschweiler (now, Morschwiller le Bas) near Mulhouse. A third factory at Sachsen had been planned, but not realised: raw materials costs had to be reduced first.[19,20] This was to be achieved by:

1 moving away from using cotton wastes from carding, combing and other machines in the cotton industry and moving towards cotton linters;
2 moving away from copper sulphate (as a reaction product with aqueous sodium hydroxide solution) and moving towards copper hydroxide;

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[*] Bronnert (German Patent 109 996, date of application; May 2, 1899), Fremery and Urban (German Patent 111 313, March 27, 1899), Fremery, Urban and Bronnert (German Patent 119 098, May 9, 1899: German Patent 119 099, May 13, 1899).

[†] Here, 'Vereinigte' means union of three groups which had a keen interest in the cuprammonium artificial silk business in Germany: the Aachen (lower Rhein) group (Fremery & Urban and the Bergisch Bank), the Elsass (middle Rhein) group (Bronnert and Th. Schlumberger), and the Glauchau (Sachsen) group (Arthur Lossow).

Table 5.3 Workforce and output of cuprammonium artificial silk in VGF in 1901 and 1911[22,23]

Year	Workforce (no. of persons)	Output (kg fibres) per day	Productivity kg/person · day
1901	376	168	0.48
1911	2517	2738	1.1
Ratio 1911/1901	6.7	16.3	2.3

3 increasing the recovery rate of ammonia to 85% and of copper to 95%;
4 changing from acetic acid and around 50% sulphuric acid coagulation to alkali solution coagulation.

Their achievements on recovery rate are not known but the above targets seem unrealistically high for the technology available at that time.

Cuprammonium rayon made by VGF ('Glanzstoff silk') appeared on the market in early 1900. VGF produced yarns of 100–200 denier, judging from their circulars and price lists.[21] This meant that the filament constituting yarn was much coarser than that of Chardonnet silk. An advertisement for cuprammonium rayon in July 1900 says:[17]

> (1) The lustre is brighter than that of natural silk. (2) The lustre is exceedingly valuable for fancy thread for weft in silk, woollen and cotton goods. (3) The fibres are largely used for laces, galloons, fringes girdles, furniture stuffs, ribbons, tricots, embroidery etc. (4) The fibre dyes equal and uniform.

The productivity of VGF in 1901 and 1911 is illustrated in Table 5.3.[22,23] Over the 10 years they increased the labour force by a factor of 6.7 and production by a factor of 16.3. The productivity more than doubled. From the start of production, VGF recorded good profits until the outbreak of World War I (Table 5.4).[24–26] VGF's technology had spread from Germany to other European countries through licensed contracts, (e.g. in France, 1899), or in the form of a subsidiary company (Austria, 1904; England, 1907).

In July 1911, Hans Jordan, Vorsitzend (Chairman) of VGF, decided to buy all the rights to the German patents for the viscose rayon process and the Donnersmarcks Kunstseide und Acetatwerke plant near Stettin at a cost of 2 million marks.[23] He aimed to convert their fibre business from the cuprammonium rayon (process), which was even at that time yielding sufficient profit (see Table 5.4), to viscose rayon. VGF explained this transition of business in terms of future prospects.[27] The production of cuprammonium rayon reached a maximum (820 tonnes) in 1912, but it stopped in 1916 because of a shortage of raw materials.[28] However, Thiele's 'stretch-

Table 5.4 Profits of VGF in 1900–1913

Year	Capital (10^4 marks)	Total profit (10^4 marks)	Net profit (10^4 marks)	Dividend (%)
1900	250	—	6.5	—
1901	250	—	—	(9)
1904	250	—	170	—
1906	250	241.1	203.1	35
1907	250	252.8	214.1	40 (40)
1908	250	287.6	209.2	40
1909	500	444.2	309.9	30
1910–12	500	—	335.9 (average)	—
1913	750	—	—	38

Reproduced from K Kamide,[8] p. 245, Table 7.8, Y Kami[24], *Recent Artificial Silk*, Meibundo, 1927, p. 141 and W E Wicht,[9] p. 35.

spinning process' developed for J P Bemberg, a powerful domestic competitor, had succeeded in commercial production of a cuprammonium rayon that had filaments as fine (1.0–1.5 den) as Chardonnet silk, and with superior physical properties. Against this, Glanzstoff silk was uncompetitive.

The years 1910–1911 constituted a remarkable turning point in the artificial silk industry. Shortly after succeeding against the nitrate process, in 1907 the cuprammonium process was confronted with almost insurmountable competition from the viscose process. It became clear in 1909–1910 that the viscose process was the best. World production of cuprammonium rayon began to decay, passing through a maximum in 1909. The conventional cuprammonium process was clearly uncompetitive economically with the new viscose process and was inferior in quality to cellulose nitrate silk.

In converting to viscose, VGF was attracted by its cheaper raw materials (e.g. wood pulp) and simpler spinning process.

5.1.2 Invention of Thiele's 'stretch-spinning' and to the present day

Edmund Thiele, an exceptional German chemist, joined J P Bemberg A G (JPB; Barmen, Germany) in 1900, to study new spinning processes. From 1904 he worked together with Emil Elsässer on this project. Thiele invented the 'stretch-spinning' method[29–32] in 1902.

Compared with cellulose derivative solutions, cuprammonium solution is not easily stretched using the apparatus employed in the viscose process and so filaments had to be spun through smaller holes. Thiele considered the use of very small diameter capillary tubes disadvantageous.[29,30]

1 Cellulose solution must be carefully filtered.
2 Higher pressures are required to force the dope through small holes.
3 Small holes block more easily.

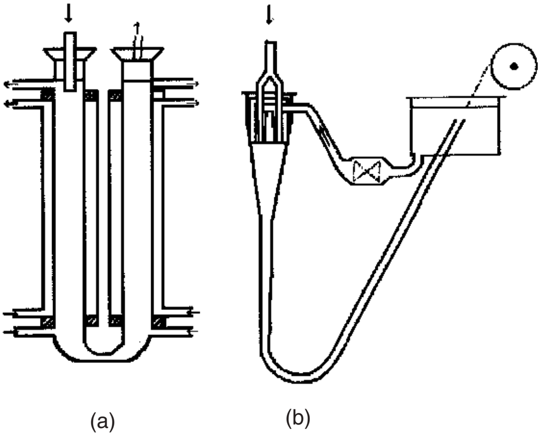
The above disadvantages, Thiele argued, would be partially obviated if a comparatively thick filament issuing from a larger opening (such as 1/4 or 1/8 th millimetre) could be drawn down by stretching. This was originally done by Lehner in nitrate silk production but such a process had never before been employed with aqueous solutions of cellulose. (The formation of the filament from cellulose nitrate solution is effected by gradual evaporation of the solvent, but precipitates immediately when cuprammonium solution makes contact with non-solvent.)

The main claims of Thiele's stretch spinning patents[29–32] are:

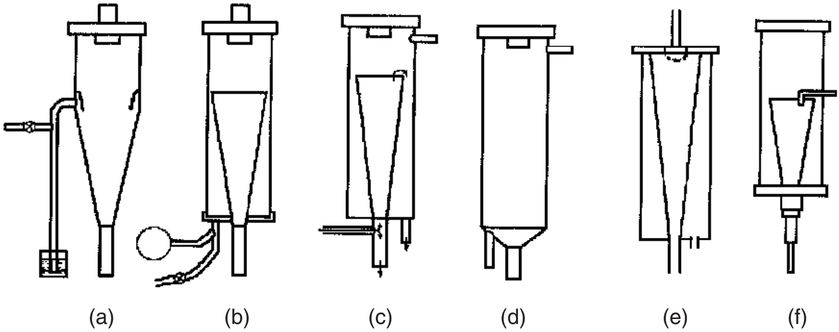
1 A process for the manufacture of filaments from cellulose solutions wherein an aqueous cellulose solution issues through comparatively large orifices into a precipitating medium that acts only slowly upon aqueous cellulose solution, the said issuing solution being substantially drawn out into fine filaments in such medium.
2 A process referred to in claim 1, using the drawing out of the cellulose solution into fine filaments to be effected by the action of its own gravity.
3 After having drawn out into fine filaments in a slowly acting precipitating medium, the filaments are subjected to the action of a more rapidly acting precipitating medium, both media coming into contact in such manner that filaments can pass directly from the slowly acting medium into the rapidly acting one.

Figure 5.3 shows Thiele's apparatus in its original form.[30,31] Thiele worked for J P Bemberg for only a few years and then moved from Barmen, where J P Bemberg's plant was situated, to Brussels, where he collaborated with R Linkmeyer, who was an entrepreneur, and filed another patent.[33] After Thiele left J P Bemberg, the engineering group, originally headed by Emil Elsaesser, continued to develop stretch-spinning technology.[34–39] Figure 5.4 illustrates the apparatus.

Surprisingly, Thiele and his successor's patents (most probably, German Patent 220 051, 1907),[34] were judged by a German court on 4th May 1907 to be anticipated by Pauly. The judgment is not easy to justify from a modern view point, because 'Pauly' was considered only to mimic the Despeissis patent (see Table 5.2) and the lack of novelty in the 'Pauly' patent was indirectly acknowledged by VGF at that time.[15] In other words, VGF won their patent defence war against J P Bemberg. This constitutes the third mystery in the history of the cuprammonium process. In this way, J P Bemberg A G had been forced to associate with VGF in the cuprammonium rayon business, although details of the above circumstances are not known.



5.3 Apparatus for 'stretch-spinning' from cellulose solution (Thiele's[31] original method). (a), (b): Thiele[31] and British Patent No 8 083 (1902).[30]



5.4 Apparatus for 'stretch-spinning' from cellulose solution (J P Bemberg Akt.-Ges.) (a), (b): German Patent 413 791 (1923),[35] (c): German Patent 413 790 (1923),[36] (d): German Patent 415 798 (1923),[37] (e): British Patent No 229 638 (1925),[38] (f): British Patent No 235 853 (1925).[39]

J P Bemberg A G founded a factory with a capacity of 500–600 kg per day of cuprammonium rayon using Thiele's procedure at Ölde near Barmen-Rittershausen. In 1916, in order to amalgamate the factories at Elberfeld (VGF) and Barmen (JPB), a mutual technical exchange was carried out and since then, cuprammonium rayon production was practically commissioned to JPB, which supplied the fibre products under the trade name of 'Bemberg'®. Glanzstoff did not reopen the production after World War I. In other words, a horizontal business division was created between VGF and JPB. Cuprammonium rayon was produced by JPB and viscose rayon by VGF. In 1925 J P Bemberg came under the control of VGF and in 1948 VGF took over 35% of the capital of JPB.

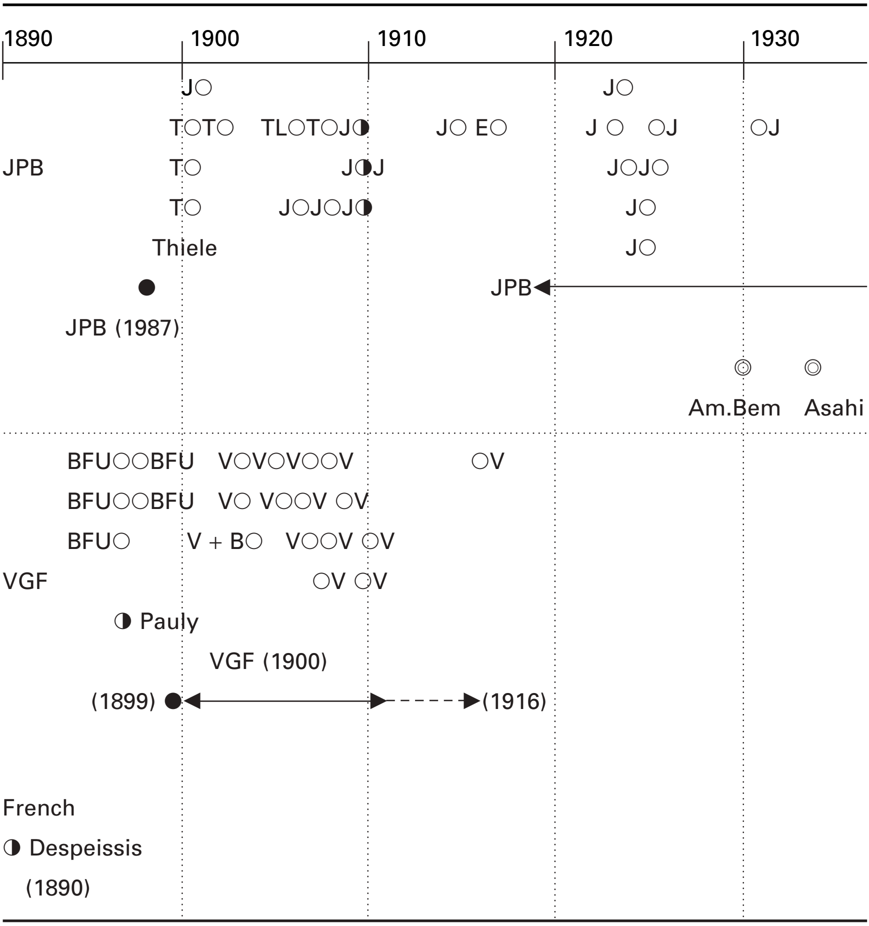
Thiele's technology was transferred to the USA (American Bemberg Corp., Elizabethton, Tennessee, 1925), Italy (Bemberg S A; Gozzano 1924), France (Le Cupro textile; Rennes), Japan (Asahi Bemberg; Nobeoka, 1928) and UK (British Bemberg; Doncaster, 1928). In 1926 Interessen Gemeinschaft (IG) Farbenindustrie A G (established in 1925) built the Dormagen factory. Beaunit Mills took over American Bemberg in 1948 as a division (Beaunit Fibers).

Table 5.5 summarizes the development and commercialization of the cuprammonium process from 1890–1930. It clearly shows that:

1 VGF and JPB started independently and almost simultaneously. VGF commercialized in 1900, but J P Bemberg succeeded in large scale production barely from 1916.
2 During the short time when Thiele worked at JPB, JPB applied for a patent (German Patent 162 866, 1900[40]). This suggests that JPB had its own engineers as well as Thiele.
3 Until 1907 JPB had obtained three patents (German Patents 162 866, 1900,[40] 174 508, 1904[41] and 220 051, 1907[34]), the last being the most technologically important, because it claims 'stretch-spinning', by which JPB could produce fibres on a large scale. Therefore, it seems probable that German Patent 220 051[34] was the main target of the legal struggle by VGF against JPB.
4 Funnels suitable for industrial use had been patented, after commencement of large-scale production and after the time of expiration of Thiele's original patents, during 1923–1925 (German Patents 408 889, 1923,[42] 413 791, 1923,[35] 413 790, 1923,[36] 415 798, 1923,[37] and British Patent 235 853, 1925[39]).

As the denier of single filaments in a yarn is decreased, the yarn exhibits superior handling quality (aesthetics) and, accordingly, can be sold at relatively high price. The denier of single filaments is also a measure of the sophistication of the production technology. Table 5.6[43] records the single filament denier of yarns that were available in several European countries in 1922. Nitrate processes had enjoyed a monopolistic position in supplying fine filaments before the commercialization of Thiele's stretch-spinning method in 1916. Viscose rayon belonged to another category competing on price rather than quality. Bemberg® competed with nitrate artificial silk. In 1922 Germany alone produced Bemberg®. The technology did not spread to other countries which continued the production of the coarser Glanzstoff-type rayon until 1924–1928. The number of single filaments in a Bemberg® thread was, in most cases, three quarters of the denier

Table 5.5 Cuprammonium rayon process in 1890–1930



●: Establishment of company; ◀- - - - -▶ Commercial production; ◑: Basic patent; ◎: Technology transfer; ○: Patent; T: Thiele; TL: Thiele-Linkmeyer; J: JPB (J P Bemberg); E: Elsaesser; BFU: Bronnert-Fremery-Urban; B: Bronnert; V: VGF (Vereinigte Glanzstoff Fabriken A G).

number: 100 denier consisted of 75 single filaments with a fineness of 1.3 denier.[45]

During the 1910s–1920s the names of the following companies were known in Germany as cuprammonium rayon producers, as well as VGF and JPB. The year in parentheses is the date established and marks indicated is the amount of capital at the time of foundation:[46] Hanauer Kunstseide Fabrik GmbH (1910; 2.5 million marks), Rheinische Kunstseide Fabrik A G (1907; 2.0 million marks), Glanzfüden A G (1910; 1.0 million marks),

Table 5.6 Single filament denier and number of filaments constituting a yarn (1922)

Process	Single filament denier			
	Germany	France	Switzerland	Belgium
Nitrate	1.4–1.8 (14–62)	—	—	—
Cuprammonium	1.2–1.7 (57–227)	6.1–8.4 (20–21)	—	—
Viscose	2.4–7.7 (31–113)	6.6–10.0 (16–23)	8.2–10.0 (11–16)	8.1, 8.4 (17, 18)

The original table (Table 8.9) of ref. 43 was constructed using data in ref. 44.
( ): Number of filaments constituting a yarn.

