

A brief history of regenerated cellulosic fibres

CALVIN WOODINGS

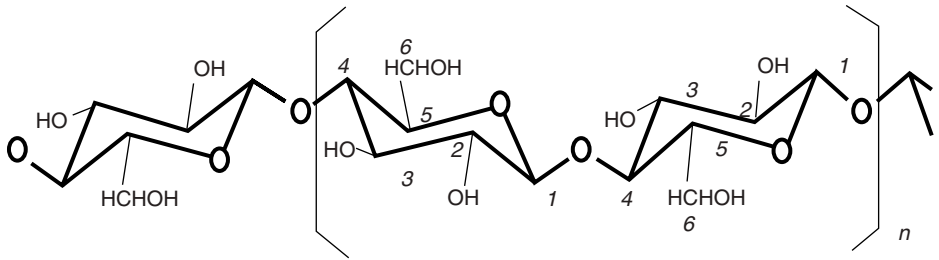
1.1 Introduction

Like so many major new materials, artificial fibres did not arise from the clear identification of a customer need followed by carefully planned research aimed at meeting that need. Visionaries foresaw the potential of artificial fibres but the amateur scientists and professional inventors who made the groundbreaking discoveries were often motivated by products unrelated to today's fibre industry. They worked without knowledge of the underlying chemistry and physics of polymers and progressed towards their goals by trial and error accompanied by careful observation.

Industrially speaking, artificial fibres had their origins in the paper industry, in war materials, and in electricity, that 'internet' of the late 19th century. However the inspiration for the artificial fibre industry is generally credited to Robert Hooke (1635–1703), an English physicist better known for his discovery of the law of elasticity and the development of improved microscopes. In *Micrographia* (Small Drawings, London, 1665) he discussed the possibility of imitating the silkworm by making 'an artificial glutinous composition [and] to find very quick ways of drawing it out into small wires for use'. He also deserves a special mention in the particular context of regenerated cellulose fibres for being the first scientist to use the word 'cell' to describe the honeycomb structure of plant matter.

Renee-Antoine de Réaumur (1683–1747) recorded in 1734 his attempts to force different kinds of varnish through perforated tin cans to form coarse filaments that hardened in warm air. He is therefore credited with the first dry-spinning process even though his extrudate was unusable as fibre. Cellulose (Fig. 1.1) itself was discovered in 1839 by a Frenchman, Anselme Payen (1795–1871) the Professor of Agricultural and Industrial Chemistry at the Central School of Arts and Manufactures in Paris, during an extensive analysis of wood. He also discovered pectin and dextrin and was the first to isolate and concentrate an enzyme – diastase.

More so then than now, silk was *the* luxury fibre and far too expensive



1.1 Structure of cellulose: a linear polymer of two anhydroglucose units with a 1-4 β-glucosidic linkage (see also Fig. 8.2-8.5).

for general use in clothing. Attempts to reduce its cost led to several abortive attempts to extrude the silkworm gum artificially, but the first indication that Hooke's idea might be realisable came in the 1840s when Louis Schwabe, an English silk weaver, developed the precursors of today's spinnerets, the nozzles with fine holes through which liquids could be forced. He extruded molten glass filaments¹ and proceeded to weave fabrics from the resulting continuous filament yarns. At the same time, in apparently unrelated developments, several continental European chemists were working with cotton and the twigs, branches and barks of assorted trees, especially mulberry (the leaves of which are the silkworm's preferred food). Charles Freidrich Schönbein is credited with the accidental discovery in 1846 that nitric acid could nitrate these cellulose sources and result in an explosive substance, 'Schliesswolle' or guncotton. This line of research was to lead to the discovery of dynamite and the founding, by Alfred Nobel in 1867, of the explosives industry. But in the early 1850s, it also led to the first successful attempt to make textile fibres from plant cellulose.

1.2 Cellulose nitrate

George Audemars of Lausanne, Switzerland dissolved the nitrated form of cellulose in alcohol and ether and discovered that fibres were formed as the resulting 'collodion' was drawn into the air. His 1855 patent² on *Obtaining and Treating Vegetable Fibres* covers the pulping of the inner bark of mulberry to extract cellulose fibre which 'may be hackled, combed, or carded, and then spun like cotton; or it may be converted into an explosive compound by the action of nitric acid, and then dissolved in a mixture of alcohol and ether, then mixed with an [ether] solution of caoutchouc, and drawn out into fine threads or filaments'.

These soft strong cellulose nitrate fibres could be woven into fabrics but had a very serious drawback that ultimately prevented their widespread use in textiles: they were very flammable.

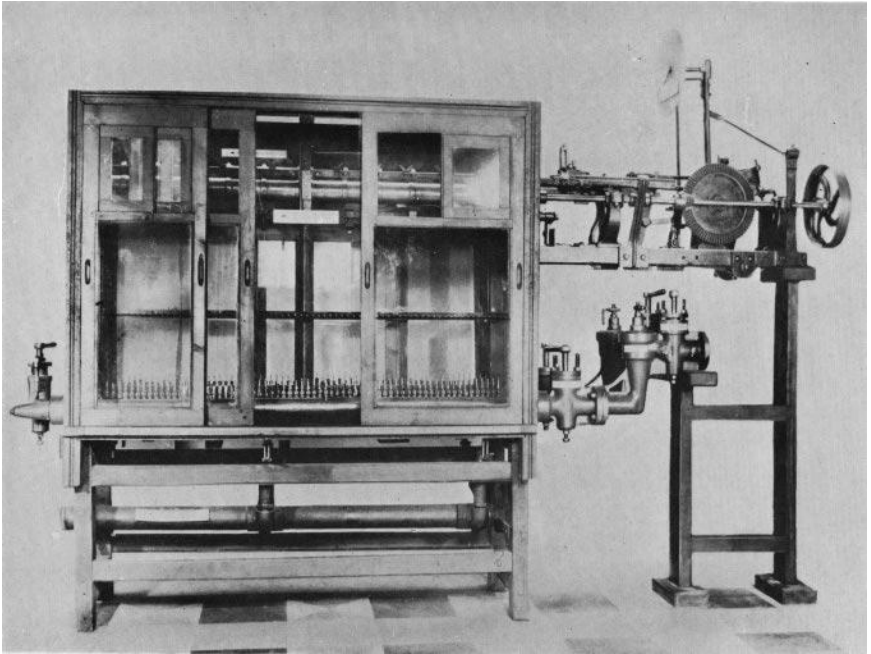
It was Joseph Swan, the English physicist and chemist, developer of the first electric lamp and inventor of bromide photographic print paper, who learnt how to denitrate the cellulose nitrate using ammonium hydrosulphate. This was part of his quest for a better carbon fibre for lamp filaments and was patented as such in 1883.³ Swan was nevertheless fully aware of the textile potential of his process, and in 1884, ‘some samples of artificial silk . . . the invention of Mr J W Swan’ were displayed at a meeting of the Society of Chemical Industry. The first fabrics made from the new artificial silk were also shown at the Exhibition of Inventions in 1885. However with carbon lamp filaments being his main focus (for which he was knighted in 1904) he failed to follow up on the textile possibilities, allowing the Frenchman, Count Louis-Marie-Hilaire Bernigaud, Comte de Chardonnet justly to become regarded as the founder of the regenerated cellulosic fibre industry.

