

## FIBERS, REGENERATED CELLULOSE

### 1. Introduction

Cellulose is the natural polymer that makes up the living cells of all vegetation. It is the material at the center of the carbon cycle, and the most abundant and renewable biopolymer on the planet. Regenerated cellulose fiber producers have converted it from the fine short fibers that come from trees into the fine long fibers used in textiles and nonwovens for over a century. Regenerated cellulose fibers nevertheless remain unique among the mass-produced fibers because they are the only ones to use the natural polymer *directly*. Polyesters, nylons, polyolefins, and acrylics all come *indirectly* from vegetation: from the polymerization of

monomers obtained from fossil fuels, which in turn are formed by the incomplete biodegradation of vegetation that grew millions of years ago.

The development of manufactured fibers is one of the great industrial successes of the twentieth century, but after 50 years of explosive growth of the original regenerated cellulosic fibers, synthetic polymer fibers now dominate the market. Natural cellulose in the form of cotton, for centuries the most important of all fibers, now takes second place to polyester. All cellulosic fibers appear relegated to little more than niches in a global textile market driven by the ready availability of cheap fossil fuels and the demand for commodity textiles. Is this relative decline of cellulose and regenerated cellulose just another example of the last stage of the growth/maturity/decline life cycle of most products or is there a possibility that, on a longer timescale, sustainable biopolymers like cellulose will prove to be a serious rival for the synthetics?

Fibers manufactured from cellulose are either *derivative* or *regenerated*. A *derivative fiber* is one formed when a chemical derivative of a natural polymer, eg, cellulose, is prepared, dissolved, and extruded as a continuous filament, and the chemical nature of the derivative is retained after the fiber formation process (see CELLULOSE ESTERS, INORGANIC). A *regenerated fiber* is one formed when a natural polymer or its chemical derivative is dissolved and extruded and the chemical nature of the natural polymer is either retained or regenerated after the fiber formation process. The difficulties of making solutions of natural cellulose from which fibers can be spun has led to most fabricated cellulosic fibers being regenerated from more readily soluble derivatives of cellulose.

Originally, the word rayon was applied to any cellulose-based manufactured fiber, and therefore included the cellulose acetate fibers. However, the definition of rayon was clarified in 1951 and now includes textiles fibers and filaments composed of regenerated cellulose, excluding acetate. In Europe the fibers are now generally known as *viscose*, the term *viscose rayon* being used whenever confusion between the fiber and the cellulose xanthate solution (also called viscose—see below) is possible. (In this article the terms *regenerated cellulosics*, *rayon*, and *viscose rayon* tend to be used interchangeably.)

All synthetic fibers are produced as continuous filaments, either as yarns or tows. Yarns are fine enough to be woven or knitted directly, but cannot be intimately blended with other fibers on the principal conversion systems used for cotton and wool. For these conversion systems, staple fibers, made by cutting the much larger tows into short lengths, are needed. Tows can also be stretch-broken into slivers or tops, which can then be drawn out and twisted into spun yarns.

Denier and tex are both weight/length measures of fiber fineness: denier is the weight in grams of 9000 m of filament, yarn, or tow; tex is the weight in grams of 1000 m. For filaments, as opposed to tows or yarns, the decitex tends to be used as the measure of fineness, 1 denier being equivalent to 1.11 decitex. Filament strengths are measured in gram force/denier (gf/den) or in centiNewtons/tex (cN/tex): 1 gf/den is equivalent to 8.82 cN/tex. Occasionally, the strength of filaments is seen expressed as N/mm<sup>2</sup> to allow comparison with engineering materials. One N/mm<sup>2</sup> is equivalent to the strength in gf/den  $\times 9 \times 9.807 \times$  the fiber specific gravity. For cellulose, the specific gravity = 1.51, so N/mm<sup>2</sup> = gf/den  $\times 133.277$ .

## 2. History

The first successful attempt to make textile fibers from plant cellulose can be traced to George Audemars (1). In 1855 he dissolved the nitrated form of cellulose in ether and alcohol and discovered that fibers were formed as the dope was drawn into the air. These soft, strong nitrocellulose fibers could be woven into fabrics but had a serious drawback: they were explosive, nitrated cellulose being the basis of guncotton (see CELLULOSE ESTERS, INORGANIC).