Sachsischen Kunstseiden Werke A G (1915; 1.5 million marks). Hanauer Kunstseide was dissolved in 1921 after defeat by VGF in a patent war and Rheinische Kunstseide was also dissolved.

In Table 5.7 the cost of production and the price of the regenerated cellulose yarns produced by three processes during 1899–1914 are collected. The table was compiled by revising Kamide's table 8.5[47] and the detailed references of the original table are omitted for simplicity. Even if the scarce and scattered data available are considered, we can presume that: (1) the prices of Chardonnet (nitrate) silk were always higher than those of VGF (cupro) silk, probably owing to the difference in fibre quality. The price of yarns produced on a commercial scale decreased in the following order: nitrate process >> cuprammonium process > viscose process. (2) The cost of fibre production decreased in the following order: nitrate process > cuprammonium process > viscose process.

Cuprammonium rayon produced in 1900–1920 had the following drawbacks, which severely limited its applications: (1) poor mechanical properties, including low tensile strength (TS), in particular in the wet state (0.3–0.5 $\mathrm{g\,den^{-1}}$); wet–dry ratio 0.1–0.25, (2) uneven dyeing and (3) high price, compared with the natural fibres. Because of (1), the products were utilized for embroidery, ribbons and strings. In the 1920s–1930s, TS(dry) exceeded 1.5 $\mathrm{g\,den^{-1}}$ and TS(wet) increased to above 0.8 $\mathrm{g\,den^{-1}}$, allowing the fibres to expand their usefulness into washable apparel applications.

The rise and fall of the leading companies producing cuprammonium rayon since the 1950s can be summarized as follows. In 1955 British Bemberg closed a cuprammonium rayon plant at Doncaster. During the 1960s five companies (except in Eastern Europe) were in operation for production of cuprammonium rayon: J P Bemberg A G (Barmen and

Table 5.7 Production cost and price of regenerated cellulose fibres for 1899–1914

Year	Nitrate process		Cuprammonium process		Viscose process	
	cost	price	cost	price	cost	price
1894	20 f/kg	25–27 f/kg				
1897		26.5 f/kg				
1899	17 f/kg	50 f/kg			2–3 s/lb (VSS)	
1900	11. 3 s/lb	12 s/lb (Tubize)				
1901						
1902				956 d/lb (120 d)		
			9.56 m/kg	14 m/kg		
1903		40 f/kg				
1904	7 s/lb	∼12 s/lb		2.5 s/lb		
1906				3 s/lb		5.6 s/lb (150 d)
1908		8 s3 d/lb (Tubize)		$2\frac{1}{3}$ s/lb		
1909						
						6.5 s/lb (150 d)
1911		20 f/kg			2 s4 d/lb (150 d)	
					24.9 d/lb	
1912	12–13 m/kg	20 f/kg	9–10 m/kg		35.9 d/lb	63.3 d/lb
					8–9 m/kg (average)	
1913			12 f/kg		2 s2 d/lb 78.4 d/lb	
1914						
1915					28.1 d/lb (180 d)	

The table was constructed on the basis of Table 8.5 of ref 47.
f: franc. (France), s: shilling (UK), d: pence (UK), m: mark (Germany).
Tubize: Davenport & Co Ltd, Chardonnet Silk Mill, Tubize, Belgium.
VSS: Viscose Spinning Syndicate, UK.
Denier of fibre is shown in brackets.

Wuppertal, Germany), Farbenfabriken Bayer (Dormagen, Germany), Asahi Chemical Industries Co (Nobeoka, Japan), Beaunit Fibers (Elizabethton, Tennessee, USA), and Bemberg S A (Gozzano, Italy). Note that all of them were originally based on the technology of J P Bemberg A G. In 1970 there were four plants producing cuprammonium rayon in the world, again excepting Eastern Europe: (1) J P Bemberg A G (Wuppertal), 27 tonnes/day; (2) Beaunit Fibers (Elizabethton), 25 tonnes/day; (3) Bemberg SpA (Gozzano), 14 tonnes/day; (4) Asahi Chemical Industries Co (Nobeoka), 80 tonnes/day (→80 tonnes/day in the 1990s). Now, only Asahi survives, although the economic environment is not very favourable, as a monopoly supplier of cuprammonium rayon.

5.1.3 Characteristic features of research and development of the regenerated cellulose fibre industry

The regenerated cellulose fibre industry, formed in the late 19th to early 20th centuries, is different from the traditional cotton and wool fibre industry which originated between the late 18th and early 19th centuries and also differs from the modern and synthetic fibre industry that developed in the mid-20th century. Regenerated cellulose is called the second generation fibre industry, cotton and wool is called the first generation, and the synthetic fibre industry is called the third generation.[48] The second generation fibre industry has common characteristics that feature in various processes.[48] Table 5.8 shows the dates that the basic patents were filed or literature was published and of the first commercial production of three kinds of regenerated cellulose fibres, all belonging to the same generation.[49] It is interesting to note that the processes of synthesis of cellulose derivatives, dissolution of the cellulose derivatives or cellulose into solvents and spinning of the solution into fibres were studied and developed at different locations. Nobody succeeded in developing the complete process in one location. If Despeissis's patent is regarded as a basic patent, it took 9 years to attain its first commercial use. The cuprammonium rayon process got off the ground 3–4 years after the first commercialization although 'true take-up' was only realized when J P Bemberg A G started large scale production by Thiele's method. In this sense, approximately 20 years elapsed before the first small-sized factory was scaled-up.

The professions of the main inventors of the regenerated cellulose fibres are summarized in Table 5.9. It is obvious that the majority are professional chemists with academic backgrounds. Fremery, Bronnert, Lehner and Müller (the last two are not shown in the table) had doctoral degrees. This is a common feature of the regenerated cellulose rayon industry.

The industrial revolution, including the textile (cotton and wool) industry, had been achieved by numerous amateurs.[50] But the operation,

Table 5.8 Basic patents and first commercial production of three kinds of regenerated cellulose fibres

Process	Basic patents			First commercial production (year)	The time the first commercialization was scaled up	Place of first commercial production
	derivatives	spinning dope	spinning			
Nitrate	1846 (Schoenbein)	1847 (Maynard)	1884 (Chardonnet)	1884	1891–1895 50 kg/day	Besançon (France)
Cuprammonium		1857 (Schweizer)[a]	1890 (Despeissis) 1897 (Pauly)	1899 1200 kg/day (1900)	1902–1903	Oberbruch (Germany)
Viscose	1892 C-B-B[c]	1892 C-B-B[c]	1898 (Stearn)	1901 600 kg/day (1903)	1910[b]	Sydowsaue (Germany)
				1904 453 kg/day	1908	Coventry (UK)

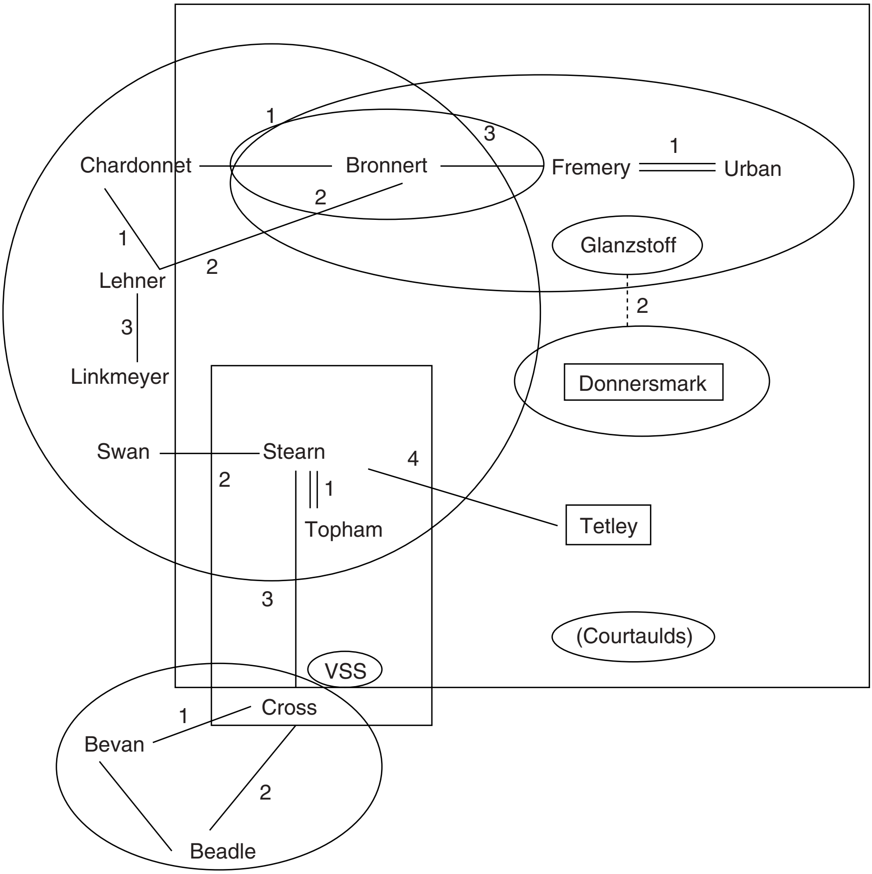
[a] in academic journal, [b] sold to VFG, [c] Cross–Bevan–Beadle.

Table 5.9 Profession of main inventors of cellulose chemical fibres

Process	Name (age when first patent obtained)	Profession
Nitrate	J W Swan (55)	Chemist, electric engineer (President of Society of Chemical Industry and Institute of Electrical Engineers)
	H B Chardonnet (45)	Scientist (Ecole Polytechnique), Count
Cuprammonium	M Fremery (38)	Chemist (Dr.)
	J Urban (34)	Engineer (Diploma-Ingenieur)
	E Bronnert (29)	Chemist (Strasbourg, Dr.)
	E Thiele (?)	Chemist (Dr.)
Viscose	C F Cross (ca.40)	Chemist (Owen's College)
	E J Bevan (ca.40)	Chemist (Owen's College)
	C H Stearn (?)	Bank clerk (self-educated chemist)
	C F Topham (?)	Technician (glass blower), inventor of genius

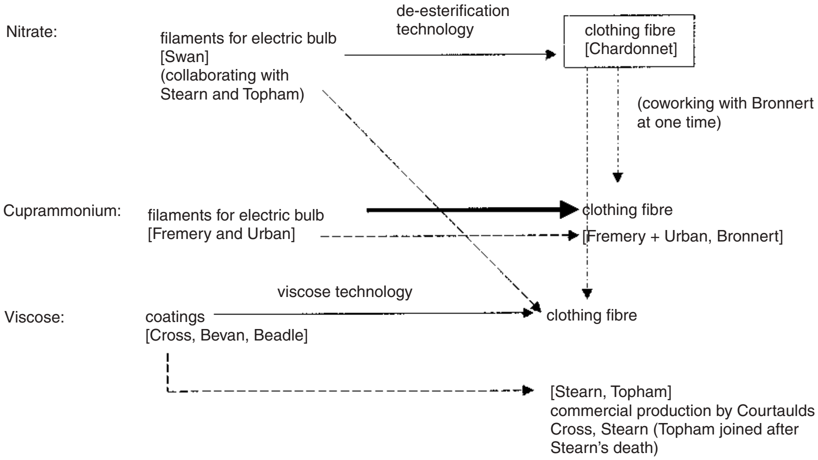
management and improvements to heavily mechanized processes required large groups of engineers who had been educated in science subjects at various levels, instead of traditional craftsmen trained by apprenticeship. In technical education, Germany and France were most advanced at that time. Nevertheless, in a relatively limited area of Lancashire, UK, many inventors who participated in the process of industrial development of natural fibres (late 18th to mid-19th centuries) worked independently, developing machines in isolation. In contrast to this, communication between developers was extremely comprehensive and complex during the development of regenerated cellulose fibres.

Figure 5.5 shows such person-to-person relationships.[51] The numbers in Fig. 5.5 indicate the order of contact between people from longest ago to most recent. For example, Bronnert once worked with Chardonnet, then with Lehner and after that joined the group of Fremery and Urban, who worked together all their lives in a kind of *Gemeinschaft*. The VGF factory at Niedermorschweiler was burnt down during World War I. After the war Bronnert left VGF to form his own company. The *gemeinschaftlich* relationship observed between Fremery and Urban was also found between Stearn and Topham. Bronnert's splendid business career is easily understood if we recall that he was an Alsatian. Processes were no longer commercialized by individuals. The groups of Fremery–Urban–Bronnert at VGF and Thiele–Elsässer at J P Bemberg contributed significantly to the cuprammonium rayon process. However, these two groups were relatively small in size, greatly different from the large research groups of gigantic contemporary multinational companies.



5.5 Person-to-person relationships between developers and entrepreneurs working on regenerated cellulose fibres. ═══ : gemeinschaftlich (comrade), ——— : gesellschaftlich (employer–employee), - - - - - : business relationships. A development group is shown by a large circle or rectangle.

The first commercial application of any rayon process was not directly concerned with textile fibres, but with electricity or coatings. Figure 5.6 shows the technological and personal relationships between the first commercial applications and the area of textile fibres.[52] In the cuprammonium rayon process the manufacturing technology of light bulb filaments was transferred, with further development, to the textile fibres. Chardonnet and Despeissis, who had intended from the first to produce textile fibres (artificial silk) directly were the exception, since France was a centre of the silk industry in Europe at that time. But Sir Joseph Wilson Swan (1828–1914) was actually the first man to commercialize rayon silk in 1883 via the nitrate



5.6 Personal and technological relationships between the commercial applications targeted initially and clothing fibres. [ ], Main developer; ( ), collaborator; ----▶, personal connection; ━▶ , strong technological connection; ▭ , clothing fibre first commercial; ┈┈▶ : technological stimulus (motivation for research); ⟶ : technological connection.

route, one year earlier than Chardonnet. Despeissis's first process could not be made commercial.

5.2 Science and technology of manufacturing processes

5.2.1 Cellulose

Cotton linter, the short fibres remaining on the surface of cotton (*Gossypium*) seed after ginning, is used exclusively for this process. It is a by-product of cotton seed oil mill production. Purified wood pulp (in particular, high α-pulp (α content > 95%) was once tried in place of cotton on a pilot scale at Asahi Chemical Industries during and immediately after World War II because of a shortage of cotton linters from overseas. It was not adopted commercially because of drawbacks in processability and the poor fibre quality,[53] both caused by the contamination of gel-like particles in the spinning solution. Cotton linter is now imported not only from the USA (Texas), but also from Mexico, Turkey, Pakistan, China, and the former Soviet Union. Raw cotton linter (with a cellulose content of about 70–75 wt% and a viscosity-average degree of polymerization (DP) = 2000–3000 (rough estimate)), is contaminated with fat, wax, proteins, pectins, inorganic materials, colouring materials, pepper trash, seeds and weeds. The composition differs markedly depending on the climate, soil and cultivating conditions under which the cotton grew. Cotton linter is purified by treating with 3–5% aqueous sodium hydroxide solution at 130–160°C for 2–6 h, and then is bleached with aqueous sodium hypochloride solution, reduced with sodium sulphite and dehydrated to a water content of ~ 50 wt%. Strong correlations are shown between the breaking strength of the filaments in the wet state and the α-cellulose content of cellulose resources.[53]

5.2.2 Ammonia

At an early stage of commercial application, ammonia produced by decomposition of ammonium sulphate as a by-product of coke production, was utilized. Nowadays, ammonia is synthesized from natural gas. Very pure liquid ammonia is transferred from the ammonia factory and diluted with water to give a 25% ammonia solution.[54]

5.2.3 Cuprammonium solution

Cuprammonium hydroxide is formed by dissolving copper hydroxide in a concentrated ammonia solution. This so-called cuprammonium solution (*cupram; Kupfer-oxyd ammoniak Lösung; Kuoxam Lösung*) is a deep blue solution in which a kind of strong bivalent base, cupric tetramine hydroxide (CTH), $Cu(NH_3)_4\ (OH)_2$, is assumed to exist,[55] but has never been isolated. The concentration of CTH increases with temperature. On the other hand, the concentration of the ammonia dimer, NH_3–NH_3 which does not react with copper hydroxide to give CTH, increases with ammonium concentration so that the concentration of CTH attains a maximum in 6N NH_4OH.[56] CTH is extremely sensitive to light and undergoes rapid photodecomposition to copper oxide, having to be stored in a cold dark place.

In practice, copper sulphate $CuSO4{\cdot}5H_2O$ (purity > 99.2 wt%, Fe_2O_3 < 0.08 wt%, Al_2O_3 < 0.05 wt%, ZnO < 0.04 wt%) is extensively employed as a copper source. Metallic oxide contamination of copper sulphate changes to insoluble hydroxide in cuprammonium solution. Copper hydroxide is produced from copper sulphate via the following routes.

5.2.3.1 Direct method for production of copper hydroxide from copper sulphate

Addition of aqueous sodium hydroxide solution to aqueous copper sulphate solution at pH > 8–9 yields copper hydroxide. However, the copper hydroxide obtained by this reaction is readily oxidized by air and has not been adopted for commercial fibre production.