Chardonnet, a scientist and professional inventor, had after all been concentrating on developing artificial silk fibres and textiles, and he did follow through to set up a company to manufacture it. His research evolved a process practically identical to Swan’s, albeit slightly later, but he nevertheless perfected the fibres and textiles in time for the Paris Exhibition in 1889. There he attracted the necessary financial backing to produce the first ‘Chardonnet silk’ from J P Weibel, a French wood-pulp producer. His first factory started up in 1892 in Besançon near to Weibel’s pulp and paper mill. His commercial process⁴ involved treating mulberry leaves with nitric and sulphuric acids to form cellulose nitrate, which could then be dissolved in ether and alcohol. This *collodion* solution was extruded through holes in a spinneret, but where Swan used a liquid coagulant, Chardonnet used warm air to evaporate the solvent and form solid cellulose nitrate filaments (see Fig. 1.2). Both Swan and Chardonnet denitrated the fibres in a separate step.

British developments began when Freidrich Lehner left the Chardonnet factory in Switzerland and set up his own business, Lehner Artificial Silk Ltd, with British capital in 1892. He wished to exploit his own patented improvements to Chardonnet’s process and collaborated with Lister and Co of Bradford Ltd, producing small quantities of cellulose nitrate yarn in 1893. (H G Tetley, the prime mover behind the development of viscose rayon, worked at Lister and Co before joining Samuel Courtauld & Co – see below)

The New Artificial Silk Spinning Co. based at Wolston near Coventry (led by Joseph Cash the Coventry ribbon weaver), also produced cellulose nitrate yarn but with much difficulty. The company went into liquidation in 1900. Their machinery was bought by Glanzstoff (see below).

Although this first artificial fibre process was simple in concept, it proved slow in operation, difficult to scale-up safely, and relatively uneconomic



1.2 The first artificial fibre spinning machine c.1889 developed by Count Hilaire de Chardonnet for cellulose nitrate fibres. The filaments were spun vertically upwards from the nozzles on the floor of the cabinet and collected on reels at the top. (Reproduced from *Courtauld's: An Economic and Social History*, Clarendon Press, 1969.)¹¹

compared with later routes. Denitration of the fibres, which was necessary to allow safe use wherever the fabrics might risk ignition, spoilt their strength and appearance. Nevertheless, Chardonnet earned and truly deserved his reputation as the 'Father of Rayon'. His process was operated commercially until 1949 when the last factory, bought from the Tubize Co in the USA in 1934 by a Brazilian company, burned down.

1.3 Direct dissolution in cuprammonium hydroxide: cupro

The second artificial silk process to be commercialised was based on a discovery made by the Swiss chemist Matthias Eduard Schweizer in 1857.⁵ He found that cotton could be dissolved in a solution of copper salts and ammonia and then regenerated in a coagulating bath. The fibre process was however invented by a French Chemist, Louis-Henri Despeissis,⁶ who worked on spinning fibres from Schweizer's solution in 1890. He extruded the *cuprammonium* solution of cellulose into water, with dilute sulphuric

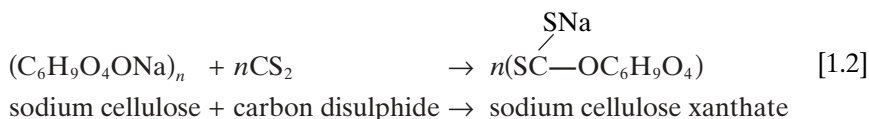
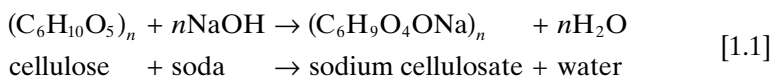
acid being used to neutralise the ammonia and precipitate the cellulose fibres.

Despeissis died in 1892 and his patent was allowed to lapse. However in 1891, the German chemist Max Fremery and the Austrian engineer Johan Urban were also using Schweizer's reagent and cotton to make lamp filaments in Oberuch near Aachen. They decided to expand into artificial silk (in German, Glanzstoff) and patented⁷ their approach in the name of Dr. Hermann Pauly to avoid attracting the attention of competitors. Pauly, a director of the technical school in Munchen Gladbach, other than lending his name, made no contribution to the development. This patent, essentially a reiteration of the Despeissis process with a practical spinning method added, was however upheld after dispute, thereby allowing Fremery and Urban to begin large scale manufacture as Vereinigte Glanzstoff Fabriken (VGF) in 1899. In 1901, a Dr Edmund Thiele working at J P Bemberg developed a stretch-spinning system. The resulting improved Bemberg[®] silk went into production in 1908. Its early commercial success owed much to the flammability disadvantages of the Chardonnet process, but it was competition from the viscose process (see below) that led to its decline for all but the finest filament products.

The process is still used today, most notably by Asahi in Japan where sales of artificial silk and medical disposable fabrics still provide a worthwhile income (see Chapter 5). However the relatively high costs associated with the need to use cotton cellulose and copper salts prevented it from reaching the large scale of manufacture achieved by the viscose rayon process. Most producers (Asahi and Bemberg excepted) had abandoned the approach by the outbreak of war in 1914.

1.4 Dissolution via cellulose xanthate: viscose

In 1891 the British chemists Charles Cross, Edward Bevan, and Clayton Beadle, working at Kew in England, discovered that cotton or wood cellulose could be dissolved as cellulose xanthate following treatment with alkali and carbon disulphide:



The treacle-like yellow solution (initially called 'viscous cellulose solution', later contracted to 'viscose') could be coagulated in an ammonium sulphate

bath and then converted back to pure white cellulose using dilute sulphuric acid. They patented their process in 1892 without mentioning fibres.