Sir Joseph Swan, as a result of his quest for carbon fiber for lamp filaments (2), learned how to denitrate nitrocellulose using ammonium sulfide. In 1885 he exhibited the first textiles made from this new artificial silk, but with carbon fiber being his main theme he failed to follow up on the textile possibilities. Meanwhile Count Hilaire de Chardonnet (3) was researching the nitrocellulose route and had perfected his first fibers and textiles in time for the Paris Exhibition in 1889. There he got the necessary financial backing for the first Chardonnet silk factory in Besancon in 1890. His process involved treating mulberry leaves with nitric and sulfuric acids to form cellulose nitrate, which could be dissolved in ether and alcohol. This collodion solution could be extruded through holes in a spinneret into warm air, where solvent evaporation led to the formation of solid cellulose nitrate filaments.

Although this first route was simple in concept, it proved slow in operation, difficult to scale up safely, and relatively uneconomical compared with the other routes. Denitration of the fibers, necessary to allow safe use wherever the fabrics may risk ignition, spoiled 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 United States in 1934 by a Brazilian company—burned down.

The second cellulosic fiber process to be commercialized was invented by L. H. Despeissis (4) in 1890 and involved the direct dissolution of cotton fiber in ammoniacal copper oxide liquor. This solvent had been developed by M. E. Schweizer in 1857 (5). The cuprammonium solution of cellulose was spun into water, with dilute sulfuric acid being used to neutralize the ammonia and precipitate the cellulose fibers. H. Pauly and co-workers (6) improved on the Despeissis patent, and a German company, Vereinigte Glanstoff Fabriken, was formed that exploited the technology. In 1901, Dr. Thiele at J. P. Bemberg developed an improved stretch-spinning system, the descendants of which survive today.

Its early commercial success owed much to the flammability disadvantages of the Chardonnet process, but competition from the viscose process led to its decline for all but the finest filament products. The process is still used, most notably by Asahi in Japan, where sales of artificial silk and medical disposable fabrics provide a worthwhile income. However, its relatively high cost, associated with the cotton fiber starting point, prevented it from reaching the large scale of manufacture achieved by the viscose rayon process.

In 1891, Cross, Bevan, and Beadle, working at Kew in the United Kingdom, discovered that cotton or wood cellulose could be dissolved as cellulose xanthate following treatment with alkali and carbon disulfide (7). The treacle-like yellow

solution could be coagulated in an ammonium sulfate bath and then converted back to pure white cellulose using dilute sulfuric acid. They patented their process in 1892 without considering its fiber-making potential. In 1893 they formed the Viscose Syndicate, to grant licenses for nonfiber end uses, and the British Viscoid Co. Ltd., to exploit the process as a route to molded materials. These companies were later merged to form the Viscose Development Co. in 1902.

In another laboratory at Kew, C. H. Stearn and C. F. Topham, who had worked for Sir Joseph Swan on lamp filaments, developed the continuous filament spinning process (8) and the machinery needed to wash and collect (9,10) the yarns. A fiber-making method was outlined in 1898, and the Viscose Spinning Syndicate was formed to develop the concept into a commercial proposition.

In 1904, the Kew laboratories were visited by representatives of Samuel Courtauld & Co. Ltd., who 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 nineteenth-century fashion for black silk mourning crepe, and the company was planning its stock market flotation. The visitors to Kew knew that Chardonnet's process was creating a lucrative market for artificial silk in France. They believed that Cross and Bevan's viscose route could make a similar fiber much more economically. Nevertheless, it took two attempts, the second to a changed Board of Directors after the flotation, before Courtaulds was persuaded to acquire the viscose process rights. On July 14, 1904, the Viscose Spinning Syndicate agreed to sell the viscose process rights and patents to Courtaulds for the sum of £25,000. A new factory was built and the first commercial production was started in Coventry, United Kingdom, in November 1905.