5.2.3.2 *Indirect method for production of copper hydroxide from copper sulphate via basic copper sulphate*

Hot (~55°C) dilute (~20 wt%) aqueous sodium carbonate solution is added to hot (~90°C) dilute (2–3 wt%) aqueous copper sulphate solution at a specific pH to give stable basic copper sulphate (BCS), $CuSO_4{\cdot}3Cu(OH)_2$ (or $CuSO_4{\cdot}2.5Cu(OH)_2$), (Equation [5.1])

$$\begin{aligned}&4CuSO_4 + 3Na_2CO_3 + 3H_2O\\&\quad = CuSO_4 \cdot 3Cu(OH)_2 + 3Na_2SO_4 + 3CO_2\end{aligned} \qquad [5.1]$$

BCS appears as crystals, suspended in the mixture. The supernatant of the mixture is then decanted, and the precipitate (slurry) is dissolved in aqueous ammonium solution, in which any copper sulphate that did not react in the first step is transformed to $Cu(OH)_2$ by reaction with sodium hydroxide, (Equation [5.2])[57]

$$CuSO_4 \cdot 3Cu(OH)_2 + 2NaOH = 4Cu(OH)_2 + Na_2SO_4 \qquad [5.2]$$

In the solution $Cu(OH)_2$ reacts with ammonium ions to give cupric tetramine hydroxide (CTH), (Equation [5.3])

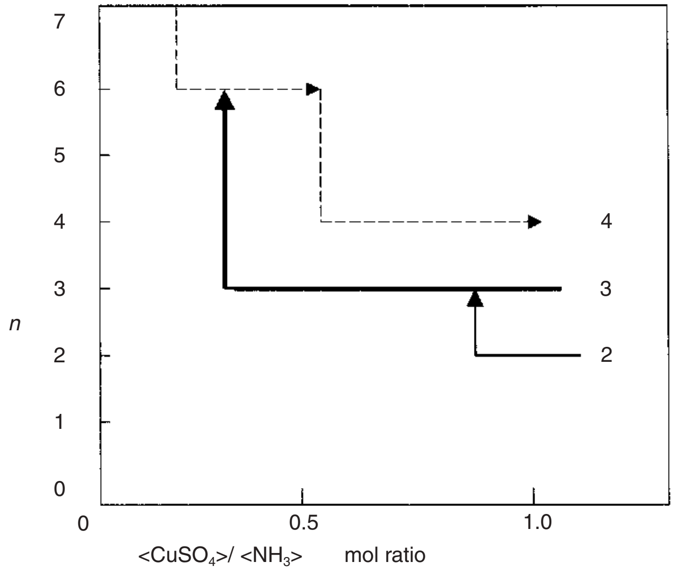
$$Cu(OH)_2 + 4NH_4OH = Cu(NH_3)_4(OH)_2 + 4H_2O \qquad [5.3]$$

In this way a cuprammonium solution is prepared. In addition to the $Cu(NH_3)_4$ ion, various copper complex ions, including ions of $Cu(NH_3)$, $Cu(NH_3)_2$, $Cu(NH_3)_3$, and $Cu(NH_3)_5$, as identified by a spectroscopic method, coexist with excess NH_4^+ in a $CuSO_4$–NH_3–H_2O system.[58] Hence, the cuprammonium solution should not be oversimplified as being aqueous CTH solution (i.e. the binary solution). The solubility of $Cu(OH)_2$ in aqueous ammonia is at most ~10 g l^{-1}.[57] The sulphate group, which coexists in the cuprammonium solution, lowers the solubility of cellulose in the cuprammonium solution, making the complete dissolution of cellulose difficult. Therefore, the sulphate content of BCS should be kept as small as possible.[59] Ammonia, which used to be a cheaper reagent than sodium hydroxide, was employed in place of sodium hydroxide.

In an alternative method, the rapid reaction of aqueous ammonium solution with copper sulphate solution at controlled pH (e.g. at pH = 8) with strong agitation was utilized for preparation of basic copper sulphate containing large amounts of $Cu(OH)_2$[60], (Equation [5.1′]), which is filtered and reacted with sodium hydroxide to yield pure hydroxide, (Equation [5.2])

$$\begin{aligned}&CuSO_4{\cdot}nCu(OH)_2 + NH_4OH \rightarrow Cu(NH_3)_{4\,\mathrm{or}\,6}SO_4 +\\&\quad (n - m)Cu(NH_3)_{4\,\mathrm{or}\,6}(OH)_2 + mCu(OH)_2\end{aligned} \qquad [5.1']$$

where $n = 6$–9.



5.7 Number of molecules *n* of the precipitate (nCu(OH)$_2$). CuSO$_4$ as a function of molar ratio ⟨CuSO$_4$⟩/⟨NH$_3$⟩ for the mixture CuSO$_4$–NH$_3$–H$_2$O at 25 °C.[58] ———— : case when NH$_3$ is added to aqueous CuSO$_4$ solution; ------------- : case when CuSO$_4$ is added to aqueous NH$_3$ solution.

In Equation [5.1′], the precipitates appear if the molar ratio of copper to ammonium, designated as ⟨Cu⟩/⟨NH$_3$⟩, is larger than 0.2. The precipitate is a basic salt, composition nCu(OH)$_2$·CuSO$_4$.[58,61–66] 3Cu(OH)$_2$·CuSO$_4$ is formed in a nearly quantitative yield over a wide range of ⟨Cu⟩/⟨NH$_3$⟩ (see Fig. 5.7). To avoid precipitation, excess ammonium ion $(NH_4)^+$ is added to the mixture. The maximum amounts of copper hydroxide and of ammonia that are attainable, which can be exhausted in forming CTH in the solution, are unambiguously determined by the solubility limit of CTH in the solution. Then, 'excess' copper hydroxide and 'excess' ammonia are defined as those existing in other forms than CTH in the solution when CTH reaches saturation.

First, Cu(NH$_3$)$_4$ SO$_4$ is formed by reaction of CuSO$_4$ with NH$_4$OH and this reacts with the remaining CuSO$_4$ by Equation [5.4]

$$\begin{aligned}&3\mathrm{Cu(NH_3)_4SO_4} + 4\mathrm{CuSO_4} + 12\mathrm{H_2O}\\&\quad = (6\mathrm{Cu(OH)_2})\mathrm{CuSO_4} + 6(\mathrm{NH_4})_2\mathrm{SO_4}\end{aligned} \qquad [5.4]$$

The composition of BCS is governed by the molar ratio ⟨Cu⟩/⟨NH$_3$⟩. Relationships between the composition of the reaction mixture CuSO$_4$–NH$_3$–H$_2$O, as expressed by the molar ratio of CuSO$_4$ to NH$_3$, ⟨CuSO$_4$⟩/⟨NH$_3$⟩, and *n* moles of the precipitate(nCu(OH)$_2$)·CuSO$_4$, formed from the mixture at 25°C, are shown in Fig. 5.7. The relationship n–$\langle CuSO_4\rangle/\langle NH_3\rangle$ differs depending on the order of mixing of the three components: whether NH_3 is added to aqueous $CuSO_4$ solution or aqueous $CuSO_4$ is added to aqueous NH_3 solution.[58] At pH 7, $n = 4$–6 is obtained.

In commercial operations, the technological and economical effects should be carefully considered in order to choose the optimum conditions. For example, in the above case basic research indicated the use of $(6Cu(OH)_2)\ CuSO_4$, but it became clear that the new process had several problems in practical operation;[67] the concentration of Cu remaining in the supernatant phase increases (the yield of BCS decreases), compared with the case where $n = 3$ and where the value of n is >5 but varies depending on the delicate operating conditions which are not easy to control. Sedimentation of BCS ($n = 4$–6) suspended in the solution is extremely slow, washing out the ammonium sulphate that adheres to BCS is difficult and as a result, the concentration of SO_4^- in the spinning solution does not decrease.

In summary the cuprammonium solution is prepared via the route shown in Equation [5.5]:

$$CuSO_4 \xrightarrow{[5.1]\text{ or }[5.1']} \underset{\text{BCS}}{nCu(OH)_2\cdot CuSO_4} \xrightarrow{[5.2]} Cu(OH)_2 \xrightarrow{[5.3]} \underset{\text{CTH}}{Cu(NH_3)_4(OH)_2} \qquad [5.5]$$

5.2.4 Dissolution of cellulose into cuprammonium solution

Cellulose is dissolved in cuprammonium solution, prepared in advance and stocked in a closed dark vessel. Cellulose is usually supplied wet to avoid possible oxidation.[68] Reducing agents such as salts of tartaric acid or sodium sulphate have been utilized to keep the quality of cellulose in solution high, but if oxygen is completely excluded, these reagents are not necessary.

In this case, the solution contains excess copper hydroxide in suspension and also excess ammonium. The dissolution of cellulose can be explained as follows:[69]

1. First, cellulose dissolves by reacting with cupric tetramine hydroxide ion CTH to form a complex, releasing ammonium ions. In the dissolving process, it is obvious that free ammonia is generated.
2. Then, excess, undissolved copper hydroxide suspended in the solution dissolves, to compensate for the amount of CTH consumed to form the cellulose complex, by reacting with (excess) ammonia to form CTH.
3. Newly formed CTH reacts with cellulose to form a complex dissolvable in the solution.

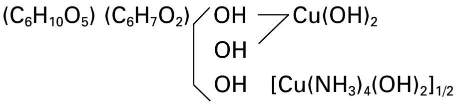
The existence of excess copper hydroxide and ammonium in solution allows us to keep the maximum concentration of CTH and, as result, enables us finally to prepare the highly viscous concentrated solution (cellulose concentration C_c is 10–12 wt%, viscosity is 1000–3000 poise at 30°C, specific gravity is 1.1 at 30°C). As the dispersion of cellulose into cuprammonium solution approaches the molecular dispersion, the viscosity of the dispersed system decreases somewhat. As dissolution of cellulose proceeds, excess copper hydroxide and excess ammonia are completely exhausted. Cellulose dissolves forming a cellulose–cuprammonium complex in cuprammonium solution.

The scientific study of the cellulose–cuprammonium solution system can be traced back to that of the alcohol–alkali–copper system in 1898 by Fr. Billnheimer.[70,71] In Table 5.10, the brief history of the research on the above systems is summarized. The cellulose complex is now considered to be cuprammonium complex coordinated preferentially to the hydroxyl groups at C2 and C3 giving a δ chelate.[78,79] In these studies, elementary analysis and spectroscopic methods such as optical rotation, optical rotary dispersion and circular dichroism were used together with UV.

Fast mixing of the appropriate amounts of copper hydroxide (or basic copper sulphate), aqueous ammonium and cellulose is now a highly effective direct method of preparing a concentrated cellulose solution for spinning. The solution is refined by filtration using a cloth of fine nickel filaments and degassed under reduced pressure to exclude air bubbles and excess ammonia from the solution. A small amount of aqueous sodium hydroxide is added simultaneously or after making the above mixture. It is assumed that with addition of sodium hydroxide the concentration of the cellulose complex increases. Dissolution of cellulose in cuprammonium solution is slightly exothermic and the temperature of dissolution is usually controlled to about 15°C. Any rise in temperature of the solution makes the dissolution rate slower. Mechanical agitation during the dissolution step is extremely important. The composition of the spinning solution is, for example, as follows: cellulose, 8–12 wt%; ammonia, 6–8 wt%; copper, 3–5 wt%.

Miyamoto *et al.*[79] indicated that in the dissolved state cellulose does not always coordinate with the cuprammonium complex. This means, that when about a half of the glucopyranose units are substituted as the diol anion salt of the cuprammonium complex, this cellulose derivative is soluble in the aqueous cuprammonium solution. If we can make the cellulose derivative described above at least copper-coordinated in a separate process, it might lead to a new way of producing the cellulose–cuprammonium solution from lower concentrations of copper and ammonia. Miyamoto *et al.* succeeded experimentally in preparing cellulose solutions using half the copper and one-third the ammonia used in the conventional procedure.

Table 5.10 Brief history of scientific research on the cellulose–cuprammonium hydroxide system

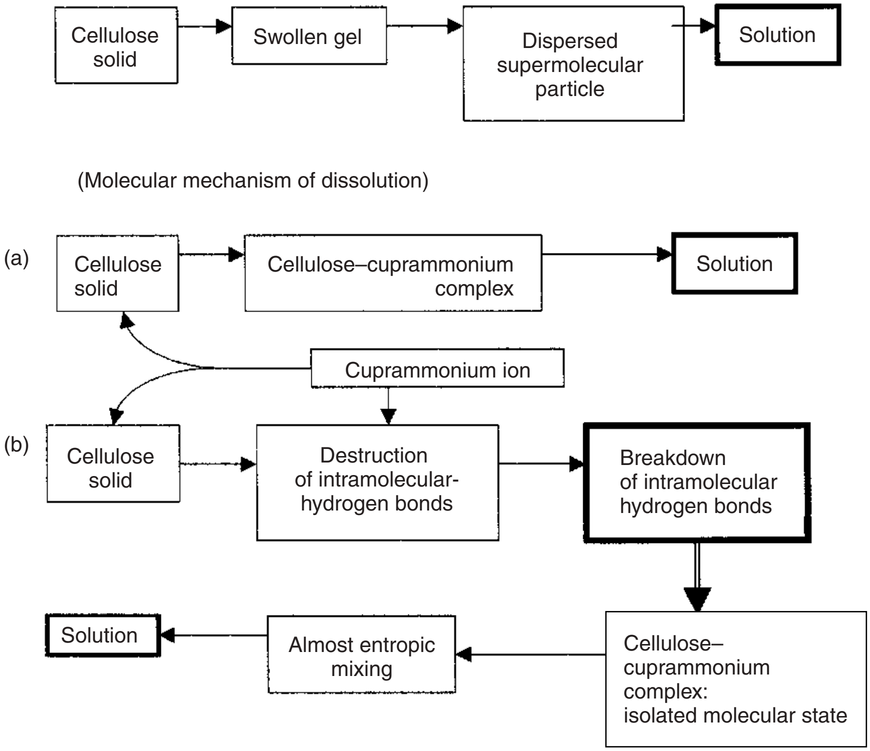
System		Complex	
(I)	Polyhydric alcohol +alkali- (sodium hydroxide) copper	Various crystalline materals	Billnheimer (1898)[70,71]
(II)	Copper hydroxide + aq.ammonia	Copper–alcohol complex soluble in aq.alkali solution $Cu(NH_3)_4(CO)_2$	Bonsdorf (1903)[55]
(III)	Glycerol + copper ethyleneamine hydroxide (copper oxide + ethylene diamine) (En)	$[(C_3H_4O_3)_2Cu]\ [Cu(En)_2]$	Traube (1911)[72]
(IV)	Cellulose + copper ethyleneamine hydroxide	$[(C_6H_8O_5)_2Cu]\ [Cu(En)_2]$ (isolated as precipitate by addition of ethanol to the system) glucose : copper = 2 : 1 (mol/mol)	Traube (1921)[73]
(V)	Cellulose + cuprammonium	$[(C_6H_8O_2)_2]^{2-}[Cu(NH_3)_4]^{2+}$ $[(C_6H_7O_5)Cu]^{2-}[Cu(NH_3)_4]^{2+}$	Traube (1921)[73] Hess–Messmer (1922)[74]
		 $(C_6H_{10}O_5)\ (C_6H_7O_2)\begin{cases} OH \\ OH \\ OH \end{cases}$ $Cu(OH)_2$, $[Cu(NH_3)_4(OH)_2]_{1/2}$	Lieser–Ebert (1925)[75]
		Copper coordinates to C2,C3 hydroxyl groups of glucose residue	Reeves (1944)[76]
		1 : 1 salt of CTH cation + diol anion at C2 and C3 positions of pyranose ring	
		Chelate coordination of copper with two hydroxyl groups	Bukhari (1968–1976)[77]
		Cuprammonium complex, coordinates preferentially to hydroxyl groups at C2 and C3, giving δ chelate form	Miyamoto *et al.* (1995)[78,79]

By what mechanism does cellulose solid dissolve into aqueous cuprammonium solution? Even in the case where cellulose or cellulose derivative solid is not easily soluble in solvents, once it is dissolved, the solution is usually stable. Cellulose–aq.cuprammonium solution is typical, so the dissolved state as an equilibrium state should be rigorously distinguished from the dissolution process. These two processes had not hitherto been distinguished for the cellulose–copper hydroxide–ammonia–water system. When cellulose solid is mixed with aqueous cuprammonium solution, cupric tetramine ion $(Cu(NH_3)_4)^{2+}$ reacts with cellulose to form the 'complex'. In this case, the cupric tetramine ion first penetrates, in particular in excess ammonia, the space between two neighbouring glucopyranose rings causing breakdown of the intermolecular hydrogen bonds. Second, the cupric tetramine ion builds the cellulose–cuparammonium complex by breaking down the intramolecular hydrogen bonds of the glucopyranose units. A cellulose molecule, in which some glucopyranose rings form a 'complex' with cupric tetramine ions, disperses molecularly into the remaining solution. The underlying mechanism of dissolution of cellulose solid into solvent is very common in cuprammonium solution and dilute alkali solutions. Cupric tetramine ion acts to break the intramolecular hydrogen bonds. Miyamoto *et al.*[79] showed that the apparent degree of breakdown in the intramolecular hydrogen bond at O_3 H-O_5' (Here, O_3H means OH group at C_3 position on a glucopyranose ring and O_5' is ring oxygen on a neighbouring glucopyranose ring) of the undissolved part of cellulose solid, treated with cuprammonium solution and regenerated with dilute acid, increased with the concentration of the hydroxyl group C_{OH}, where cuprammonium complex is ionized. Their results suggest that cuprammonium ion breaks the intramolecular hydrogen bonds. It is now clear that the dissolution of cellulose does not depend on the formation of a 'cellulose-complex with a definite composition'. The cellulose-complex can be considered to play in dissolution as a kind of strong solvated solute, interfering effectively with the reassociation of dispersed cellulose molecules.