Cross and Bevan had set up a partnership as analytical and consulting chemists to serve the pulp and paper industry in 1881. They collaborated with the Swedish inventor of the sulphite pulping process, C D Eckman, to help the British paper industry develop a wood pulp alternative to the cotton and linen rags that were then the main raw materials of the paper trade. As a natural extension of their work on pulping chemistry, and cotton mercerising* they became interested in dissolving cellulose and the 1892 patent application, entitled *Improvements in Dissolving Cellulose and Allied Compounds*⁸, was the result. In 1893 they formed the Viscose Syndicate to grant licences for non-fibre end-uses, and in 1896 the British Viscoid Co Ltd was formed to exploit the process as a route to moulded materials. These companies were later merged to form the Viscose Development Co in 1902. Early licences were granted to papermakers and calico printers for the use of viscose as a coating or size, and to makers of artificial leather and artificial flowers.

In another laboratory at Kew, Charles Henry Stearn and Charles Fred Topham developed the continuous filament spinning process and the machinery needed to wash and collect⁹ the viscose yarns. The two had met in about 1874 in Liverpool where Topham was helping his father blow glass for Stearns spectrum tubes and radiometers. At the time Stearn was a cashier in the Liverpool branch of the Bank of England but also an amateur scientist specialising in high vacuum technology. In 1877 Stearn was collaborating with Joseph Swan on the electric lamp, Stearn taking the carbon filaments from Swan's experiments in Newcastle, inserting them in tubes made by Topham in Rock Ferry, and evacuating them at home. In 1889 with a workable lamp filament still eluding Swan and Stearn, Stearn left to direct the Zurich Incandescent Lamp Co of Zurich and London, also at Kew. In 1893, on seeing the viscose patent, he immediately recognised the potential of the process as a cheap route to the now successful Chardonnet silk, and contacted Cross with a view to commencing fibre spinning developments.

His work on spinning equipment culminated in 1898, when, describing himself as an electrician, Stearn patented¹⁰ filament manufacture 'by projecting the [viscose] solution [of cellulose] into a precipitating solution such for instance as alcohol, brine, chloride or sulphate of ammonia or other suitable precipitant.'

In order to finance the development of a commercial spinning process from these ideas, Cross and Stearn set up the Viscose Spinning Syndicate Ltd, incorporated in May 1899. Alfred Nobel (explosives) and Andrew

*John Mercer's 1850s process of using caustic alkali to finish cotton fabric, later (1894) found to be capable of making cotton look like silk if the process was carried out under tension.

Pears (soapmaker, and Beadle's father-in-law) were among the first shareholders. The continental European rights went to a group of German businessmen who had set up *Continentale Viskose GmbH* in 1897. The Viscose Spinning Syndicate under Cross and Stearn was keen to attract buyers and sell the process, an attitude that inhibited the necessary development of a deeper understanding of the fundamentals of cellulose dissolution. D C Coleman¹¹ describes the syndicate as 'a curious assemblage of talent and inexperience . . . that managed to be neither a research laboratory nor a production pilot-plant'.

The next few years were fraught with difficulty as the original process was repeatedly shown to be inconsistent and largely uncontrollable. Economics went uncalculated and the consequences of toxic gases and viscose solidifying in sewers were ignored. Filaments produced by spinning into the then favoured alkaline bath were so weak they could only be collected in Topham's specially devised spinning box.¹² Topham's box, later to be regarded as one of the fundamental breakthroughs leading to successful commercialisation of the viscose process, would have appeared unnecessary had acid spinning baths been developed earlier (as they were in Europe). However the box is still relevant to this day as a gentle way of collecting high quality yarn without incurring the strain applied by bobbin systems. His candle filter¹³ (to remove particles from the viscose prior to spinning), spinning pump¹⁴ (to allow careful control of filament size), and his development of hot acid fixing were however key, if underrated, process improvements.

The first licensee to discover the inherent unreliability of the early viscose process was Prince Donnersmarck, the majority shareholder of the *Continentale Viskose Co* who in 1902 decided to set up a plant, using equipment commissioned from Dobson and Barlow, at Settin, near his pulp and paper mill in Altdamm. It started production in August 1903 but despite heavy investment in machines and men failed to exceed 100 kg per day of yarn output over the next two years. His managers became frequent visitors to Kew, but despite free access to the latest technology, they continued to struggle.

An American chemist, Dr Arthur D Little of Boston, had also visited Kew in 1899, and with a Philadelphia businessman, Daniel Spruance, had acquired the US rights to the Cross, Bevan and Beadle patent. They were instrumental in setting up the *Cellulose Products Co* in the USA to make viscose solutions in 1900, and in 1901 set up the *General Artificial Silk Co* to spin fibres – acquiring rights to the Stearn spinning patent. Five years of difficulty later, the rights were bought by Silas W Petitt, Spruance's attorney, for \$25 000. He dissolved the original companies but continued the project as the *Genasco Silk Works* until his death in 1908.

The *Société Française de la Viscose*, who like the pioneering

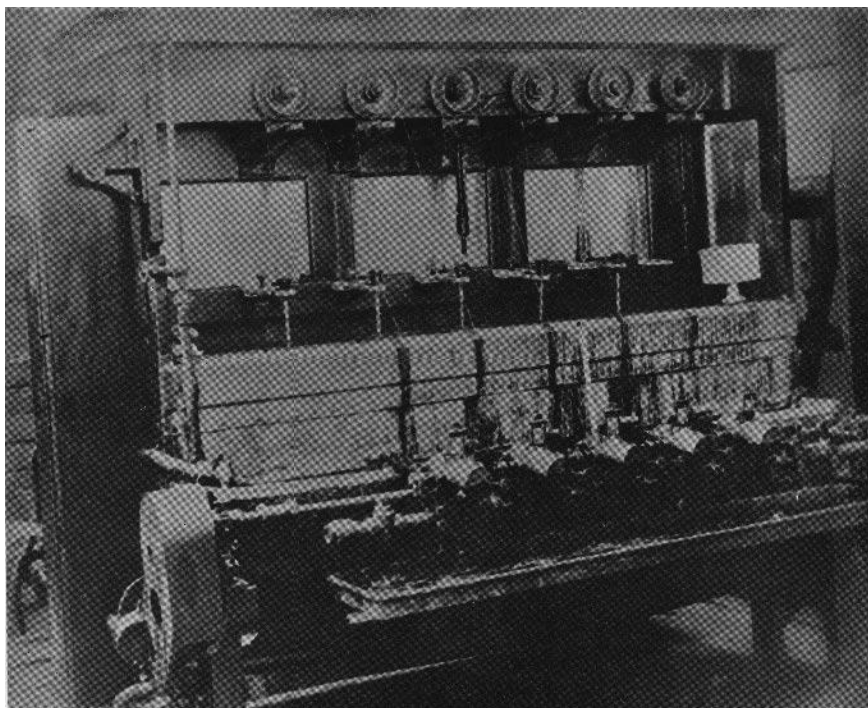
Donnersmarck, ordered three Dobson and Barlow spinning tables with 50 spindles each, acquired the French rights. Their factory commenced operation in the summer of 1903, but like Donnersmarck, they failed to exceed 100 kg per day output by 1905.