The acquisition of the rights to the viscose process became one of the most profitable investments of all time. Interest in the new fiber was intense, and growth of production capacity was exponential. By 1907, the Courtauld company was selling all the artificial silk it could produce and proceeded to expand into the U.S. market. In 1910 they formed the American Viscose Co. and in 1911 started the first U.S. viscose factory at Marcus Hook. By 1939, Courtaulds had six factories in the United States, seven in the United Kingdom, one in France, one in Canada, and joint ventures in Germany and Italy.

From 1920 to 1931, after the expiration of the viscose patents, world output increased from 14,000 to 225,000 t per year, as more than 100 companies entered the cellulose fiber field. In Europe, Vereinigte Glanzstoff Fabriken (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 United States the new entrants included Du Pont (with help from CTA), Tubize, Chatillon, American Enka, The Industrial Fiber Corp. (later The Industrial Rayon Corp.), American Glanzstoff (later North American Rayon), and American Bemberg.

By 1941, as the first synthetic polymers were being converted into fibers (nylon and later polyester), regenerated cellulosic fiber production had risen to 1,250,000 ton. It continued to expand into the 1970s recording its highest ever annual output at 3,856,000 ton in 1973. Since then a steady decline has occurred

as more and more end uses switch to the cheaper synthetic fibers based on oil valued at little more than the costs of extraction.

### 3. Applications

The original yarns were marketed as silk substitutes for use in apparel, hosiery, lace, home furnishings, ribbons, braids, and in a whole range of fabrics using blends with cotton or wool yarns. As the end uses expanded beyond silk replacement, the harsh metallic luster of the yarn proved disadvantageous, and dull "matt" fibers had to be developed. Oil dulling was invented (11) in 1926, and an improved method using titanium dioxide was developed (12) in 1929.

Commencing in the late 1930s, new developments to make very strong yarns allowed the viscose rayon to replace cotton as the fiber of choice for longer-life pneumatic tires. The pace of this line of development increased during World War II, and by the 1960s a significant part of the production of viscose yarn was for tires and industrial applications.

From 1910 onward waste filament yarn had been chopped into short lengths suitable for use on the machinery designed to process cotton and wool staples into spun yarns. In the 1930s new plants were built specifically to supply the staple fiber markets. During World War II the production of staple matched that of filament, and by 1950, staple viscose was the most important product. The new spun-yarn outlets spawned a series of viscose developments aimed at matching the characteristics of wool and cotton more closely. Viscose rayon was, after all, silk-like. Compared with wool it lacked bulk, resilience, and abrasion resistance. Compared with cotton, it was weaker, tended to shrink and crease more easily, and had a rather lean, limp hand.

For wool outlets, coarser crimped staple fibers were developed. By the late 1960s these were widely used in the new tufted carpets, which for a period became the single largest application for the cellulosic fiber. For cotton outlets, two distinct lines of development were undertaken, the first being to boost the strength and modulus of rayon so that it could match that of cotton, and the second to alter the shape of the fiber to give bulkier, more cotton-like textures. High wet modulus (HWM) rayons of two types were developed. Staple versions of the tougher tire-yarn fibers (modal HWM fibers) were introduced for use in industrial textiles, and for blending with the rapidly growing synthetics. This class was later subdivided into the low, intermediate, and high strength variants (LWM, IWM, and HWM) as producers tuned the process to market niches. Polynosic HWM fibers with even better wet stability and higher wet modulus were introduced to blend with the better grades of cotton.

In the 1960s and 1970s, viscose producers in Europe, the United States, and Japan made various attempts to make rayon behave more like cotton in both woven fabrics and specialty papers. Avtex (U.S.) and Kurashiki Rayon (Japan) commercialized inflated-collapsed paper-making fibers. Courtaulds (U.K.) developed a range of hollow fibers, of which two were commercialized. The first, having an uncollapsed tubular shape, found worthwhile new business in thermal underwear. The other, having an unevenly collapsed tube shape and a very high absorbency, enjoyed large sales in sanitary protection products. These

hollow fibers were replaced in the late 1980s by I- and Y- shaped solid fibers that performed as well as the hollow versions in the main applications.