So, the key factors governing dissolution of cellulose are (1) breakdown of supermolecular (especially, intramolecular hydrogen) bonds in the solid and (2) formation of strong solvation (or interaction). Figure 5.8 shows schema of speculative concept of dissolution of cellulose into aqueous cuprammonium solution.

5.2.5 Fundamentals of wet-spinning

The fundamental technological concept behind the wet-spinning of cuprammonium rayon is the complete separation of the following three steps, stretching (deformation), coagulation (solidification) and regeneration. This is essential to produce better quality fibres with high productivity.



5.8 Dissolution of cellulose into aqueous cuprammonium solution: (a) classical concept, (b) new concept.

In the Despeissis[7] and VGF[10] patents, the last two steps are completely mixed together and indistinct and the first step is practically absent; Thiele intended to separate the first two steps from the latter, although the degree remained far from the ideal state. The Asahi Chemical Industries Co have developed an advanced and highly sophisticated process along the lines of the above concept (see Table 5.11).

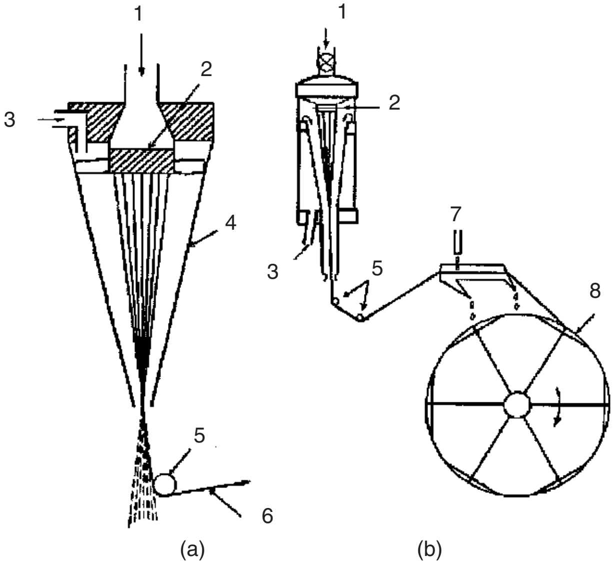
5.2.6 Dynamics of stretch-spinning

Stretch-spinning, first used commercially by J P Bemberg A G (Germany) in the 1910s has been extensively developed in Germany, the USA and Japan. Viscous dope is extruded under pressure through a die (nickel or stainless steel), that has holes 0.6–1.6 mm in diameter, into a glass or plastic funnel flowing with degassed and de-ionized, warm spinning water (*Fall wasser*). The dope coagulates very gradually in the funnel and is stretched hydrodynamically up to some hundreds times, forming fibres which emerge

Table 5.11 Revolution in wet-spinning technology

Stage	Relation between three steps	Apparatus	Inventor(s) (period)
I	Coagulation + regeneration (no stretching)	Single bath	Despeissis, VGF (1890–1910)
II	Stretching + coagulation–regeneration	Funnel + bath	Thiele (JPB) (1900–1940)
III	Stretching–coagulation–regeneration	Double or triple funnel system + bath	Asahi (1950–1990)

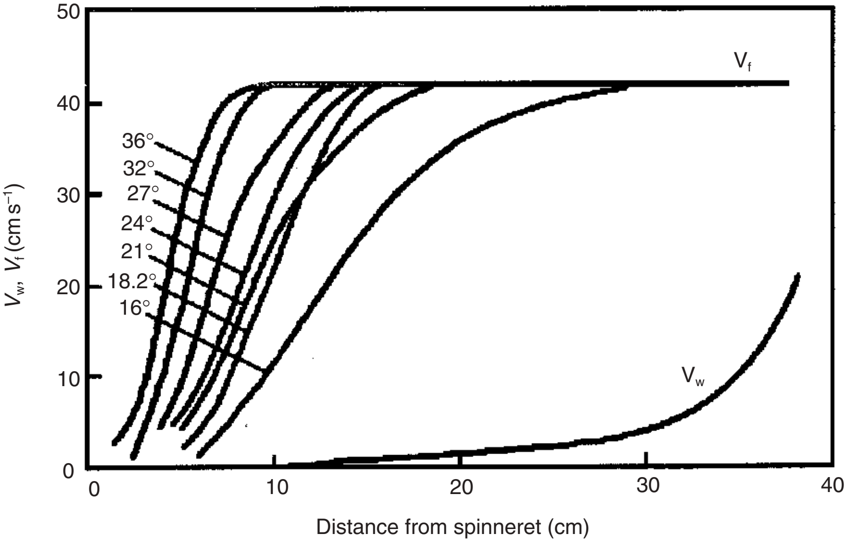
+, simultaneously; –, separately.



(a) (b)

5.9 Stretch-spinning showing funnel (a), and hank-type spinning machine (b). 1: spinning solution; 2: spinneret; 3: spinning water; 4: funnel; 5: guide; 6: blue yarn; 7: dil. acid; 8: hank.

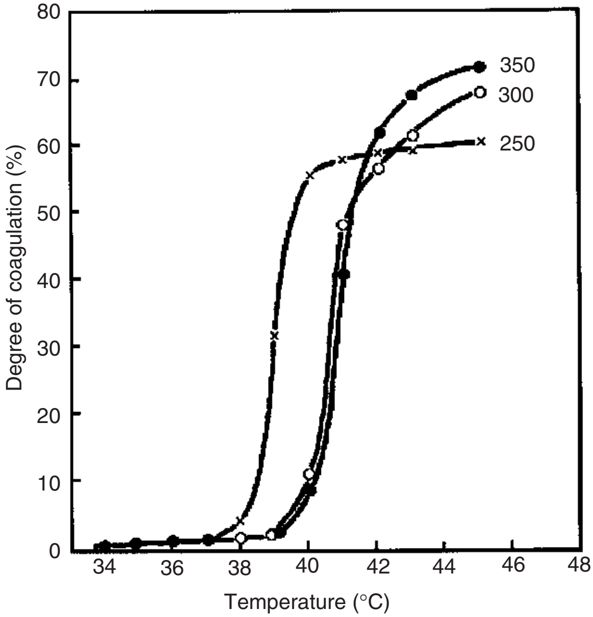
from the lower end of the funnel (Fig. 5.9(a)). The filaments are drawn round a rod to separate them from the entrained spinning water that they are carrying. The spinning funnel design has advanced remarkably in the last 70 years (see Fig. 5.17) and a more complete separation of drawing (deformation) and coagulation processes, which Thiele dreamed of a hundred years ago, has now been successfully realized in practice by Asahi (Nobeoka, Japan). Note that use of a single funnel does not allow effective separation.



5.10 Line velocity of running liquid thread V_f and of the spinbath V_w plotted against distance from spinneret. The numbers indicate the temperature (°C) of the spinbath.[81]

The cellulose–cuprammonium complex is supposed to be decomposed during drawing in the funnel by hydrolysis removing part of the copper and about 70–80% of the ammonia from the complex, giving the copper–cellulose complex compound known as 'blue yarn'.

Five forces act on the running thread[80] (1) gravity (density of the threads), (2) buoyancy (density of the spin bath), (3) friction between the threads and the spinning water owing to their velocity difference, (4) surface tension on the boundary of thread and water, and (5) tension, generated from the take-up roll and applied on the filament. These forces are balanced in steady state operations. The density difference between thread and water is quite small, in particular at the inlet region of the funnel where the direction of gravitational force is opposite to that of buoyancy, so that forces (1) and (2) are negligible. The frictional force (3) is a predominant factor in controlling the drawing of filament in the funnel. Force (3) varies depending on the shape and length of funnel, the spinning velocity and the denier(diameter) of single filaments. Except very near the inlet region, the velocity of thread is greater than that of spinning water (Fig. 5.10).[81] The surface tension is also minimal. The region between the inlet to the middle part of the funnel plays an important role in controlling the quality of fibres. Provided that all other operating conditions are kept the same, the coagulating rate increases with an increase in cellulose concentration in the



5.11 Degree of coagulation of threads, as measured by their ammonium content, as a function of temperature of the spinbath. The numbers show the flow rate (ml/min) in the spinbath.[84]

spinning solution and of the temperature of the spin bath[82,83] (Fig. 5.11) and with a decrease in the ammonium concentration. A low coagulation rate results in occasionally insufficient coagulation of the running thread within a funnel. A high coagulation rate indicates that the coagulation completes relatively high up in the funnel (Fig. 5.9) and the spinning tension increases, giving fibres with an irregular cross-section, which have poor yarn qualities such as low tensile strength and low tensile elongation. Viscosity-spinning solution too low is difficult to stretch in a funnel and solution too high up is not suitable for in-pipe transportation and filtration (in other words, processability is poor).

The characteristic of the 'flow stretching' process can be summarized as:

1 Use of a larger pore (~0.8 mm diameter) die becomes possible.
2 Use of a highly viscous spinning liquid becomes necessary.
3 Yarns can be made from high molecular weight cellulose and have better physical properties.
4 Fibres can be made with relatively uniform cross-section, with no microscopically visible skin unlike viscose rayon fibres (see Fig 5.24(b)).

5 No evolution of gas during coagulation. (In the viscose rayon process the decomposition of cellulose xanthate is accompanied by unavoidable evolution of toxic gas.) No microscopic voids in the final fibres.
6 Very fine fibres are achieved by high stretching.

Thiele anticipated points 1, 2 and 6 in his patent specifications.[29]

The thread, after leaving the lower end of the funnel, runs into a small bath containing sulphuric acid (5–10 wt%), where the cellulose is completely regenerated. Very pure sulphuric acid is supplied for this purpose.

5.2.7 Commercial stretch-spinning process

Hank spinning (or reel spinning) was first used commercially before the 1940s. In this process the untwisted yarn is wound up in a hank as illustrated in Fig. 5.9(b). The yarns are twisted in the form of skein before weaving. These additional operations are very labour intensive and expensive. The yarns made by the hank process have relatively lower tensile elongation. The centrifugal (or Topham box) collection method, in which the thread is wound in twisted form (the early viscose rayon process) gives yarns with better mechanical properties. For cuprammonium yarns this replaced the Hank spinning process during the 1930s and it was suspended (by Asahi) in 1943. The yarns were supplied to the weavers in the form of cake, which demanded careful handling, otherwise the fine filaments broke. It was discovered in the mid-1940s that a careful choice of the spinning conditions produces slightly self-bonding fibres (i.e. yarns in which the constituent filaments adhere to each other slightly owing to their self-adhesive properties, but after weaving the adhesion of filaments can be removed in a finishing step on the woven cloth). With this technique new ‘Hank process’ yarns can be woven without any further twisting. The Hank process therefore was revived during the 1950s, overtaking the centrifugal process, which was actually abolished in 1957 (by Asahi), being replaced by a continuous process, in which untwisted yarns are collected on ‘cheeses’. The Hank process still survives although its importance has diminished considerably.

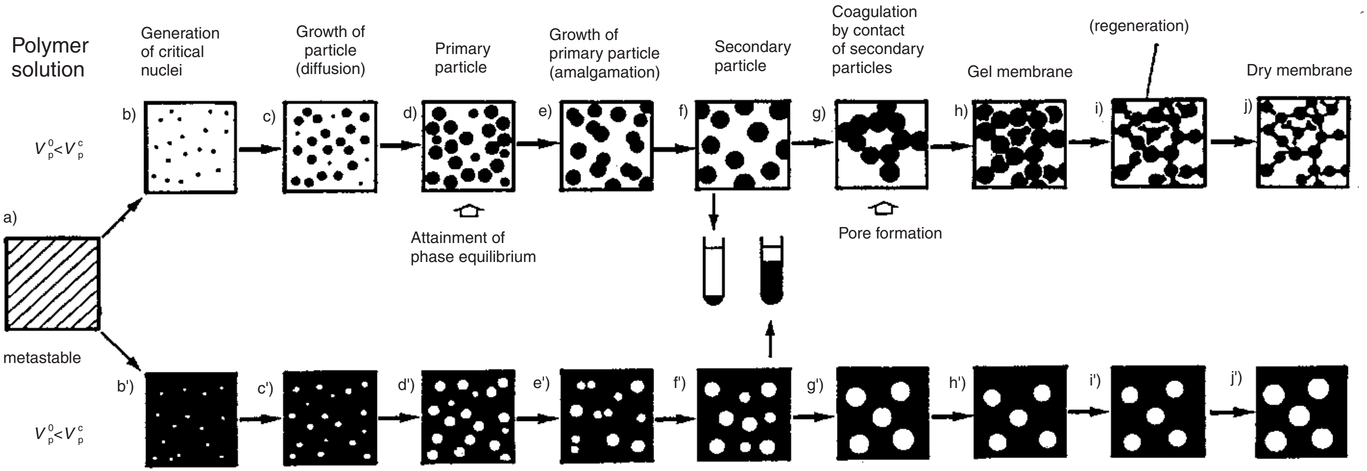
5.2.8 Thermodynamics of wet-spinning

Coagulation that occurs during the spinning process is a kind of phase separation. From the 1970s–1990s the thermodynamics of phase separation in polymer solutions was extensively studied for multicomponent polymer–solvent or polymer–solvent–non solvent systems.[85] Kamide and co-workers showed that when the initial polymer concentration (i.e. the solution concentration at the instance of phase separation) V_p^0 is smaller than the critical concentration V_p^c, the polymer-rich phase separates as small particles suspended in a medium (i.e. a polymer-lean phase) and these particles grow by amalgamation. Phase separation is a sequential occurrence of the following elementary steps (Fig. 5.12).[86] Figure 5.12 shows (a) generation of critical nuclei,[87] (b) growth of particle (diffusion),[85,87] (c) attainment of phase equilibrium (primary particle),[85,87] (d) growth of primary particles by amalgamation,[85,88] (e) formation of secondary particles,[85,88] (f) coagulation by contact between secondary particles,[85,88] (g) the coagulated membrane,[85,89,90] (h) regeneration and drying.[85,89] Detailed molecular mechanisms of the above steps were disclosed by Kamide, Iijima and their co-workers.[87–93]

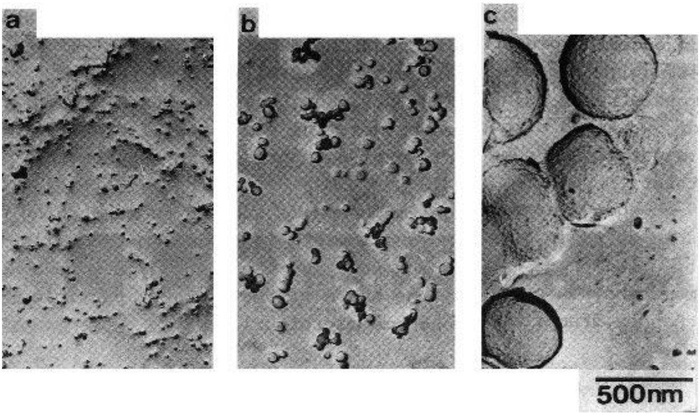
In wet-spinning, the shape of the secondary particles changes dramatically to microfibrils. Stretching a non-coagulated thread of cellulose cuprammonium solution may be regarded as simple flow of the spinning solution, mixed with a few of the initial steps in Fig. 5.12. When tension is absent, the interstitial space between particles gives a porous structure, that is, pores are formed by contaction of the secondary particles. The delicate control of the morphology of the fibre was achieved successfully in the case of simple polymer solutions such as the acrylonitrile/methylacrylate copolymer–aqueous nitric acid system.[94] It is easily assumed that the wet-spinning process of cellulose cuprammonium solution may obey the above-mentioned thermodynamic mechanism, but the cellulose–cuprammonium solution system is tremendously complicated to study. For example, the spinning solution is composed of a cellulose–cuprammonium complex, cupric tetramine hydroxide (CTH), ammonium ion, copper ion, hydroxide ion, non-ionized ammonia, water, and so on, and the composition of each component, which is not yet fully understood, varies depending on the nature of starting materials, and on the temperature of the coagulating liquid. If some specific solvents other than water and acid are chosen as coagulant, macroscopical liquid–liquid phase separation occurs even for cellulose–cuprammonium solution.[95] Acetone provides an example and the phase-diagram of this system was investigated by approximating the cellulose–cuprammonium solution + acetone system as a quasi-quaternary system ((cellulose + copper) + ammonia + water + acetone).[95]