In February 1904, the Kew laboratories were visited by Henry Greenwood Tetley of Samuel Courtauld & Co Ltd. Courtauld were silk weavers looking for new raw materials and new opportunities to grow. The success and profitability of Samuel Courtauld had been built on the 19th century fashion for black silk mourning crepe, and the company was planning its stock market flotation. The visitors to Kew knew that Chardonnet's now established cellulose nitrate process was creating a lucrative market for artificial silk in France. Having also visited Donnersmarck's plant in Germany, they believed that Cross and Bevan's viscose route could make a similar fibre at about a third of the manufacturing costs of the Chardonnet's route. Nevertheless, it took two presentations, the second to a changed Board of Directors after the flotation, before Courtauld was persuaded to acquire the viscose process rights.

On 14 July 1904, the Viscose Spinning Syndicate agreed to sell the viscose process rights and patents to Courtauld & Co for the sum of £25 000. Courtauld took over the Kew laboratories to gain practical experience in the new technology while constructing a production plant. In September 1904 they gained full access to the technology developed by the Société Française de la Viscose, and in December took delivery in Kew of a 12-end Dobson and Barlow viscose yarn pilot line (Fig. 1.3). Siemens Timber Yard by the canal in Foleshill, Coventry, England was acquired, and the Kew equipment transferred to Coventry in August 1905. The first small samples of Coventry viscose filament yarn were shown to the Courtauld Board in November 1905.

While the first fabrics were woven in March 1906 at Courtauld's Halstead Mill in Essex, Coventry's output was largely put to waste. By August 1906, only 25% of the yarn produced was saleable and the Courtauld board were advised that any expansion of the plant would be folly. The problem was largely due to the tender nature of the yarns emerging from the alkaline ammonium sulphate spinning bath but its solution, an acid-salt bath, was emerging from work in the Donnersmarck plant in Germany and at Société Française de la Viscose in France, and, via the technical exchange with the French, at Courtauld & Co in Coventry.

It was Dr Paul Koppe, the technical manager of Donnersmarck's plant, who took out the first patent (May 1904) on what later became known as the Müller spinbath, a mixture of sulphuric acid and another soluble salt. Donnersmarck, a major shareholder in the Viscose Spinning Syndicate, presumably realising this crucial new discovery would devalue the licence being acquired by Courtauld from VSS, had the patent withdrawn. It was



1.3 The first commercial viscose spinning machine (c. 1904) supplied to Samuel Courtauld and Co by Dobson Barlow Ltd. This was a double-sided machine, the other six spinning positions being out of view. A white Topham-Box is shown (out-of-position) on the right. (Reproduced from *Courtaulds: An Economic and Social History*, Clarendon Press, 1969.)¹¹

reapplied for in May 1905 (Germany) and April 1906¹⁵ (Britain), this time in the name of Dr Max Müller. By then the alkaline bath process that Donnersmarck had proved unworkable had been safely sold to Courtauld.

Courtauld's first attempt to get the British Müller patent revoked was made jointly with the other European viscose producers and failed in May 1907 in a judgment with curious consequences. The British judge, apparently confused by the complexities of the case, concluded that while the sulphuric acid concentration could vary over the full range claimed in the patent, the salt level always had to be at saturation. So in Britain, lower concentrations of the salt were deemed outside the Müller patent but in the rest of Europe, Donnersmarck's competitors were much more constrained. Courtauld opted for a sulphuric acid/ammonium sulphate/sodium sulphate spinbath with appropriate salt concentrations in mid-1907, and were never challenged by Donnersmarck.

Spinbath evolution in Coventry continued apace with progressive improvements in yarn quality. The addition of glucose¹⁶ in 1907 followed by the progressive removal of the costly ammonium salt in 1909 and the fundamental breakthrough¹⁷ achieved by adding zinc sulphate in 1911 firmly established Courtauld's lead in the new technology. The yield of first quality yarn increased to around 40% in 1907 and 4 years after taking over the Kew operation, early in 1908, the Courtauld viscose business had its first profitable month. By 1911, with the zinc additions to the spinbath, more than 90% of Coventry yarn was meeting the original first quality standard, but by then the standards in use had been re-based to allow further progress.

The acquisition of the rights to the viscose process by Courtauld was to become one of the most profitable investments of all time, and the opening up of the American market was the key to this greater success. Just before he died in 1908, Silas Pettit the owner of the Genasco Silk Works in the USA entered into a royalty agreement to allow Courtauld to sell Coventry yarn in his territory. After his death, his son, John Read Pettit Jnr decided to sell up. He travelled to Coventry in May 1909 and on 3 June reached agreement with Tetley to sell Courtauld the US plant and rights for \$150 000. The Courtauld board, by then fully convinced of the enormous potential of the process and encouraged by the take-off in US demand for the Coventry yarn, approved the deal on the same day.

On 6 August 1909, the US government applied a duty of 30% to the imported Coventry yarn, but by then Tetley had visited the USA and decided to start production there. Fifty acres of land were purchased in November 1909 and the American Viscose Company registered on 15 March 1910 at Marcus Hook in Pennsylvania. It was set up as a private company with shares bought in cash by Samuel Courtauld and Co, UK. The new US company acquired the rights to the viscose process from Courtauld in exchange for further shares. George Henry Rushbrook, the Courtauld company secretary became the first President. The first yarn was spun on 23 December 1910.

From 1910 to 1920, with the Courtauld viscose patents in force and the production technology developed to provide quality yarn at competitive prices, Tetley's 1904 vision became reality. Donnersmarck's plant in Germany, the originator of the Müller process, failed to achieve Courtauld's level of first quality and was bought out in 1911 by Vereinigte Glanzstoff-Fabriken, the leading producer of cuprammonium silk.

That they too appreciated the superiority of the viscose route, simply underlines the fact that by 1910, viscose was emerging as the winning fibre process. Viscose yarn output may only have been a third of the cellulose nitrate production and a half of the cuprammonium output, but technology and economics were now clearly in its favour. VGF had, in 1908–1910, set up a British cuprammonium plant at Flint on the River Dee to protect

their rights to operate the cupro patents in Britain. While at the time Courtauld did not feel this a significant threat, the VGF acquisition of the Donnersmarck viscose process a year later sounded the alarms. In 1911, Courtauld informed VGF they would be prepared to reach a 'general understanding between the makers of cuprammonium and viscose artificial silks.'