#### 4. The Viscose Process

The main raw material required for the production of viscose is cellulose, a natural polymer of D-glucose (Fig. 1). The repeating monomer unit is a pair of anhydroglucose units (AGU). Cellulose and starch (qv) are identical but for the way in which the ring oxygen atoms alternate from side to side of the polymer chain (beta linkages) in cellulose, but remain on the same side (alpha linkages) in starch.

Cellulose is the most abundant polymer, an estimated  $10^{11}$  t being produced annually by natural processes. Supplies for the rayon industry can be obtained from many sources; but in practice, the wood-pulping processes used to supply the needs of the paper and board industries have been adapted to make the necessary specially pure grade. Of the  $3 \times 10^8$  t of wood used by the paper and board industry (13) in 1989, about  $6 \times 10^6$  t were purified to provide the  $2.5 \times 10^6$  t of dissolving pulp required by the viscose processes.

The trees used to make dissolving pulp are fast-growing hard or soft woods farmed specifically for their high quality pulping. For example, *Eucalyptus grandis* is farmed in relatively poor agricultural areas but grows from seedling to maturity in 7–10 years. It yields about  $0.62 \text{ kg/m}^2$  (2500 kg/acre) per year of cellulose for fiber-making, compared with the best cotton fiber yields of  $0.074 \text{ kg/m}^2$  (300 kg/acre) per year obtained from prime agricultural land. After sulfite or prehydrolyzed Kraft pulping, the cellulose wood fibers, liberated from the lignin, pass through a sequence of purification stages, eg, chlorination; hot caustic extraction; hypochlorite, peroxide or chlorine dioxide bleaching; and cold caustic extraction.

The final properties of the rayon fiber and the efficiency of its manufacturing process depend crucially on the purity of the pulp used. High tenacity fibers need high purity pulps, and this means pulping to get up to 96% of the most desirable form of cellulose (known as alpha cellulose), and removing most of the unwanted hemicellulose and lignin. Cellulose molecular weight must be tightly controlled, and levels of foreign matter such as resin, knots, shives, and silica must be very low. Of the two main pulping processes, the sulfite route produces higher yields of lower alpha, more reactive pulp, suitable for regular staple fiber. Prehydrolyzed kraft pulps are preferred for high strength industrial yarn or modal fiber production. The highest purity pulps, up to 99% alpha

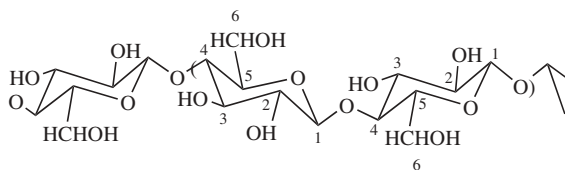
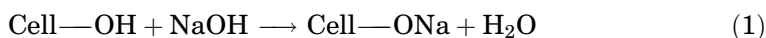


Fig. 1. Anhydroglucose units with 1–4 beta linkages as in cellulose.

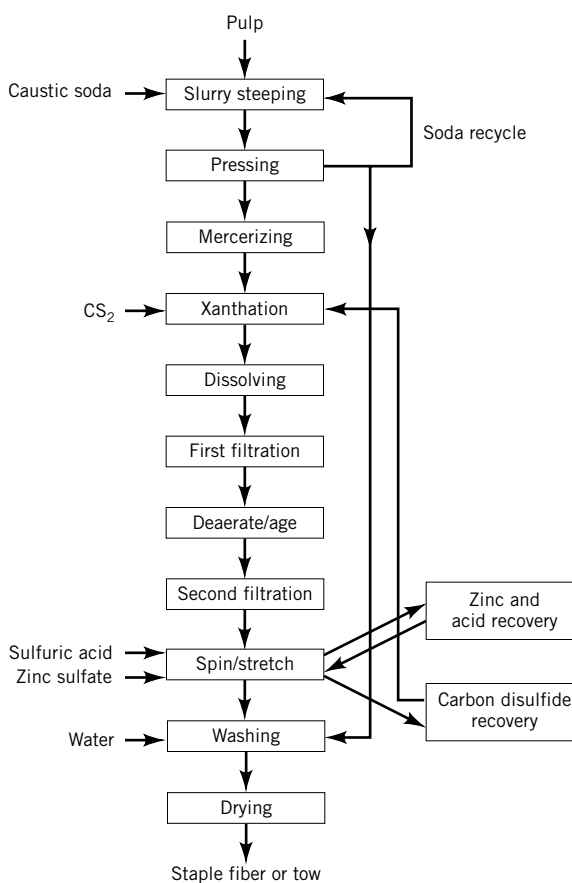
cellulose, are obtained from cotton fiber. These are no longer used in viscose production but are now the main raw material for cuprammonium rayon.