Figure 5.13 shows electron micrographs of particles in cellulose–cuprammonium solution coagulated by an aqueous ammonia–acetone mixture.[96] Phase separation of the above cellulose solutions obeys the particle growth mechanism shown in Fig. 5.12.[97]

If we stop the process of coagulation half way, the secondary particles can be separated.[95] Using the cellulose–cuprammonium–coagulant system, microporous hollow fibre membranes were developed[98] and are commercially produced by Asahi at Nobeoka. Iijima *et al.* studied the phenomenological effects of solvent-casting conditions on the pore

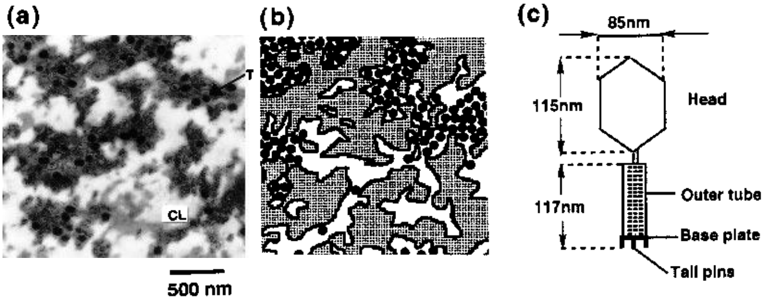


5.12 Elementary steps in porous membrane formation by the microphase separation method. V_p^o, polymer volume fraction of the solution when the phase separation occurs; V_p^c, polymer volume fraction of critical solution point.[89]

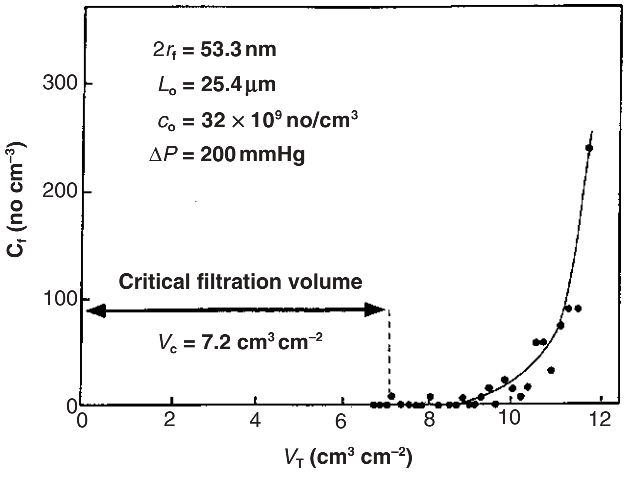


5.13 Electron micrographs of particles in cellulose cuprammonium solution coagulated by aqueous ammonia–acetone mixture (steps d, e, and g in Fig. 5.12). (a) primary particles (step d); (b) intermediate stage of the conversion of primary particles to secondary particles (step e); (c) the secondary particles in contact with each other (step f); starting solution (the weight fractions of cellulose, W_{cell}^{S}; copper, W_{cu}^{S}; ammonia, W_{NH3}^{S} and W_{H2O}^{S} are 0.08, 0.316, 0.1122 and 0.7762, respectively). Composition of coagulant, acetone/ammonia/water (30.00/0.56/69.44, wt/wt/wt).[94]

characteristics of cellulose membranes regenerated from cuprammonium solution. The acetone concentration $W_{acetone}$ of the system is one of the most important factors determining phase separation characteristics like the two-phase volume ratio (i.e. the volume ratio of the polymer-lean phase to the polymer-rich phase) and the composition at the point of phase separation. The ammonium concentration, W_{NH3}, in the cellulose/cuprammonium/acetone/water system influences the size of the secondary cellulose particles. Membranes consisting of large secondary particles have a larger mean pore size, and this fact agrees well with the prediction of Kamide's lattice theory[90] on pore size distribution. Iijima *et al.* also studied the supermolecular structure and virus separability of regenerated porous cellulose membranes.[92] According to them, a porous cellulose membrane has a 'cavity-vein' structure (Fig. 5.14). Viruses were captured by two different mechanisms: accumulation in cavities and blocking in narrow veins. Viruses moved downstream in the membrane, leaving in the filtrate, however, without exceeding a 'critical' filtration volume V_c, the porous cellulose membrane achieved complete rejection of viruses from the filtrate (i.e. aqueous serum protein mixture such as blood) (Fig. 5.15).[92] V_c depends on filtration pressure and virus concentration in the filtrand (i.e. supplying liquid).



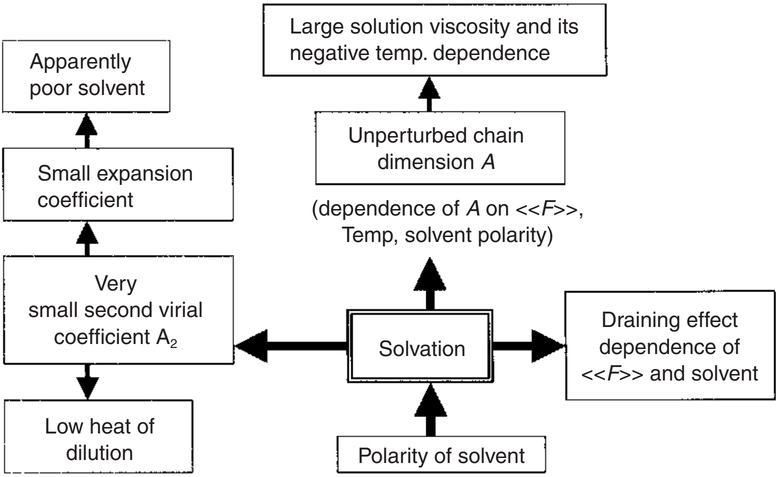
5.14 Cross-section of a porous regenerated cellulose membrane and captured viruses in the membrane. (a) transmission electron micrograph of a cross-section of porous regenerated cellulose hollow fibre membrane: pore diameter by flow rate method 2 $r_f = 41$ nm; a T4 phage suspension was filtered through the membrane by perpendicular filtration at a pressure difference $\Delta P = 200$ mmHg; brackish particle (T) T4 phage; white area (CL) cellulose; grey area, pore; (b) schematic representation of cavity-vein structure: shadowed area, cellulose; black particle, virus particle; (c) sketch of T4 phage.[92]



5.15 Change in virus concentration C_f during filtration.[92] The volume of each fraction was ca. 0.2 ml, V_c was 27.2 ml cm^{-2}, $2r_f$ was 53.3 nm, C_o is concentration of virus, L_0 is thickness of membrane, V_T is total volume of rinsed saline water per unit area of membrane during rinsing, ΔP is pressure difference.

5.2.9 Molecular characterization of cellulose and its derivative solutions

Until the late 1970s, very few comprehensive and reliable studies on the molecular characteristics of cellulose derivatives (CD) had been reported,



5.16 Relationship between solvation and some characteristic features of cellulose derivatives solutions[99] (≪*F*≫ is the total degree of substitution).

because of experimental difficulties encountered in the determination of the substituent groups, fractionation, and the removal of gel-like materials from the solution. Moreover, the experimental data, that had been obtained unsystematically for some cellulose and CD solutions, could not be explained reasonably in terms of the known and established solution theories applicable to many synthetic flexible polymers. For this reason, the molecular characterization of cellulose and CD remained unsolved even in the 1970s. During the 1980s–1990s, the molecular properties of cellulose and its derivatives (in particular cellulose acetates) solutions were synthetically studied.[99–101] Needless to say, these studies were very valuable providing basic knowledge for planning in an industrial fibre-forming process. Unfortunately, cellulose–cuprammonium solution had not until then been a target of this kind of study except at a rather primitive stage of research in the 1930s–1940s.

Common phenomenological features of cellulose and CD solutions are: (1) a small second virial coefficient, (2) a low heat of dilution, (3) a large solution viscosity and (4) its negative temperature dependence. These can be reasonably and consistently explained by solvation (Fig. 5.16), which had been quantitatively evaluated by adiabatic compressibility and nuclear magnetic resonance measurements.[99]

Table 5.12 collects some molecular parameters of cellulose solutions. The table was constructed from tables 11 and 13 from Kamide and Saito[99] and table 7 from Kamide and Saito.[102] From Table 5.12 we can conclude: (1) cellulose dissolves molecularly in cadoxen, FeTNa and 6 wt% aqueous LiOH,

Table 5.12 Some typical molecular parameters of cellulose solutions

Molecular properties	Cellulose		
	cadoxen	FeTNa	6 wt% (LiOH)
$K_m \times 10^2$ (cm^3 g^{-1})[a]	3.85	5.31	2.78
a[b]	0.77	0.78	0.79
X[c]	0.2–2.2	0.3–2.9	—
$A \times 10^8$ (cm)[d]			
method 2B[e]	1.53	1.96	2.18
method 2D[f]	—	2.27	—
method 2G[g]	1.57	2.17	2.13
method 2K[h]	1.56	2.07	2.13
most probable	1.55	2.12	2.15

[a,b] Parameters K_m and a in the Mark–Houwink–Sakurada equation; between the limiting viscosity number[η] and the molecular weight M: $[\eta] = K_m M^a$.

[c] Draining parameter, X defined by $X = (3/2\pi)^{1/2}(d/a')N^{1/2}$ (where a' is the length of a link, d is the hydrodynamic diameter of segment in pearl-necklace model, N is the number of segments). If $X \gtrsim$ 10–20, the polymer chain can be regarded as a solvent-impermeable sphere.

[d] Unperturbed chain dimension.

[e] From the linear expansion factor calculated from the second virial coefficient, M and radius of gyration $<S^2>^{1/2}$.

[f] From $<S^2>^{1/2}$, M and the non-Gaussian unperturbed chain a_2.

[g] From [η], a_2 and the molecular dependence of parameter $\Phi(a_\Phi)$.

[h] From K_m, a, a_2, and a_Φ.

(2) cellulose molecule behaves as Gaussian chain in the above solvents in the unperturbed state, (3) the excluded volume is small, but the draining effect can never be ignored. Not only the physical properties shown in Table 5.12, but also many other properties of the above solutions show similarities to those of CD solutions (see Table 5.10[99], Table 5.11[99], Table 5.13[99], and figs. 6.3.8[99] and 6.3.9 from Kamide and Saito[99]). In other words, cellulose complex solutions like cellulose–cadoxen and cellulose–FeNa solutions have the same features as those of CD solutions, which have been investigated more systematically. Judging from the similarity between parameters K_m and a in the Mark–Houwink–Sakurada equations (see Table 5.12, footnotes a and b), solutions of cellulose in aqueous NaOH, cuoxam (cuprammonium hydroxide), cuen (cupriethylenediamine hydroxide) and EWNN (iron–tartaric acid–sodium complex solution) may behave similarly.

5.2.10 Continuous spinning process

The continuous wet-spinning process is defined as a process in which the extrusion of the spinning dope, and the final winding of the thread on to a normal textile package, take place continuously on one machine or on an integrated set of machines which, to all intents and purposes, form one machine.[103] From 1905 the improvement of spinning apparatus including solidification, drying and winding was carried out at VGF under the guidance of Eduard Boss (1877–1935; he joined VGF in 1905 and married Fremery's daughter).[104–106]

According to Barker and Alleston,[103] the continuous process can be classified as follows:

5.2.10.1 Simple continuous method

This consists of guiding yarn over and under rollers. The original idea was proposed by the Société Française de la Viscose (SFG)[107] in 1906 and by J Foltzer[108] in 1908. Both remained just ideas until commercialized by J P Bemberg before the end of the First World War: in the 1940s J P Bemberg operated their machines for spinning direct to warping beams and produced about 1000 tonnes of warps by the end of the war.[109] This was called the Dureta method.[110,111] Afterwards J P Bemberg developed the process with the collaboration of I G Farbenindustrie (later Farbenfabriken Bayer).[103] Their process consisted of a spinning machine (400 ends, 12.8 m long), a washing machine (8.5 m long) and a drying machine (4.4 m long) (overall length 25.4 m). The threads were formed into a sheet, passing through acid treatment and into a wash bath in this form. After sizing and drying they were wound on to a beam.[101] The Farbenfabriken Bayer operation at Dormagen used this type of continuous spinning machine, selling the product under the trade name of Cupresal®.[112,113]

5.2.10.2 Continuous belt method

The yarn is dropped on a very slowly travelling belt in a loose spiral form and transferred through various treatment baths on the belt. Boss proposed this method in 1906,[103,114,115] but it was not commercialized. Forty years later, difficulty in controlling the tension and shrinkage in the above method was pointed out.[101] In 1972, Miyazaki *et al.* at Asahi invented[116] this technology and in the 1980s–1990s Asahi succeeded in applying it commercially, which will be described in more detail in Section 5.2.12.

5.2.10.3 Advancing reel or helical reel method

An early suggestion for the use of a reel was made in VGF's patent literature in 1910.[117,118] In 1932 William Henry Furness invented an advancing reel method with a specially designed reel suitable for the cuprammonium rayon process (United States Patent No 1770750 (1930) and Japanese Patent No 101 379 (1933)).[119,120] The Furness method was taken over by the Industrial Rayon Corp (USA)[103,121,122] and commercialized in 1938 for high-tenacity rayon production.[122] The success of the commercial application of this method is mainly due to use of a chemically resistant small plastic reel and the isolation of each treatment to one or more small advancing reels.[103]

5.2.10.4 Simple roller method

In 1952 Hugo Hofmann invented a continuous machine,[123] which was purchased by Beaunit Mills and used commercially at Elizabethton, Tennessee.[124]

Table 5.13 summarizes the progress of continuous spinning technology. Note that in the 1950s the spinning speed of this technology was, without exception, in the range of $< 70\,\mathrm{m\,min^{-1}}$.

Some properties of the end products of regenerated cellulose fibres depend greatly on the residual internal strain, which was fixed in the fibre in the spinning and finishing process, and in particular, in the tension-drying step, and which when released brings about significant shrinkage in the after-treatment process (e.g. the drying step of scoured cloth). Therefore, the properties of the products produced by the continuous process are usually different from those produced by hank or cake processes. The operating conditions of continuous spinning and after-treatment processes and their formulae for the filaments produced by the continuous method should be optimized.

Asahi's continuous process originated in the USA.[125] The process that was licensed in 1953 from Beaunit fibres gave untwisted, hard yarns wound on to a beam, unsuitable for rewinding and mainly used only for knitting. This continuous process had first to be improved by coating the yarns with carefully chosen softening oil before drying in order to produce soft fibres. In this way, continuously spun yarns successfully widened the end-use application in woven fabrics, resulting in closure of the cake-yarn process. Both hank and cake processes were batch processes, and were extremely limited in the face of the dramatic improvements in the processability and yarn quality that were urgently demanded in the 1950s–1960s in order to compete economically with newly developing synthetic fibres. That the production of untwisted cuprammonium fibres in the factory was not to be a fatal disadvantage was due to significant technological advances in winding and weaving machines during the 1950s, and due to a change of fashion to bright yarns. The continuous spinning process conformed to the 'faster, cheaper, better' philosophy quite well.

Table 5.13 Development and commercialization of the continuous wet-spinning process of cuprammonium rayon 1900–present

Class	Method	Fundamental idea or patent(s)	Commercial process
I	Simple continuous method	(1) Société' Française de la Viscose; DP Nr 192 406 (1906)	JPB (afterwards jointly with IG) 1940s–1950s
		(2) Foltzer J; DP Nr 209 923 (1908)	Barmen (Dureta method)
		(3) DP Nr 763 735 (1940) ⟹	JPB (Dureta method) Bayer (ex IG) Dormagen
II	Continuous belt method	(1) Boss E (VGF), DP Nr 235 134 (1906)	
		(2) Miyazaki, *et al.*, USP No 3 689 620 (1972) ⟹	Asahi, Nobeoka 1980s–1990s
III	Advancing reel or helical reel method	(1) VGF, DP Nr 239 822 (1910)	
		(2) Furness W, USP No. 180 0828 (1931); JP No 101 379 (1931) ⟹	Industrial Rayon Corp (USA) (Viscose)
IV	Simple roller	(3) Hofmann H, US Patent 2 587 619 (1952) ⟹	Beaunit Mills Elizabethton ↓ 1953 Asahi Chem. Nobeoka

⟹ Commercialization, → transfer of technology.

5.2.11 Technology innovation in the conventional spinning process

The spinning velocity is a good measure of the sophistication of the production technology. On continuous machines, high velocity cannot be attained by improving the spinning process alone, but requires innovation in many other areas, closely correlated with spinning speed, such as purification of cellulose and preparation of a highly uniform spinning solution.

During the 1920s–1940s, the spinning velocity in the plant operation was far below $50\,\mathrm{m\,min^{-1}}$. From 1940–1965, numerous energetic attempts were made to improve productivity in the manufacture of fibres, based on the fundamental concept of wet-spinning already described.