The outcome was a consortium of three groups, a German Group (VGF, Austrian Glanzstoff and Donnersmarck, an Anglo-American Group (Samuel Courtauld and Co, The American Viscose Company, and British Glanzstoff at Flint) and a Latin Group (The French, Italian, Belgian, Swiss and Spanish companies). All technology was to be shared, prices fixed, production quotas allotted, and each group would sell yarn only in its own area. While this 'protocol' was signed and put into effect at the end of 1911, it was never converted into a formal contract. It was nevertheless observed in principle if not in detail and provided some marketing consistency and stability at a crucial time. It also allowed faster technical progress by sharing rather than restricting access to innovations, it kept prices high, and it did not prevent the leading exponent, Courtauld, from obtaining even higher prices than its competitors. Only Courtauld had silk weaving know-how allowing them to open up the woven fabric market with a yarn quality the other consortium members could not match (see Chapter 9: Applications development).

The extraordinary success of Courtauld's venture is illustrated in Fig. 1.4 and 1.5.

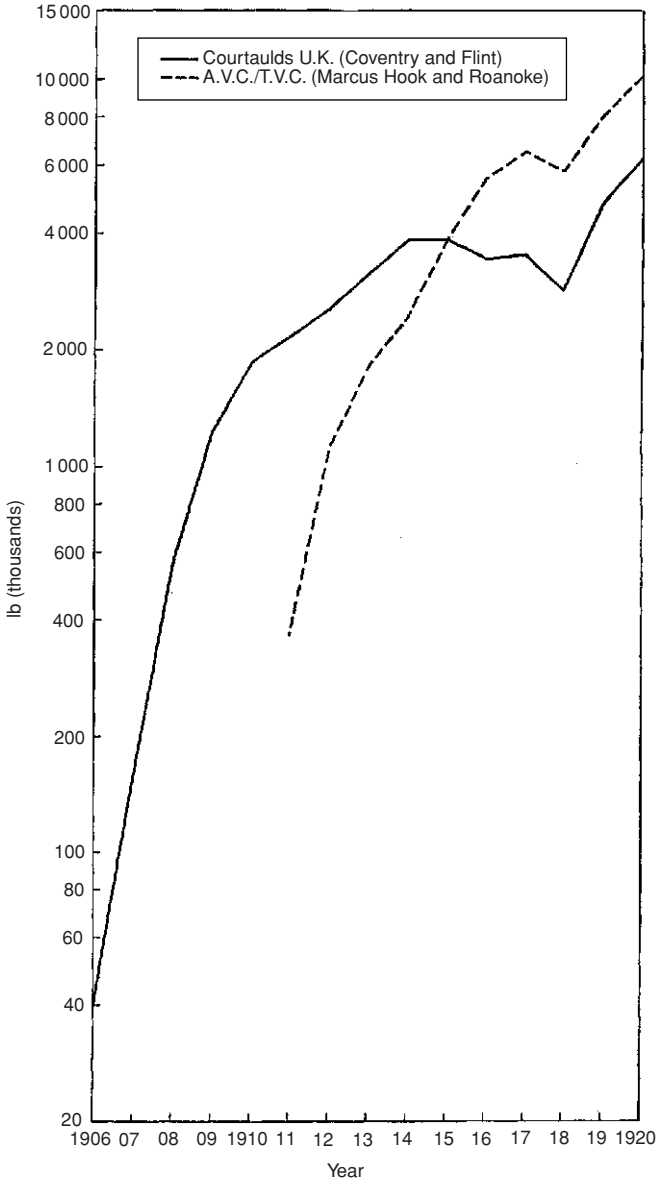
From 1920 to 1931, after the expiry of the viscose patents, world output increased from 14 000 to 225 000 tonnes per year, as more than 100 companies entered the artificial fibre field. In Europe, VGF (Germany), Enka (Holland), I G Farben (Germany), Snia Viscosa (Italy), Comptoir des Textiles Artificiels (CTA – France), Rhodiaceta (France), Tubize (Belgium) and Chatillon (Italy) were among the new starters.

In the USA the new entrants included DuPont (with help from CTA), Tubize, Chatillon, American Enka, The Industrial Fiber Corporation (later The Industrial Rayon Corporation), American Glanzstoff (later North American Rayon) and American Bemberg.

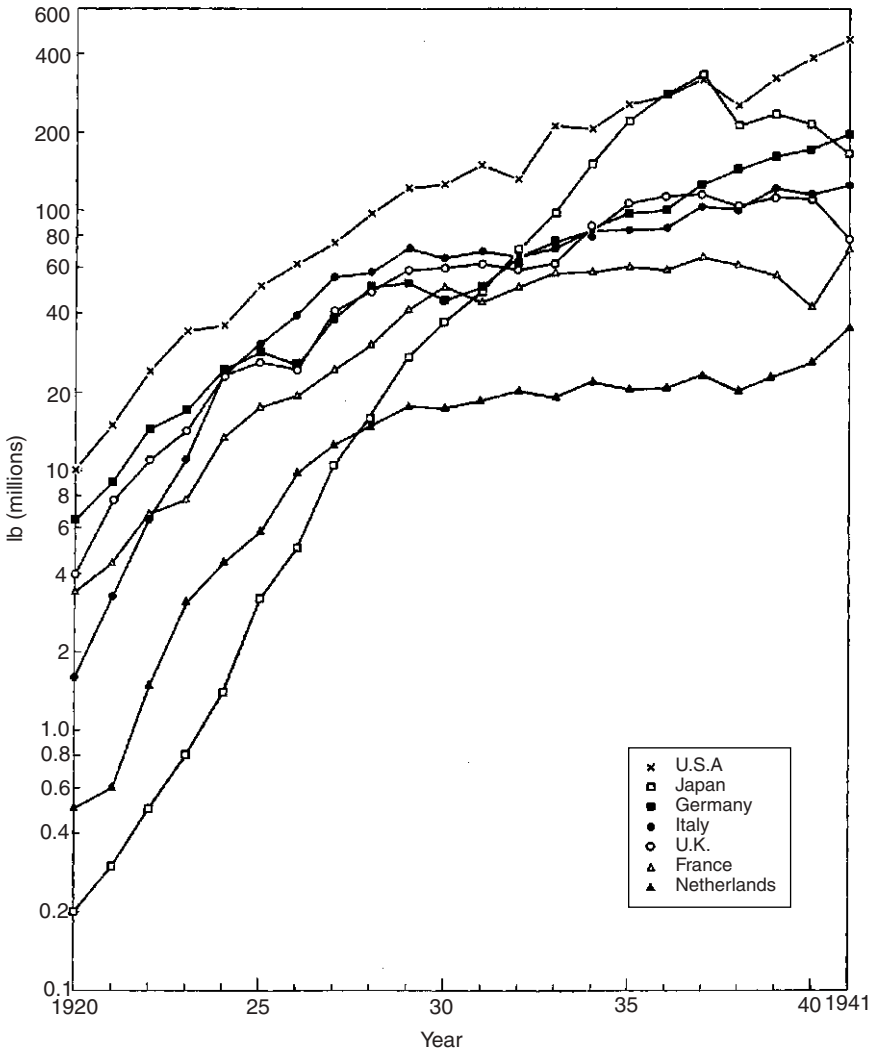
By 1939 Courtauld had six factories in the USA, seven in the UK, one in France, one in Canada, and joint ventures in Germany and Italy.