The flow diagram for the viscose process is given in Figure 2. The sequence of reactions necessary to convert cellulose into its xanthate and dissolve it in soda used to be performed batchwise. Fully continuous processes, or mixtures of batch and continuous process stages, are more appropriate for high volume regular viscose staple production.

**4.1. Steeping.** Sheet, roll, or suitably milled flock pulp is metered into a pulper along with vigorously stirred 18% sodium hydroxide solution at 50°C. The resulting slurry, containing about 5% finely dispersed pulp, passes to a buffer tank from which it is metered to a slurry press that sieves out the swollen fiber and returns the pressings soda for concentration correction and reuse. The cellulose reacts with the soda as a complex alcohol to form the sodium salt or alk-cell.



The blanket of alk-cell leaving the slurry press is shredded, and if necessary cooled, before being conveyed to mercerizing (the ripening or aging process).



**Fig. 2.** The viscose process.

Hemicelluloses left over from the cellulose pulping process tend to accumulate in the steep soda, and levels of up to 3.0% are tolerable, depending on the type of fiber being produced. Equilibrium hemicellulose levels may prove to be too high for the production of stronger fibers, and in this case steps must be taken to purify the soda, eg, by dialysis, prior to reuse. In any case a proportion of the soda from the presses is filtered for later use in dissolving and washing; the steep liquor itself is corrected to the required concentration by the addition of fresh hemicellulose-free strong soda.

**4.2. Mercerizing.** Alk-cell mercerizing (or aging) is ideally carried out on a conveyor belt running through a temperature-and humidity-controlled tunnel. Towers, silos, cylinders, or even extended treatment in shredders are used as alternatives to belts. During mercerizing, oxidative depolymerization of the cellulose occurs, and this reduces the molecular weight to a level where the final viscose viscosity and cellulose concentration are within acceptable ranges. The optimum conditions for a given pulp depend on the details of the equipment and the cost-quality balance required by the business. The aging temperature is generally around 50°C, and the humidity is adjusted to prevent any drying of the alk-cell. Catalysts such as manganese (a few parts per million in steep liquor) or cobalt have been added to the steep soda to accelerate the aging process (14) or to allow lower temperatures to be used. Catalyzed aging on a conveyor takes 3–4 h, and at the end of the belt, the alk-cell is blown or conveyed to a fluid-bed cooler.

Whatever system is used, tight control of the aging process is essential for good quality viscose solutions, because the viscosity of the viscose depends on it. Varying viscosity can play havoc with all subsequent operations up to and including spinning. Productivity gains achieved by high-temperature or catalyzed aging tend to be accompanied by increased viscosity variability and reduced reactivity in xanthation.

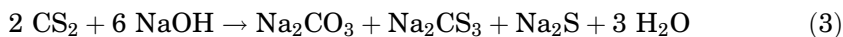
**4.3. Xanthation.** The viscose process is based on the ready solubility of the xanthate derivative of cellulose in dilute sodium hydroxide. The reaction between alkali cellulose and carbon disulfide must therefore be as uniform as possible to avoid problems with incompletely dissolved pulp fibers that will later have to be filtered out of the viscous solution.

In theory, for regular rayon manufacture only one of the hydroxyl groups on each pair of anhydroglucose units needs to be replaced by a xanthate group, ie, the target degree of substitution (DS) is 0.5, which to achieve without waste would need 23% CS<sub>2</sub> on cellulose.