The following are key criteria for improving the conventional process:

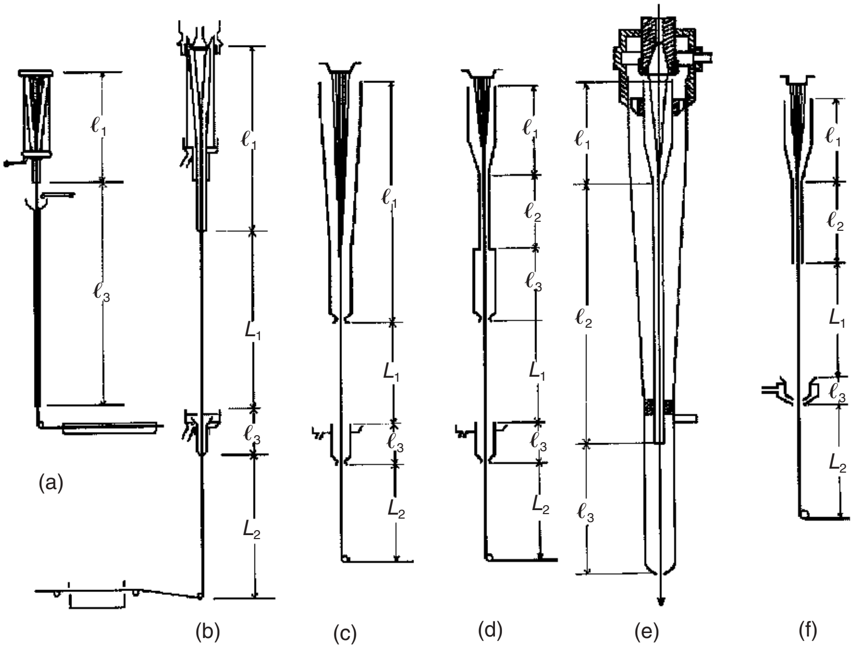
1 A small frictional resistance between thread and coagulation bath (i.e. bath resistance).
2 Uniform drawing (stretching) of liquid thread with little or no coagulation.
3 Sufficient coagulation of the running thread under the low tension.

Figure 5.17 shows 'stretch-spinning' apparatus invented at Asahi during the 1950s–1970s for increasing the spinning velocity. In 1950 Munakata and Maeda proposed the introduction of a long narrow guiding pipe as a second coagulating bath positioned under the spinning funnel.[126] In this patent, the pipe was expected to accelerate rather than coagulate the thread. In the patents that followed, this idea of a 'two-step funnel method' was advanced.

In 1954, Suwa, Mihara and Nagao invented a second type of funnel coagulation bath, to which fresh coagulating liquid is constantly supplied and which is positioned at a distance from the first upper funnel, adjustable according to the spinning speed.[127] They controlled stretching in the free dropping zone before the coagulation bath.

In Nagao's patent in 1956,[128] the second bath is a 'liquid brake', slowing down the half-coagulated thread. This idea developed into a liquid injector. In order to control the tension applied to a running thread, selecting the coagulating bath length (ℓ_1 and ℓ_2 in Fig. 5.17(c)) and free dropping length (L_1 and L_2 in Fig. 5.17(c)) was shown to be effective.[128]

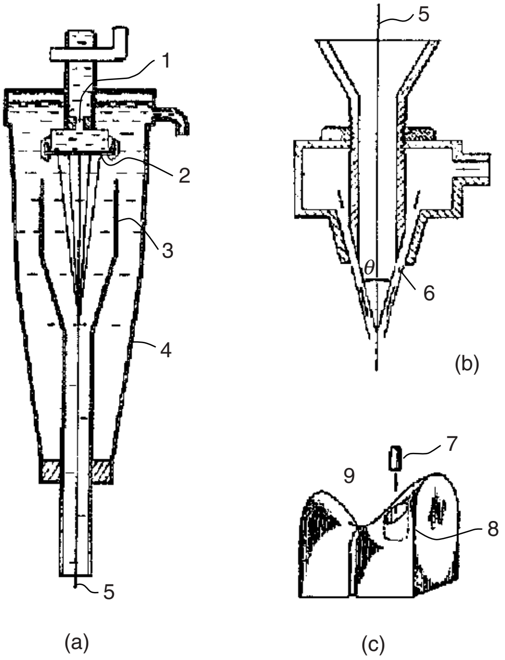
In 1962 Aizawa and Ishida proposed a stretching apparatus consisting of a conical tube (ℓ_2), long straight tube (ℓ_2) and a coagulation zone (ℓ_3) (Fig. 5.17(d)), wherein the flow rate of the coagulating liquid is suddenly diminished, thereby permitting completion of the coagulation in a relaxed state.[129] They showed how this method could produce cuprammonium rayon, which is superior in both tenacity and elongation (particularly the latter), having a homogeneous cross-section and easy resin finish. In 1969 Naniwa invented a method, where a liquid retarding the coagulation of the liquid thread is



5.17 Stretch-spinning apparatus invented at Asahi during the 1950s–1970s. (a) Munakata-Maeda (1950);[126] (b) Suwa-Mihara-Nagao (1954);[127] (c) Nagao (1956);[128] (d) Aizawa-Ishida (1962);[129] (e) Naniwa (1969);[130] (f) Makita *et al.* (1972).[131]

supplied to a first bath and a coagulating liquid is supplied to a second bath. For this purpose two kinds of spinning water, differing in temperature, are supplied to each bath[130] (a double spinning water method).

Makita *et al.* invented in 1972 an injector to decrease the speed of the running thread below the funnel-type stretching tube midway down the free-dropping zone[131] (Fig. 5.17(f)). Using this method, the maximum spinning velocity attainable technically was estimated to be 700–800 m min^{-1}, and the maximum operation velocity, by which fibres can attain the quality approved for commercial products, was about 500 m min^{-1}. In 1972 Miyazaki *et al.* proposed a double-funnel type stretching tube (see Fig. 5.19),[116] in their new continuous spinning process (Net process), which will be described later. The distance L_1, measured from the lower end of the minor funnel and the upper part of the spray unit, together with the conditions (feed and temperature) at the primary liquid bath substantially affect the spinnability of the filament. The length L_2, measured between the lowest part of the spray unit and the level of the movable deflector pin, as well as the conditions (feed rate and temperature) at the secondary coagulating bath substantially influence the coagulation properties of the filaments.[116,131]



5.18 Enlarged view of a spinneret-funnel assembly (a), liquid injector (b) and trough of a saddle guide (c). 1: spinneret; 2: extrusion orifice; 3: inner funnel; 4: outer funnel; 5: thread; 6: ring nozzle; 7: supply nozzle; 8: liquid-receiving blind hole; 9: thin filament passage groove.

In 1986 Moroe and Iwase invented an apparatus consisting of a stretching nozzle, which enables the running liquid to stretch up to several thousand times instantly at its outlet, a liquid injector and a gas injector to separate the thread from the coagulating liquid.[132] Using this invention the production of fibre became possible at 1000–1500 m min^{-1}.

The most advanced process at present consists of a spinneret-funnel assembly (double-funnel type), a liquid injector (as a brake), and a gas injector (as a separator) (Fig. 5.18).

(1) Spinneret-funnel assembly (double-funnel type)

The spinneret is provided with a number of fine orifices, each of which has a bore diameter of 0.8 mm (Fig. 5.18(a)). The spinning solution is supplied by a metering pump through a filter, and a feed pipe from reservoir, to inlet pipe, fitted with an on-off control cock, and a reduced inlet opening.
(2) Hydraulic braking and secondary bath liquid injection unit (liquid injector). Figure 5.18(b) shows the unit that provides a liquid braking effect on the liquid entrained by the filaments, which emerge from the spinneret-funnel assembly, shown by a single line in Fig. 5.18(a). This unit comprises an inside guide funnel and outer box-shaped casing member, concentrically

arranged to inject a thin liquid ring jet of coagulating liquid towards the running bundle of continuous filaments.

5.2.12 Innovation of continuous process: development of the Net process

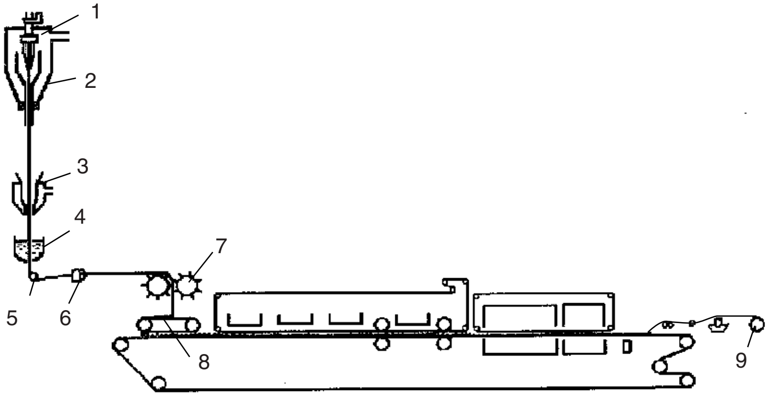
When Asahi introduced Beaunit-type machines in 1954, the take-up velocity was 73 m min^{-1}. When the two-step funnel method, developed by Asahi, was combined with the original continuous process, the spinning velocity increased up to 81 m min^{-1} (1961). Two years later the continuous finishing section was improved by Asahi and also introduced to the plant, and the spinning velocity attained to 95 m min^{-1}. In 1966 the two-stage spinning water method was invented at Asahi and the spinning velocity increased up to 110 m min^{-1}. In 1971 Asahi developed the vacuum-free drop-spinning method and the spinning velocity reached 130–150 m min^{-1}. In 1974 the epoch-making continuous process (Net process) was brought into commercial operation at a velocity of 380–500 m min^{-1} (see next section).

When the whole operational speed of the yarn manufacturing plant is above 400 m min^{-1} the following three major problems occur:

1 First there is an unacceptable number of broken filaments and considerable generation of 'fly' in the spinning and after-processing stages. This is because the entrained bath liquid impinges on the secondary bath pool, which leads to disturbance of the pool and poor filament quality. A process and method for eliminating such liquid disturbance in the secondary bath pool is therefore necessary.
2 Second, it is difficult to provide tension-free yarn for the after-treatment. Then, a process and apparatus for reducing tension is needed.
3 The third problem is that filament breakage is substantial and unacceptable. It is caused by contact between the extruded and coagulated filaments and the stationary filament guides (pins or combs), which are subjected to a gradually increasing deposit of copper hydroxide that will become the harder copper oxide. This hard oxide deposit, when accumulated on the contacting surface of the guide, will cause filament breaks, whose frequency increases as the spinning velocity increases.

To overcome these problem, Miyazaki *et al.* proposed the new 'Net' process[116] (Fig. 5.19).

According to their invention, the filaments leaving the spinneret (1) in a vertically downward direction pass through a first coagulating bath (double-funnel type) (2) and the fluid entrained by the filaments increases by means of a concentric angular-directed jet (liquid brake) (3) of fluid prior to passage through a second coagulation bath (lower funnel) (4). The filament may then pass over a bar which changes the direction of the filament and removes



5.19 Continuous wet-stretch-spinning process (Net process).[116] 1: spinneret; 2: double-funnel type coagulation bath; 3: liquid jet brake; 4: second coagulation bath; 5: guide bar; 6: saddle guide (see, Fig. 5.18(c)); 7: roll; 8: travelling web; 9: cheese.

entrained fluid. Further coagulation bath treatment may be provided by passage through the saddle guide (6) (see also Fig. 5.18(c)) prior to passage between a pair of vane-type rolls (7) that shake the remaining bath fluid from the filaments. The filaments are then loosely deposited on a travelling web (8) for further treatment. Specific apparatus for carrying out the process includes elastic-covered vanes on the rolls and several decelerating fluid jet arrangements. Here the cross-section of a lower funnel (3) is shaped like a cup opening out at the bottom. The stationary arranged guide bar (5) serves to guide the filaments so as to deflect their passage from the vertical to a substantially horizontal position leading them to a saddle stationary filament guide (6). Regeneration is by a dip treatment for the filaments in aqueous sulphuric acid solution on the saddle guide. The tensioned state of filaments can be transformed by a conveyer (8) into a perfectly loose state, which can be maintained through the after-treatment stages. The yarns are finally wound up into cheeses. The process can be operated at the rate of 500–1000 m min^{-1} (the maximum operation velocity for a long run may be 500 mm min^{-1}). The processability of the process was recently improved by Moroe and Iwase[132] to allow 1500 m min^{-1} operation. This process is now in extensive commercial use at the Nobeoka Plant of Asahi (Japan). Even now, the continuous spinning process continues to be developed.

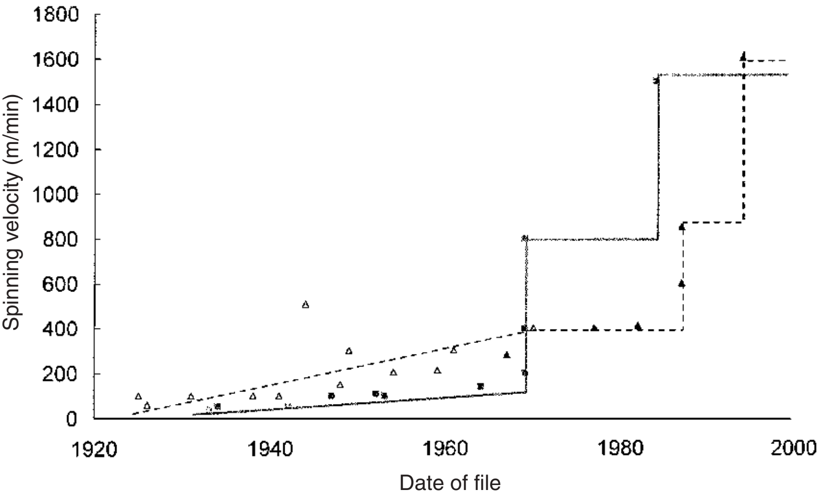
5.2.13 Staple fibre and other products

At present, the factory production of cuprammonium rayon is carried out overwhelmingly by the ordinary continuous yarn spinning process and the new continuous yarn spinning process (Net process). However, Asahi started Bemberg staple fibre production in 1960, spun-bond nonwoven fabric in 1974, hollow fibre for artificial kidneys (i.e. blood dialysis) in 1975, and hollow fibre membrane for blood filtration (Planova®) in 1985. The first two are fruitful new applications of the Net process for textile filaments. The last two result from fundamental research on the phase separation thermodynamics of the cellulose–cuprammonium solution system (see Section 5.2.8).

5.2.14 Spinning velocity

At the early stage of development of rayons, the spinning velocity V_s had not attracted the attention of development engineers, and V_s was in the range of several to 10 m min^{-1}. In fact, spinning velocity was mentioned in very few patents. For example, among about 300 Japanese patents, registered between 1905 and 1940 on regenerated cellulose fibres, only nine patents described the spinning velocity. This situation did not change until the 1950s. We could find only six patents that disclosed V_s, between 1941–1949. In contrast to this, 60 patents described the spinning velocity between 1950 and 1965.