From the 1920s onwards, sales grew explosively, but the rayon process evolved in a more or less predictable manner. Discoveries enabling the production of stronger yarns led to the development of the tyre-yarn process and, driven by the war and a massive expansion in automobile use in the 1940s and 1950s, this technology boomed.

The introduction of staple fibre, which could be converted on traditional textile spinning equipment, was crucial to continued expansion in the 1930s



1.4 Growth of Courtauld's viscose filament yarn output: 1906–1920. The 1911 American investment (American Viscose Corporation/The Viscose Company) rapidly overtakes UK output. Despite the viscose success, in 1911 cellulose nitrate was still the world's leading fibre with a 40% share, viscose and cuprammonium yards having 30% each. (Reproduced from *Courtaulds: An Economic and Social History*, Clarendon Press, 1969.)¹¹



1.5 Regenerated cellulose filament yarns: 1920–1941. Expiry of the key viscose patents allows global growth. (Reproduced from *Courtaulds: An Economic and Social History*, Clarendon Press, 1969.)¹¹

but did not involve any startling innovations. However, what had been devised as a route for getting extra value out of yarn waste (chopping it into short lengths and selling it to cotton spinners as a cotton diluent) ultimately outsold the original continuous filament yarns and resulted in many new factories being built in the 1950s and 1960s. Staple fibre is dealt with in Chapter 9: Applications development.

By 1941 as the first synthetic polymers were being converted into the first nylon and polyester fibres, world production of viscose rayon had risen to 1250000 tonnes.¹⁸ It continued to expand into the 1970s recording its highest ever annual output at 3856000 tonnes in 1973. Since then a steady decline has occurred as more and more end-uses switch to the now cheaper synthetic fibres based on oil.

Also in 1973, the century's leading exponent of viscose technology, Courtaulds, who, since the late 1960s had realised that the end was near for viscose, began to explore new ways of converting cellulose into fibre. This is our next subject.

The current position of regenerated fibres in the market and a complete listing of the world's regenerated cellulose fibre plants at the close of the 20th century is given in Chapter 10.

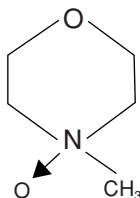
1.5 Direct dissolution in amine oxide: lyocell

Lyocell technology was pioneered in the USA by Eastman Kodak and American Enka, but it was Courtaulds in the UK who persisted with development until a commercially viable fibre process emerged. Furthermore, Courtaulds did it at a time in its history when the very wisdom of continued involvement, not just in cellulose but in any fibre or textile activity, was being called into question.

As early as the mid-1950s, Courtaulds believed the future of viscose to be so unattractive that it started to divert viscose profits not only into other fibres, but also into totally unrelated businesses.

By the late 1950s, despite accounting for 80–90% of Courtaulds earnings, the reality of viscose's decline was becoming apparent. The usual remedies, reducing costs, improving quality, selling more aggressively and internationally were yielding diminishing returns so the board's reaction was a new strategy¹⁹ involving:

- 1 developing new internal sources of profit, i.e. utilising the viscose wet-spinning expertise to move into wet-spun acrylic fibres ('Courtelle'), and opening up a vast, and with hind-sight, transient, new market for a coarse and tough viscose in tufted carpets ('Evlan')
- 2 developing new external sources of profit by acquisitions in 'related but different' products, in reality British Celanese (cellulose acetate fibres and related products) and Pinchin Johnson Paints (later renamed International Paint)
- 3 developing greater market power by acquiring key elements of the rest of the fibre value-chain – 'Verticalisation' – resulting most notably in the acquisition of the Lancashire Cotton Corporation Ltd and Fine Spinners and Doublers (representing about 35% of the entire Lancashire cotton industry).



1.6 Structure of *N*-methyl morpholine *N*-oxide.

Of these three, (1) was least favoured with funds. Furthermore, little emphasis was placed on modernisation* of regenerated cellulose fibre production methods to counteract the intertwined problems of synthetic fibre expansions, rising costs and diminishing returns. The demise of viscose thus became a self-fulfilling prophecy. The leading exponent of the technology turned its back on cellulose at a crucial time in its history, a time in fact when new ways of dissolving cellulose were already evident in the research work of other organisations.