The desired reaction is



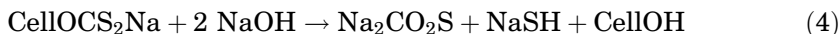
but side reactions between the CS<sub>2</sub> and the NaOH also occur, one of which is



It is the sodium trithiocarbonate from this side reaction that gives the viscose dope its characteristic orange color.



In addition to the cellulose xanthate [9032-37-5] forming reaction, equation 2 being reversible, cellulose can reform by



Clearly, free sodium hydroxide in alkali cellulose leaving the slurry presses causes problems in xanthation, and the presses have to be operated to minimize reactions 3 and 4.

Carbon disulfide [75-15-0] is a clear colorless liquid that boils at 46°C, and should ideally be free of hydrogen sulfide and carbonyl sulfide. The reaction with alkali cellulose is carried out either in a few large cylindrical vessels known as wet churns, or in many smaller hexagonal vessels known as dry churns. In the fully continuous viscose process, a Continuous Belt Xanthator, first developed by Du Pont, is used (15).

In a large wet churn operation, a weighed batch of alk-cell (5–10 t) is charged into the churn, which is then evacuated. Carbon disulfide (0.5–1 t) is admitted over a 20-min period and vaporizes in the partial vacuum. Churns are rotated slowly to encourage the solid–vapor interaction or they are stirred with a large slow-moving paddle. The reaction with alk-cell is slightly exothermic, and churns are generally cooled to maintain the temperature between 25 and 30°C. Under these conditions the xanthation reaction is completed in about 100 min and its progress can be monitored by observing the partial vacuum redeveloping as the gas is adsorbed by the solid.

About 25% of the CS<sub>2</sub> is wasted in side reactions (eg, eq. 3), and this means that to achieve the ideal 0.5 DS, the CS<sub>2</sub> charge is about 30% by weight of the cellulose. Higher charges (up to 50%) are needed for the strongest high wet modulus rayon production. Lower charges are possible if steps are taken to increase the reactivity of the alk-cell, or to suppress the undesirable side reactions, or to ensure that viscose filtration is good enough to cope with more undissolved material.

The incomplete accessibility of the cellulose molecules in alk-cell prevents complete xanthation, ie, the formation of the trixanthate, no matter how much CS<sub>2</sub> is used. The trixanthate would imply a DS of 3, sometimes known as a gamma value of 300 CS<sub>2</sub> groups per 100 AGUs. In practice, gamma values over 100 are hard to achieve in the churn, but levels up to 200 can be reached by a combination of churn addition and liquid CS<sub>2</sub> injection into the viscose where the cellulose accessibility is at its greatest. For regular staple production, gamma values tend to be around 50 at the churn and 30–35 at spinning.

At the end of xanthation, any remaining traces of CS<sub>2</sub> are flushed from the wet churn prior to, or in some cases by, admitting a charge of the dissolving or mixer soda in order to commence dissolution. For a dry churn operation, the vessel is opened to allow the golden xanthate crumbs to be discharged into a separate mixer.

**4.4. Dissolution.** Cellulose and its derivatives dissolve more easily in cold alkali than in hot, and the initial contact between cellulose xanthate and the mixer soda should occur at the lowest temperature possible. Two percent NaOH at no more than 10°C is admitted to the wet churn and the paddle speeded up to wet out all the crumb prior to discharge. Some of the required mixing soda

charge can be retained to wash out the churn before restarting the cycle. Discharge occurs, through cutters that eliminate any large lumps of agglomerated xanthate, into the batch tank where dissolution is completed. Here it is stirred for about 2 h to allow the xanthate to dissolve. The mixing conditions are crucial. High shear mixing certainly speeds up the process but can cause local heating, which can regenerate cellulose from the xanthate.

The final composition of the solution is controlled by the ratio of xanthate to mixer soda, the concentrations of cellulose and NaOH in the xanthate, and the concentration of NaOH in the mixer soda. For regular staple processes the cellulose/soda ratio is within the range 8.5:6.0 to 10.0:5.0, the latter tending to give lower quality viscose solutions. High quality textile yarns require a 7.5:6.5 ratio, whereas the strongest high wet modulus processes use a 6.0:6.0 ratio. Here lower cellulose concentrations are necessary to allow the use of higher molecular weights (less mercerizing), which allow higher strength development.