Figure 5.20 shows the change in the spinning velocity, described in the patent literature, in the production of cuprammonium and viscose rayons,



5.20 Improvement in the spinning velocity of cuprammonium and viscose rayons. ————: cuprammonium rayon; -------------: viscose rayon; ■: cuprammonium rayon (Asahi); □: cuprammonium rayon (others); ▲: viscose rayon (Asahi); △: viscose rayon (others).

plotted against their file date. V_s of cuprammonium rayons remained below 100 m min^{-1} until 1945–1950, reached c. 100 m min^{-1} in the 1950s and c. 150 m min^{-1} in the 1960s, and then started to increase markedly in the late 1960s to 800 m min^{-1}, and 1500 m min^{-1} was recorded in 1984. A similar change was also observed for viscose rayon. It is clear that a great technological advance has occurred since the late 1960s and is still in progress. The trends observed in Fig. 5.20 correlate well with the change in the operation velocity at the plant: 73 m min^{-1} in 1954, 81 m min^{-1} in 1961, 95 m min^{-1} in 1963, 110 m min^{-1} in 1966, and 139–150 m min^{-1} in 1971.[133] The above change also corresponds to commercial introduction of new technology like the two stage-funnel method, continuous finishing, the double- (or multiple-) spinning water method, and the dropping method.[133]

5.2.15 Recovery of waste materials

The economic significance of recovery of the solvents used in the process was well recognized even at the beginning of its commercial use. For example, VGF described in the complete specification of British Patent No 1283 (1905) that 'The economical value of the process above described resides in the fact that both the ammonia and copper can be recovered from the acid solution'.[134] The acid solution, in this case, is the regenerating bath liquid and VGF considered the recovery of waste materials only from the regeneration bath at that time. In November 1945 Hegan and Ingham reported that Bayer's Wuppertul plant recovered copper from the bath by precipitation, but did not recover ammonia.[135]

The recovery rate of copper by Asahi improved from c. 70% in 1930 to 99.9% in the 1980s (Table 5.14). The following developments were made in this period:

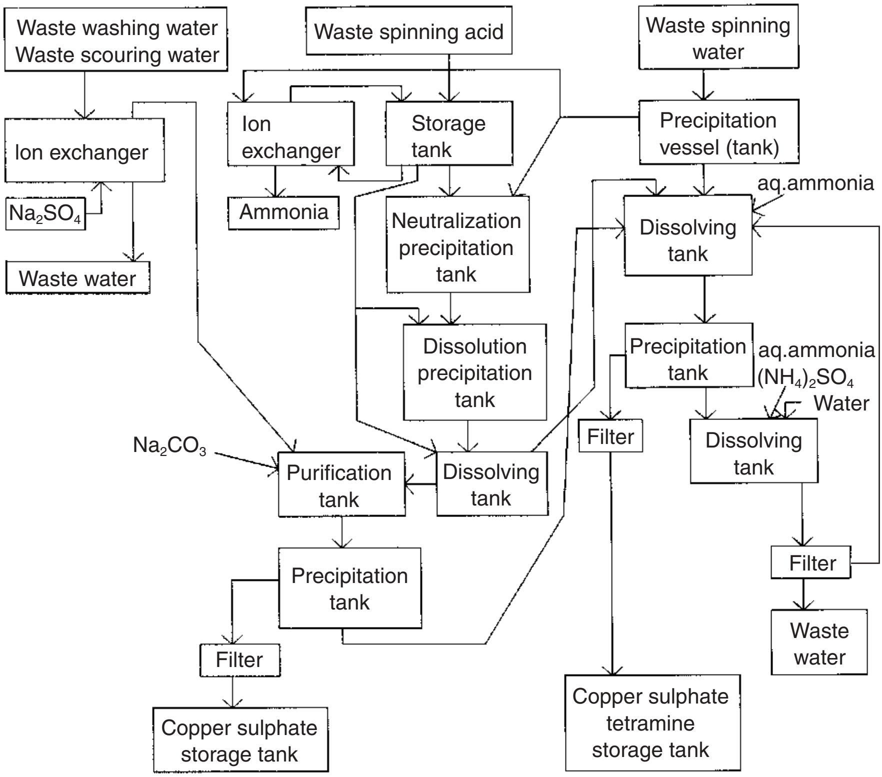
Table 5.14 Copper recovery rate at Asahi

Year	Recovery rate (%)
~1930	70–75
1940	75–80
1945	80–85
1948	85
1951	96
1961	99
~1970	99.7
~1980	99.9

Data from Asahi.[133]

1 quick sedimentation of small amounts of copper in suspension
2 filtration by a sand filter, then partial replacement of sand with active charcoal
3 positive use of CTH formed by adding ammonium in the recovery process
4 use of ion-exchange resin, whose function has been upgraded over 40 years.

Figure 5.21 illustrates the copper recovery system of Asahi. Note that at the Nobeoka plant the waste materials from all the production processes (filaments, staple fibres, nonwoven fabrics and hollow fibre membranes) are recovered totally and the optimum operating conditions of the recovery plant are determined considering the production plan of various cuprammonium cellulose products and the seasonal factors. The recovery of waste materials is now not done for economical reasons, but for environmental protection. Cuprammonium cellulose fibres are now manufactured almost entirely without new copper input.



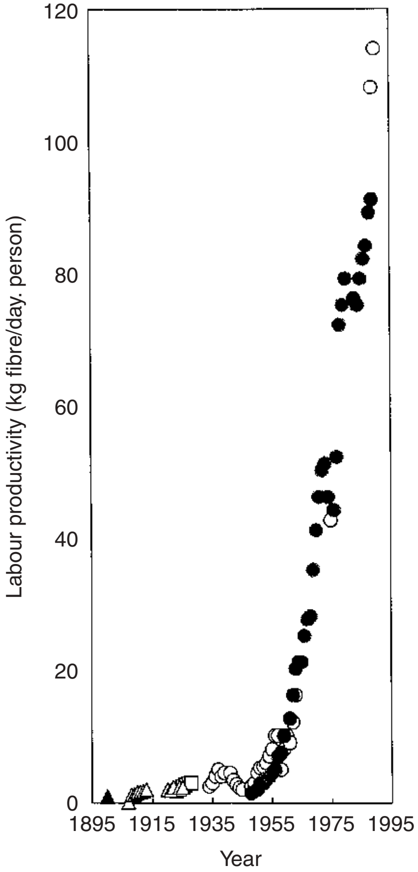
5.21 Copper recovery system (Asahi Chem. Industries).

In contrast, the recovery of ammonia is difficult, although enthusiastic attempts were made for many years. For example, Asahi established as early as 1935 the first commercial plant in the world for the recovery of ammonia, where ammonia was effectively evaporated from the waste from spinning water and then absorbed by sulphuric acid in the form of ammonium sulphate.[136] Then, at Bayer's Dormagen plant, distillation of ammonia from waste spinning water under reduced pressure was developed[137–139] (see also German Patent 738 115). Now, ammonium is recovered by ion-exchange, if necessary in combination with the above distillation method, and is used directly for preparation of the spinning solution and partly used in plant for miscellaneous neutralizing agents.

5.2.16 Labour productivity and advances in technology

Figure 5.22 shows the plots of the labour productivity, plotted as kilograms of fibre per day-person, for cuprammonium and viscose yarns versus year. Starting from 0.48 kg-fibre/day-person in 1901 (see Table 5.3), the productivity of the cuprammonium rayon process has changed over 100 years, passing through three phases: phase I (before World War II) where there was a very gradual improvement through choice of optimum operating conditions; phase II (during World War II when the factory system was virtually destroyed; and phase III (after the war) which has seen explosive advances caused by the development of novel processes. The cuprammonium process made progress in parallel with the viscose process, now attaining approximately 100 kg-fibre/day-person, which is about 200 times the amount at the beginning of commercial production and about 20 times that of the pre-war zenith.

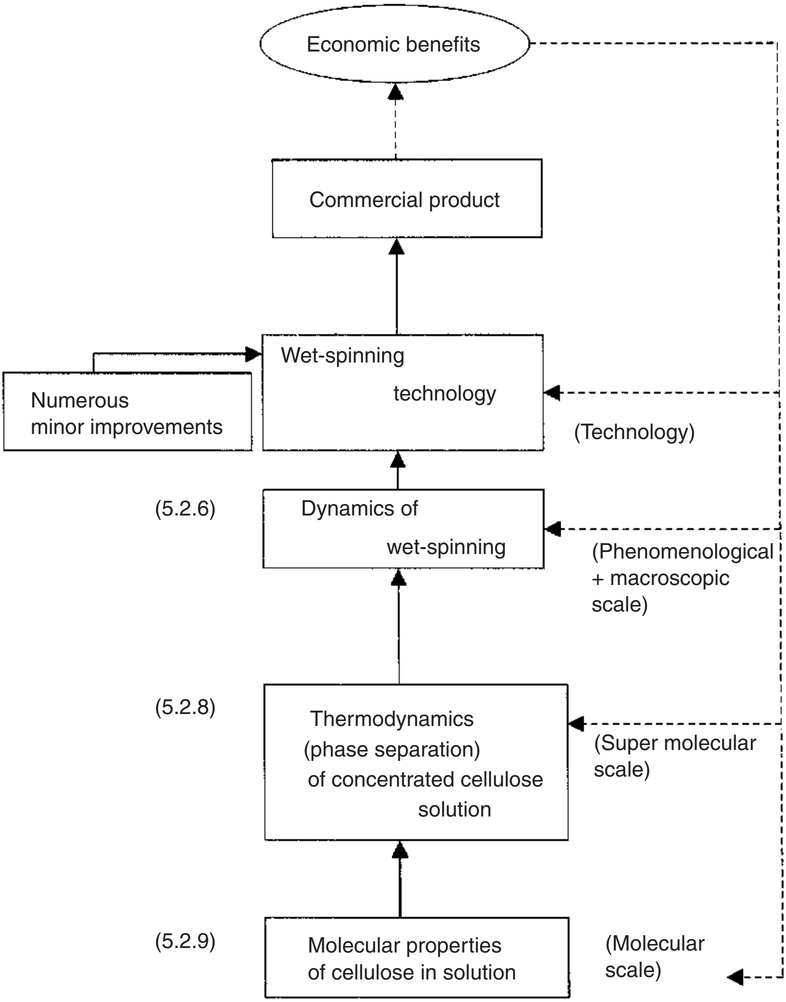
Harrop made a rather stereotypical comment on the Japanese rayon industry between the wars saying that 'Japanese engineers displayed a remarkable ability both to imitate engineers in other countries and also simplify and improve the ideas of others'.[143] His comment may be properly applicable to any countries whose industrial conditions are behind the most advanced and who have an eager desire to level up their native industries. For example, from Roman times to immediately before the industrial revolution England operated a variety of textile technologies such as fulling (from Rome, 2nd–3rd century), weaving (wool from Flanders, 11th–15th century); worsted from the low countries, 13th and 16th century; silk from France, 17th–18th century; and cotton (in the form of fustian) from the low countries, 17th century, and dyeing and finishing (wool from the Netherlands, 17th century).[144] Harrop commented only on the conditions essential to 'catch-up' with modern technology, but not satisfactory conditions. Other than this, nobody has explained reasonably why any one country (or one company) has been prosperous up to the present time, inventing and



5.22 Labour productivity of cuprammonium and viscose rayons from 1901–1990: ▲: VGF (Germany; cupra);[140] △: Courtaulds (UK: viscose);[140] □: Teikoku Jinken (Teijin) (Japan: viscose);[141] ○: Asahi (Japan: viscose);[142] ●: Asahi (Japan: cupra).

developing wide expertise, which even Despeissis or Fremery, Urban or Thiele could not have imagined. This success in revolutionary innovation of wet-spinning technology for cuprammonium rayon production owes much to the continuous and very long-term investment in fundamental research and technology. It is not due to cheap labour and a genius for imitation!

Figure 5.23 demonstrates the hierarchy of development from basic research to process development in the cuprammonium cellulose fibre industry. Research and development (R&D) covers several different disciplines, ranging from the molecular to the technological level. After World War II, the three lower levels flourished remarkably. The achievements gained in the fundamental disciplines were transferred to higher ones (as



5.23 Science and technology of wet-spinning of cuprammonium solution. Numbers in parentheses indicate section numbers.

shown by the solid lines in the figure), leading directly to innovation in process or products, although transfer and communication were often difficult, owing to the lack of common language among the groups belonging to various disciplines. Broken lines in the figure represent capital investment in R&D, which motivates and/or rewards achievement. Provided that the R&D machine works well, a continuous cyclic flow will occur (i.e. positive circulation) and in addition, if the R&D machine can be quickly modified to respond to external change, enduring circulation can be anticipated with some confidence. At present, without the basic research underpinning the hierarchy, no revolutional progress can be anticipated. Cuprammonium processes are no exception. As early as 1907–1911 many people engaging in the business of cuprammonium artificial silk, judged that the cuprammonium process had no future. Now, it is widely considered that the regenerated cellulose fibre industry, including the cuprammonium process is out-of-date and has no interest for young scientists or engineers.

This industry is, however, very artistic and the process involves numerous minor improvements as well as the remarkable innovations described in this chapter. The former are not usually published or patented, but their contribution to the industry should never be underestimated. In this sense, the motivation of the workforce operating the plant is just as important to the success of the plant. The plant is in fact an accumulation of tiny, but invaluable pieces of 'know-how', gained by a large number of 'nameless' workers. However, it should not be assumed that any entrepreneur can readily enter this business nowadays through simply purchasing the patents in question or reading the relevant scientific and technological documents.

5.2.17 Production output

Table 5.15 collects the production output data for cuprammonium rayon from 1920–1940. The last column denotes the world output of all kinds of rayon. J P Bemberg and Asahi produced more than half of world output of cuprammonium rayon in the 1930s. Output of cuprammonium rayon was 3.46% of total rayon production in 1930, decreasing to 2.62% in 1935 and 1.85% in 1939/1940. At present (1990s), only a few percent is estimated for cuprammonium rayon (filaments and staple fibres) within world rayon production. The official record of annual production of cuprammonium rayon in Japan is tabulated in Table 5.16. The last column of the table is the world production of rayons. Unfortunately, the records of countries other than Japan are not separated from those of viscose rayon. Now, Asahi produces approximately 90% of the world's cuprammonium fibres. Its total world production can be roughly estimated at c. 20 000–25 000 tonnes per year.

5.3 Morphology and properties

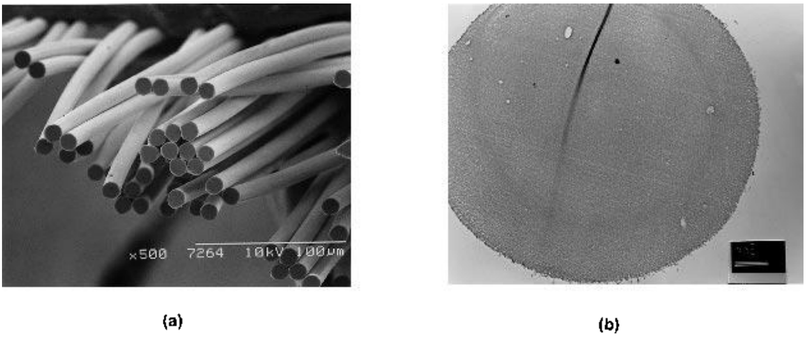
5.3.1 Morphology

Figure 5.24(a) is a scanning electron micrograph of cuprammonium rayon. The denier of a filament is about 1.4, the filament surface is very smooth and the denier is uniform. Figure 5.24(b) is an electron micrograph of the cross-section of a filament, which was sampled immediately after regeneration and not dried after spinning. Cuprammonuim rayon has a

Table 5.15 Production output of cuprammonium rayon (1920–1940)

Year	Output (1000 tonnes)			
	J P Bemberg[a]	Asahi Chemical	World[d]	World[e] (all rayons)
1920	—	—	—	15
1922	0.440	—	—	
1923	0.500	—	—	
1924	0.520	—	—	
1925	1.000	—	—	
1926	1.000	—	—	
1927	1.960	—	—	
1928	2.291	—	8.2	
1929	2.507	—	8.1	
1930	1.836	—	7.2	208
1931	1.371	0.390[b] (0.345)[c]	5.9	
1932	1.605	1.900 (1.893)	5.8	
1933	2.504	2.670 (2.659)	9.6	
1934	3.488	3.440 (3.425)	12.5	489
1935	3.468	4.460 (4.443)	12.8	
1936	—	5.220 (5.112)	16.7	
1937	—	5.120 (5.088)	16.3	
1938	—	(4.979)	18.0	
1939	—	(4.047)	20.8	
1940	—	(3.558)	—	1127

[a] Yamazaki;[145] [b] Yamazaki Part 1, Chapter 3, 4.2;[146] [c] Ishii *et al.*;[147] [d] Lieser p. 59;[148] [e] Ishii (from Textile Organon).[149]



5.24 (a) Scanning electron micrograph of cuprammonium rayon (Bemberg®); (b) electron micrograph of cross-section of cuprammonium rayon (Bemberg®) sampled immediately after the regeneration stage and not dried.

Table 5.16 Production output of cuprammonium rayon in Japan (1947–1998)

	Output (10^3 tonnes/year)		
Year	Filament[a]	Staple fibre[a]	World (rayons)
1947	0.270	—	949[b]
1950	3.523	—	1612 (664)[c]
1955	6.391	—	2278 —
1960	14.587	1.044	2608 (937)
1965	18.429	3.020	3338 —
1970	27.124	3.360	3431 (991)
1975	22.508	1.474	— (821)
1980	22.080	3.480	— (828)
1985	21.970	1.590	— (690)
1990	24.925	0.831	— —
1995	20.626	1.536	— —
1998	19.218	1.678	— —

[a] *Year Book of Textile Statistics*;[150] [b] *History of Japanese Chemical Fiber Industry* (cited from *Textile Organon*);[151] [c] World Rayon Filaments Production.[152]

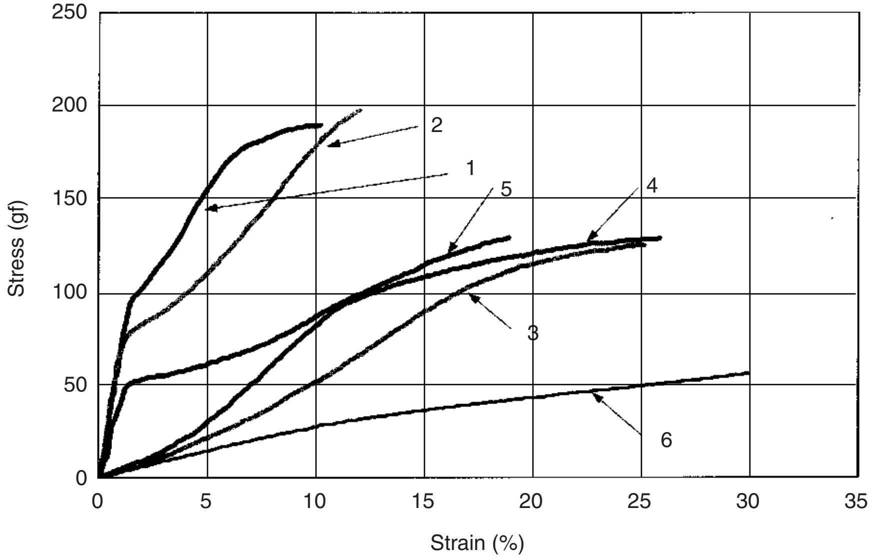
Table 5.17 Mechanical properties of cuprammonium rayon filaments (75 denier/45 filaments)

Mechanical properties	Bemberg	
	Continuous	Continuous (NP)
Tensile strength (g/d) (dry)	2.5	2.7
Tensile elongation (%) (dry)	12	13
Tensile strength (g/d) (wet)	1.6	1.6
Tensile elongation (%) (wet)	26	26
Wet shrinkage (%)	–0.5	2.4
Boil shrinkage (%)	5–6	1–2

circular cross-section and no visible skin, but does have a microscopically thin outer skin, which is more porous, when undried, than the compact inner part. A cuprammonium rayon filament can be regarded approximately as a fine flexible uniform cylinder. This morphological character is apparently responsible for the superior feel and brightness of the fibres.