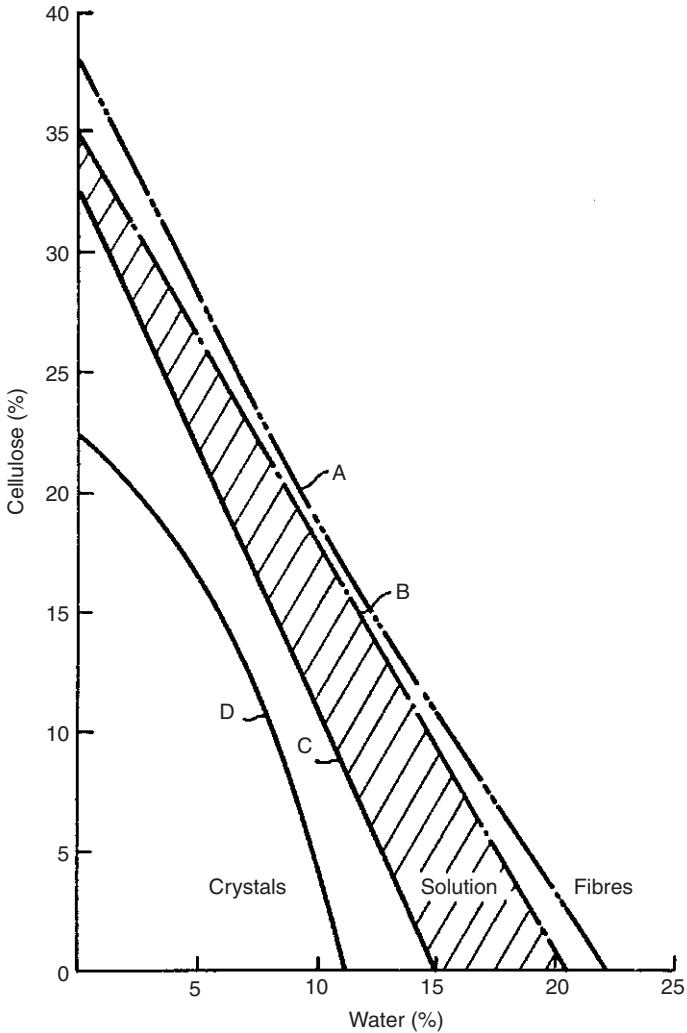
Reviews of this early work on direct dissolution are provided by Turbak^{20,21} who, in Chapter 7 of this volume, records the efforts to dissolve cellulose directly as a *base* using phosphoric, sulphuric and nitric ‘protonic’ acids, or using zinc chloride, thiocyanates, iodides, and bromides as Lewis acids. However, despite early promise, the problems of developing fibre production routes using these systems have, with the single exception of the amine–oxide route, so far proved insurmountable.

The amine–oxide solvent, later to become the focus of Courtauld’s most costly development project, and the most acrimonious patent battle since the dispute over the Müller bath in 1910, had in fact been discovered back in 1939 by a pair of Swiss chemists, Charles Graenacher and Richard Sallman.²² But it was not until 1969 that Dee Lynn Johnson of Eastman Kodak described the use of cyclic mono(*N*-methylamine-*N*-oxide) compounds (e.g. NMMO: see Fig. 1.6) as a solvent-size for strengthening paper²³ by partially dissolving the cellulose fibres.

Other Johnson patents^{24,25} covered the preparation of cellulose solutions using NMMO and speculated about their use as dialysis membranes, food casings (sausage skins), fibres, films, paper coatings, and nonwoven binders.

NMMO emerged as the best of the amine–oxides and a team at American Enka demonstrated its commercial potential in the late 1970s. In their laboratories in Enka, North Carolina, Neil Franks and Julianna Varga,^{26,27} developed a way of making a more concentrated, and hence

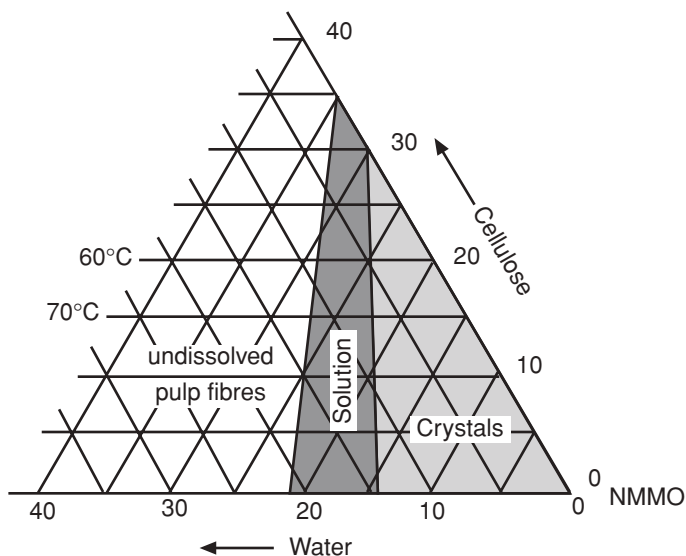
* Projects described as ‘modernisation’ were in fact common, but their scope was restricted largely to taking cost out of viscose dope making, often with losses of quality, by automating the original process.



1.7 Dissolving cellulose in NMMO and water mixtures. (Reproduced from *USP 4 196 282*.)²⁷

economical, solution of cellulose, by carefully controlling the water content of the system.

Figure 1.7 shows that the concentrations of water and cellulose where complete dissolution of the cellulose occurs (at 95°C), lie between lines B and C. Between lines A and B there can be 95% confidence that the solution would be free from undissolved cellulose fibres, and to the right of line A, undissolved cellulose fibres are bound to be present. Similarly,

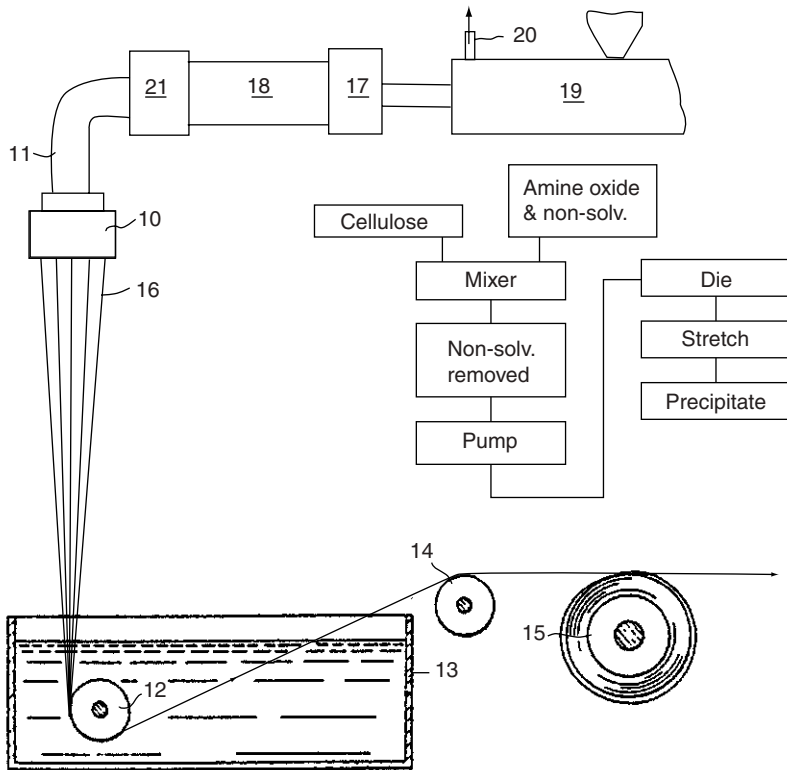


1.8 Ternary diagram showing the effect of temperature on the dissolution of cellulose in NMMO. (Reproduced from Spinnable solutions of cellulose in amine oxides, R N Armstrong, C C McCorsley and J K Varga, *Proceedings of the 5th International Dissolving Pulp Conference*, TAPPI, 1980.)³²

between C and D there is a 95% chance that crystals of undissolved NMMO will be present, and such crystals will always be present to the left of line D. Figure 1.8 shows the same information in the more familiar ternary diagram form.