It is possible to add modifiers or delustrants at the dissolving stage. However, modern viscose dope plants feed several spinning machines, which are often expected to make different grades of fiber. It is therefore now more common to add the materials needed to make special fibers by injection close to the spinning machines.

**4.5. Viscose Aging, Filtration, and Deaeration.** After the dissolution step, the viscose cannot be spun into fibers because it contains many small air bubbles and particles. Furthermore, the degree of xanthation is too high, with too many of the xanthate groups in positions dictated by their accessibility and not in the ideal positions for uniform dissolution.

Dexanthation, and the redistribution of xanthate groups into the most favorable positions on the cellulose molecules, occurs automatically as the viscose ages. For regular staple fibers the process takes about 18 h, but for the stronger fibers, shorter times and more difficult spinning conditions have to be tolerated. During this aging process, eq. 2 goes into reverse and the xanthate groups attached to the 2- and 3- positions on the AGU (Fig. 1) hydrolyze 15–20 times as fast as those on C-6. Transxanthation occurs (16); the unoccupied C-6 hydroxyl competing with reaction 2 for the CS<sub>2</sub> that is leaving C-2 and C-3. The reactions favoring more spinnable viscose are in turn favored by aging for longer times at the lowest possible temperature. Cold viscoses are unfortunately much more viscous, and therefore harder to filter and deaerate.

Filtration of viscose is not a straightforward chemical engineering process. The solution of cellulose xanthate contains some easy-to-deal-with undissolved pulp fibers, and also some gel-like material that is retarded rather than removed by the filters. The viscose is unstable and tends to form more gel as it ages. Its flow characteristics make the material close to the walls of any vessel or pipe move more slowly, get older, and gel more than the mainstream viscose. So while filtration can hold back gels arising from incomplete mixing, new gels can form in the pipework after the filters.

The removal of particles that would block the spinneret holes occurs in several stages. The traditional plate-and-frame first-filters dressed with disposable multilayers chosen from woven cotton, cotton wadding, or wood pulp have now been replaced by durable nylon needlefelts that can be cleaned by automatic backwashing (17). Second filtration, usually after deaeration, is also changing

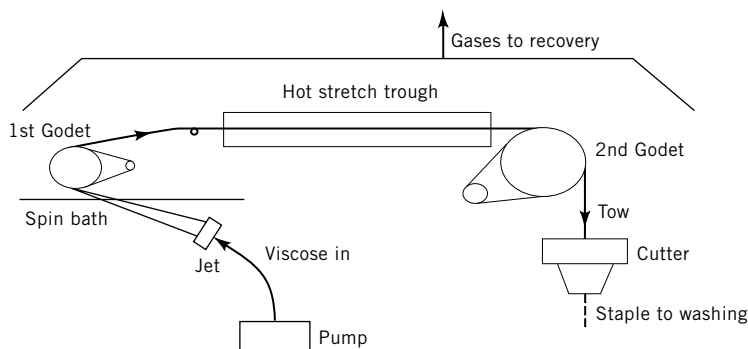
to fully automatic systems with sintered steel elements that do not need manual cleaning. Third-stage filtration, close to the spinning machines, is used to provide a final polishing of viscose quality, but is only justifiable for the premium quality fibers. All processes nevertheless use small filters in each spinneret to catch any particulate matter that may have eluded, or been formed after, the main filter systems.

Continuous deaeration occurs when the viscose is warmed and pumped into thin films over cones in a large vacuum tank. The combination of the thinness of the liquid film and the disruption caused by the boiling of volatile components allows the air to get out quickly. Loss of water and  $\text{CS}_2$  lower the gamma value and raise the cellulose concentration of the viscose slightly. Older systems use batch deaeration, where the air bubbles have to rise through several feet of viscose before they are liberated.