5.3.2 Mechanical properties

Figure 5.25 illustrates the stress–strain curves of cuprammonium and viscose rayons. Some typical physical properties are collected in Table 5.17.



5.25 Stress–strain curves of cuprammonium and viscose rayons at 20 °C (relative humidity 65%, 84 dtex). Curve 1, Bemberg (continuous process) dry; curve 2, Bemberg (net process) dry; curve 3, Bemberg (net process) wet; curve 4, Bemberg (continuous process) wet; curve 5, viscose (cake) dry; curve 6, viscose (cake) wet.

Note that mechanical properties depend, to some extent on the spinning and after-treatment conditions, and the mechanical properties of the commercial products are designed to fit the end-use. Cuprammonium rayon has higher tensile strength (TS) and lower tensile elongation (TE) than viscose rayon, whose TS ranges from 1.7–2.3 g denier^{-1} and TE from 18–24%. Table 5.18 shows TS in wet and in dry cuprammonium rayon from the 1950–1990s. The ratio of TS in the wet state to that in the dry state (W-D ratio) is now 0.70–0.73, compared with 0.45–0.55 for viscose rayon. It is to be noted that TS (wet) exceeded 1.5 g in the 1970s.

5.3.3 Hydrophilic properties

Figure 5.26 is a contour map of equilibrium water content (W_c) plotted against environmental temperature and humidity.[154] In the lower humidity and lower temperature region ($T < 40°C$ and <60%), W_c is temperature-dependent. In the high humidity region (>80%), W_c is humidity dependent.

Table 5.18 Wet–dry ratio of TS of Asahi Bemberg fibres (75 denier)

Year	Method	Tensile Strength (g/d)		Ratio
		dry	wet	
1951	Hank	2.03	1.22	0.60
	Centrifuge	2.14	1.31	0.61
	Continuous[a]	2.10	0.93	0.44
1961	Continuous	2.17	1.03	0.47
	Continuous[b]	2.14	1.32	0.62
1976	Hank	2.18	1.31	0.60
1977	Continuous	2.54	1.64	0.65
1978	NP	2.54	1.55	0.63
1988	Continuous	2.46	1.73	0.70
1998	Continuous	2.56	1.88	0.73

Data from Munekata in *Chemical Fibers*, 1956, p. 281 (data were obtained in 1951);[153] *30 years History of Asahi Bemberg Plant*, 1962, and data from Asahi Bemberg plant.
[a] America Bemberg made; [b] Beaunit Mills made.

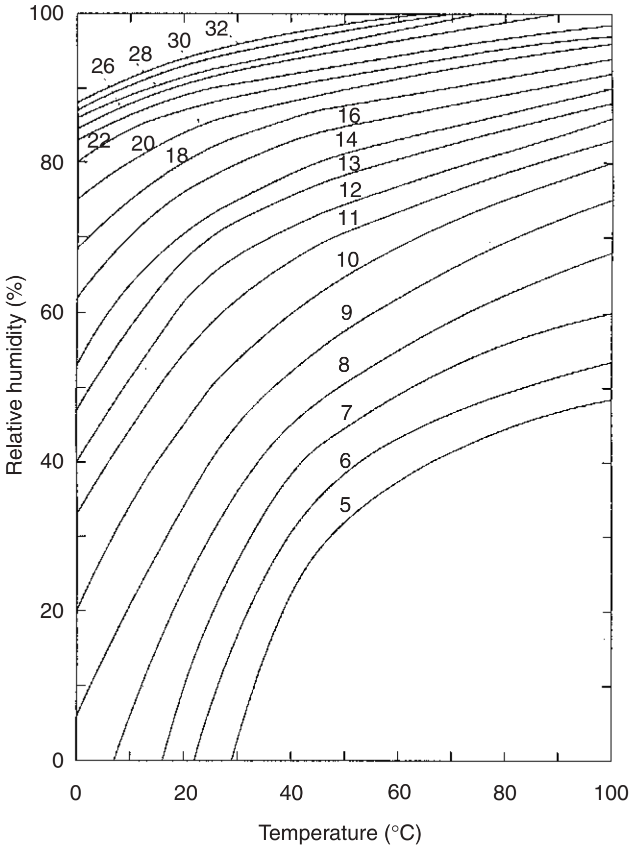
5.4 Products and application

5.4.1 Filaments and staple fibres

Table 5.19 collects correlations between process and products of filaments, staple fibres, and non-woven filament cloth. Table 5.20 summarizes end-uses of fabric and knitted materials made from filaments and staple fibres and their characteristics. Cuprammonium rayon fabrics have the following features when they are worn: (1) high water content, (2) low tribo-electric voltage, (3) moisture absorbing and releasing ability, (4) no cling, (5) less ravelling, (6) no stickiness, (7) smooth wearing through sleeve, (8) low friction coefficient, (9) low noise at rubbing with lining, (10) good pliability, (11) excellent dynamic drape behaviour, (12) good iron setting ability, and (13) excellent wearing comfort. These are closely correlated to the fineness, circular cross-section and hydrophilic properties of fibres, and these are more manifest when wool is used as a face side fabric, to which cuprammonium rayon cloth is added as lining.

5.4.2 Nonwoven fabric

Cuprammonium filaments constituting nonwoven fabric are almost perfectly round, adhering to each other at some places. Self adhesion is formed during the sheet forming and refining process. Bemliese,® a trade



5.26 Relationship between the equilibrium water content of cuprammonium rayon filaments (75 denier/45 filaments)[154], relative humidity and temperature. The numbers denote the equilibrium water content (%).

Table 5.19 Commercial products and their manufacturing methods (Asahi Chemical Ind. Co.)

Type	Method	Registered name	Spinning velocity (m min^{-1})	Products (dtex)
Filament	Hank	Bemberg	50–70	22–330
	Continuous		90–170	17–165
	Continuous (not process)		400–1000	84–165
Staple fibre	BF		100–150	1.4–3.3
Nonwoven filament cloth	Wet-spunbond	Bemliese	30–50	15–60 (g m^{-2})

Table 5.20 End-uses and characteristics

	End-uses	Characteristics
Bemberg® fabric, knitted	a. Lining b. Lingerie c. Dress fabric (velvet, outer, inner) d. Native costume (duppatta, saree) e. Interior (curtain)	a. Superior hydroscopicity and anti-static b. Extremely soft touch and fine texture c. Silk-like brilliance and dyeability
Bemliese® nonwoven fabric	a. Domestic uses (cosmetic puff, wet wiper, tea bag) b. Medical uses (hospital swab, towel) c. Industrial uses (clean room wipe, industrial wipe) d. Agricultural uses (seeder tape, seeder net)	a. Binderless (pure cellulose) b. Sanitary and soft c. Dust- and lint-free d. Highly liquid absorbent and retentive e. Anti-static f. Ecologically safe
Hollow fibre	a. Artificial kidney	a. High strength b. Easy to produce thin-walled membrane c. Little protein and blood corpuscle due to high hydrophilicity d. Heat resistant and γ-ray resistant e. Safety and long-term actual results

mark of Asahi, is distinguished from other cellulosic nonwoven fabrics, because it is made of continuous filaments of pure cellulose and has no binder. The following characteristics are due to the sheet forming component and water-jet treatment: (1) residue-free, (2) lint free, (3) non-toxic, (4) high absorbency and high liquid retention, (5) anti-static electricity, (6) biodegradable, (7) bulky and soft, (8) uniform thickness and density.

Being lint-free, soft, flexible and hygienic with a high capacity, Bemliese® has various applications as follows: (1) consumer uses: cosmetic puff, wet wiper, tea bag, various kinds of disposable uses, (2) medical uses: hospital swab, towel, gauze, adhesive bandage, (3) industrial uses: clean room wiper, industrial wiper, (4) agricultural uses: seed tape, covering net for sowing.

Characteristics and end-uses of Bemliese® are also summarized in Table 5.20.

5.4.3 Cuprammonium cellulose hollow fibre membrane

As most old cellulose industrial products were replaced by synthetic polymers, cellulose and its derivatives were continuously forced to attain new markets for their survival. For this reason, a broad open-minded approach was helpful. One attractive market for cellulose is undoubtedly the membrane business. Cellulose membranes have the longest history of use in the membrane industry[155] and even now are keeping their top position.[156] Unlike regenerated cellulose fibre, cellulose membranes are superior because of the following properties: (1) chemical stability, (2) safety (biological compatibility), (3) low price, (4) high tenacity in the wet state, enabling the preparation of thin membranes, (5) ease of control of pore size, ranging from 1–100 mm in diameter, and (6) porosity.[155,156] In comparison with synthetic polymer membranes, cellulose membranes have: (1) large removability of low-molecular-weight nitrogen metabolites such as urea, (2) better balance of material permeability and water ultrafiltration rate, and (3) high dimensional stability and good processability in module manufacturing.[157] Now, most cellulose membranes are hollow-fibre membranes. The traditional technology of regenerated cellulose fibres for textiles combines well with membrane science and technology.

The cuprammonium process is the most lucrative because a tremendously wide range of variation in the sequential steps of dissolution–deformation–coagulation–regeneration is possible. However, the target markets have changed, for example, from packing material (i.e. sausage skin) and moisture-proof cellophane to separation media such as haemodialysis and ultrafiltration (UF).

There are two types of cellulose membranes with respect to their morphology: symmetrical and asymmetrical membranes – cellophane (viscose rayon) and cuprammonium cellulose membranes for haemodialysis are typically symmetrical membranes. Asymmetrical cuprammonium cellulose hollow fibre membrane developed in the 1980s–1990s is now used as a virus separation medium.

5.4.4 Artificial kidney

Cuprammonium cellulose hollow fibre membranes are utilized as one of the main elements in a blood purification device, the hollow fibre artificial kidney (AK), produced and sold by Asahi Medical Co Ltd (Tokyo, Japan), a subsidiary of Asahi, which was first in the world to produce a dry-type hollow-fibre artificial kidney commercially in 1974. During the 25 years or so that have followed, regenerated cellulose hollow fibre membranes have been considerably improved in the following areas:[158,159] (1) pin hole, (2) break-down during dialysis, (3) membrane thickness (100 μm → 7 μm), (4) purity (low molecular weight non-cellulosic component), (5) sterilization method, and (6) biological compatibility. There are two types of artificial kidney that use cuprammonium hollow fibres: the AM-SD series (conventional hollow fibres) and the AD-BIO series (biocompatible AK with standard and middle-flux ranges). In the latter series, the biocompatibility of the cellulose membrane is improved by polyethylene glycol grafting technology. Specifications for AK are as follows: surface membrane, 0.8–2.0 m^2; inner diameter, 180 µm; membrane thickness membrane, 15 µm. Ordinary haemodialysis membranes are believed to have a mean pore diameter of 2–3 nm. Biocompatible membranes have a larger mean pore size (4–10 nm). The sieving coefficient S_c, is defined as the ratio of substrate in the filtrate to that in the supplying solution of β_2-microglobulin (molecular weight 11 800; molecular size c. $4.5 \times 2.5 \times 2.0\,\text{nm}^3$) = 0.6 and S_c of albumin = 0.02.

The world market for artificial haemodialysis apparatus was roughly estimated to be 7.2×10^7 units/year in 1999. Cuprammonium cellulose membrane occupies a 35% share, and cellulose acetate membrane has a 24% share.

5.4.5 Virus removal filter

In 1987 Asahi Chemicals developed the BMM (Bemberg Microporous Membrane) process as a new technology for effective removal of viruses. Asahi marketed its filter under the trade name Planova®. Planova® is a validated virus removal filter used in the purification of various plasma-derived and biopharmaceutical products such as globulin, blood coagulation factors and interferon. Planova® 'has been filed with the Biologic Master File of the US Food and Drug Administration.

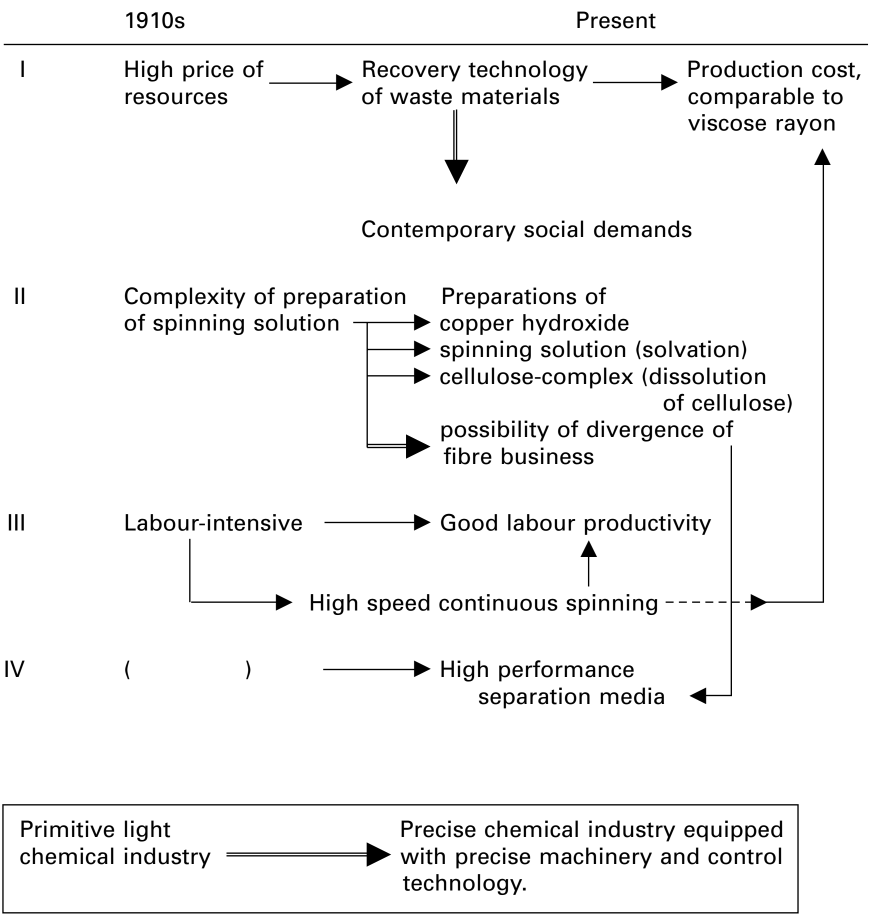
Planova®'s features are: (1) the effective removal of known and unknown viruses and other contaminants by a size exclusion mechanism, (2) a high recovery rate of proteins owing to the hydrophilic nature of the membrane, (3) a high filtration rate and a large filtration capacity, (4) the availability of two filtration methods: dead-end and tangential (i.e. parallel flow) filtrations,[160] (5) various filter sizes.

Three types of membrane are on the market: Planova 15 N (mean pore size, measured by the water flow rate method, 15 ± 2 nm), Planova 35 N (pore size 35 ± 2 nm; virus removal filter) and Planova 75 N (mean pore size, 72 ± 4 nm) used as a prefilter.

5.5 Conclusion and future prospects: does the cuprammonium rayon industry have a future?

Table 5.21 summarizes three major drawbacks of the cuprammonium rayon industry in the 1910s and their solutions in the 1990s. During these 90 years

Table 5.21 Drawbacks of the cuprammonium rayon process encountered in the 1910s and at present



the cuprammonium process made a slow metamorphosis from a primitive light chemical industry to a precise chemical industry.

Cellulose is synthesized from carbon dioxide and water and is biodegradable, being the most abundant naturally occurring organic compound. Therefore, there is no doubt about the very long term future of the cellulose industry after complete exhaustion of fossil fuels, although we cannot tell exactly when this will happen. The problem is whether the existing cellulose industry, including the cuprammonium rayon process, which at present is under fierce competition from synthetic polymers, can survive until that time. Cellulose is an earth-friendly material, but the regenerated cellulose fibre industry is heavily handicapped by the huge areas of land and amounts of water required. These are the negative legacy of the 19th century.

Now is a time of global free competition (laissez-faire; this does not mean fair competition) with people trying to make immediate profit, or make a fortune overnight. We may expect some specific improvements to arise from basic research and technology, which is now being accelerated. The next hundred years' history of the cuprammonium process may differ greatly from that of the last hundred years.

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