Clarence C McCorsley III, also at Enka, developed the key elements of several possible commercial processes. In one, cellulose pulp sheets were soaked in NMMO solution, and after mild heat and vacuum treatment to adjust the water content, the ground-up sheet was fed to an extruder from which fibres could be spun.²⁸ In another, the solution was made in a large mixer prior to casting it as thick film, freezing it solid, and grinding it up into chips for later extrusion.²⁹ In a continuous process (Fig. 1.9), a vented extruder fed directly with the ground-up wood pulp and NMMO, mixes the ingredients, creates the solution by removing excess water and volatiles through the vent, and feeds the spinning pumps.^{30,31}

Both American Enka³² and Courtaulds set up pilot plant work in the early 1980s with the objectives of developing the fibre spinning and solvent recovery operations. Courtaulds commercialised first and this, and the continuing development of lyocell is dealt with by White (Chapter 4), who from the outset of practical work in 1979, led the lyocell development effort at Courtaulds.



1.9 Clarence McCorsley's lyocell spinning system c. 1979: Dope (containing 15–20% cellulose and at about 115°C) in the extruder barrel (19) is forced through a filter (17), a static mixer (18) to a metering pump (21) and on to the spinneret (10). Filaments (16) pass through an air gap into water in tank 13.

American Enka decided not to commercialise the process and stopped the research in 1981, probably because at that time engineering issues associated with the difficulty of avoiding exothermic reactions looked too hard to resolve economically. However when Courtaulds had demonstrated practical solutions to the many problems discovered during American Enka's early work, they (Enka that is, now part of Akzo Nobel) re-entered the field with the continuous filament version of the lyocell process under their brand name 'Newcell'. The Akzo deal with Courtaulds involved their gaining access to Courtaulds' technology in exchange for granting Courtaulds rights to use some of the key steps in the early patents mentioned above.

Coming right up to date, Akzo Nobel acquired Courtaulds in 1998, and formed Acordis Fibres, bringing together in one company all the key lyocell

technology. However, Akzo Nobel had earlier granted a lyocell licence to Lenzing, the Austrian viscose fibre maker, allowing Lenzing to enter the field with a very similar process to Courtaulds. The ensuing patent litigation between Lenzing and Courtaulds was to prove costly to both companies.

Lenzing obtained a patent in the USA for a process, some aspects of which had been operated by Courtaulds for many years, and indeed were used in production at Courtaulds Tencel® plant in Mobile. Courtaulds naturally objected, and applied for summary dismissal of both the US and the subsequent European patent. In Europe, the Munich court would not allow the Lenzing patent to be dismissed summarily and the case went to trial. Courtaulds won, and Lenzing's European patent was disallowed with no right of appeal. In the USA, the Lenzing patent was summarily dismissed, but Lenzing appealed successfully, winning the right to another costly trial. At this point the two companies reached a settlement out of court. The lyocell patent estates of both companies were pooled, to be available royalty free to both companies. It is perhaps worth noting that the settlement only covered patented technology. There was to be no sharing of 'know-how' gained in the operation of the process, which at the time, had only been commercialised by Courtaulds.

1.6 Other routes

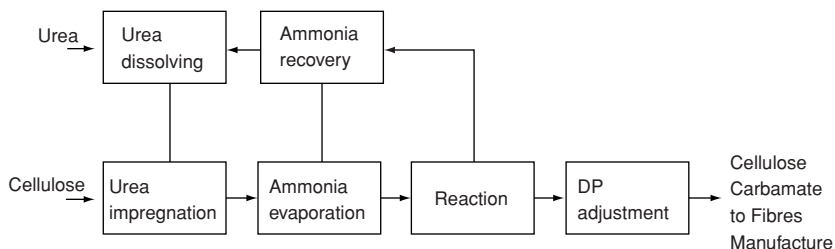
Work on other routes to cellulosic fibres has continued, in some cases driven by a desire to utilise the large capital investment in the xanthate route and hence cost less than a completely new fibre process.

The Finnish viscose producer Kemira Oy Saeteri collaborated with Neste Oy on the development of a carbamate derivative route. This system was based on the original work of Hill and Jacobsen³³ who showed that the reaction between cellulose and urea gave a derivative which was easily dissolved in dilute sodium hydroxide:



Neste patented an industrial route to a cellulose carbamate pulp³⁴ which was stable enough to be shipped into rayon plants for dissolution as if it were xanthate. The carbamate solution could be spun into sulphuric acid or sodium carbonate solutions, to give fibres which, when completely regenerated, had similar properties to viscose rayon. When incompletely regenerated they were sufficiently self-bonding for use in papermaking. The process was said to be cheaper than the viscose route and to have a lower environmental impact (Fig. 1.10).³⁵ It has not been commercialised, so no confirmation of its potential is yet available.

Chen, working on a small scale at Purdue University, claims that



1.10 Manufacture of cellulose carbamate pulp for spinning on viscose equipment. (Reproduced from *Cellulose Carbamate* PIRA International Conference, 1987).³⁵

solutions containing 10–15% cellulose in 55–80% aqueous zinc chloride can be spun into alcohol or acetone baths to give fibres with strengths of 1.5–2 g den⁻¹. However, if these fibres were strain dried (i.e. stretched) and rewetted whilst under strain, strengths of 5.2 g den⁻¹ were achieved.³⁶

Kamide (see also Chapter 5 on cuprammonium rayon) and co-workers at Asahi have been applying the steam explosion³⁷ treatment to dissolving pulp to make it dissolve directly in sodium hydroxide.³⁸ In technical papers,³⁹ they claimed a solution of 5% of steam-exploded cellulose in 9.1% NaOH at 4°C being spun into 20% H₂SO₄ at 5°C. The apparently poor fibre properties (best results being 1.8 g den⁻¹ tenacity dry, with 7.3% extension) probably arise because the fibres were syringe extruded at 75 den per fil. Asahi felt at the time that this would be the ultimate process for large scale production of regenerated cellulose fibres but in reality its use appears to be confined to the production of thickeners.

Chanzy, Peguy and co-workers at the Plant Macromolecules Research Centre (CERMAV-CNRS) in Grenoble studied the cellulose/NMMO system in depth;⁴⁰ one paper indicates that further strength increases can be obtained by adding ammonium chloride or calcium chloride to the dope.⁴¹

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