The correct viscose age or ripeness for spinning varies according to the type of fiber being made. Ripeness can be assessed by establishing the salt concentration necessary to just coagulate the viscose dope. The preferred test uses sodium chloride (salt figure) although the alternative method (Hottenroth number) is based on ammonium chloride.

**4.6. Spinning.** Properly filtered and deaerated viscose of the right salt figure can be coagulated into filament by pumping it through a suitable orifice (jet or spinneret) into a coagulating bath. The forming filaments are pulled through the bath by the first godets, which in some systems also serve as an anchor against which stretch can be applied by the second godets or traction units. The assembly of pumps, spin baths, jets, godets, stretch baths, traction units, and ventilation systems is known as the spinning machine. It can take many forms depending on the type of fiber being made and the priority given to achieving a geometrically similar path for the tows from each jet. Figure 3 illustrates one end of a staple fiber-spinning machine that would have hundreds of ends making up the final tow entering the cutter.

Jets for continuous filament textile yarn are typically 1-cm-diameter gold-platinum alloy structures with 20–500 holes of 50–200- $\mu\text{m}$  diameter. Tire yarn jets are also 1 cm in diameter but typically use 1000–2000 holes to give the required balance of filament and yarn denier. Staple fiber jets can have as many as 70,000 holes and can be made from a single dome of alloy or from



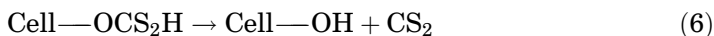
**Fig. 3.** One “end” of a staple fiber-spinning machine.

clusters of the smaller textile or tire yarn jets. The precious metal alloy is one of the few materials that can resist the harsh chemical environment of a rayon machine and yet be ductile enough to be perforated with precision. Glass jets have been used for filament production, and tantalum metal is a low cost but less durable alternative to gold-platinum.

The basic chemistry of fiber formation is however independent of the hardware. Spin-bath liquors are mixtures of sulfuric acid (5–15%), zinc sulfate (0.05–7%), and sodium sulfate (10–28%) controlled at temperatures ranging from 30 to 60°C. They are circulated past the jets at carefully controlled rates and fully recycled. The liquid filament emerging from the jet coagulates at the interface between acid bath and alkaline viscose to form a cuticle, and later a skin, through which the rest of the coagulation and regeneration is controlled. This regeneration mechanism causes the skin-core nonuniformity, which is characteristic of regular rayon fiber cross sections.



As coagulation proceeds into the center of the forming fiber, the outside regenerates to cellulose at a rate dependent on the temperature and composition of the bath.



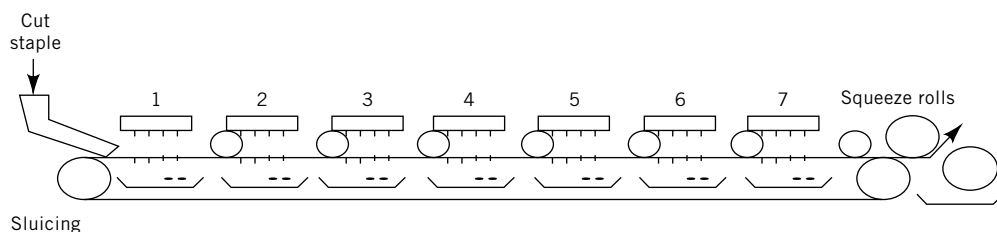
In processes making regular staple fiber, eqs. 5 and 6 occur practically simultaneously, but in high wet modulus processes, reaction 5 predominates in the spin bath, with reaction 6 occurring while stretching the filament in a hot water or steam bath. The carbon disulfide liberated in spinning and stretching can be recovered from the extracted air and from the spin-bath liquor.

Zinc salts are added to the spin bath to slow down the regeneration reaction by forming a less easily decomposed zinc cellulose xanthate intermediate. This allows greater stretch levels to be applied and results in fibers with thicker skins. There is still uncertainty as to whether the zinc cellulose xanthate gel acts by hindering acid ingress or water loss. High levels of zinc in the spin bath allow the production of tough fibers for tire reinforcement and industrial use.

**4.7. Washing and Drying.** In staple fiber production the filaments from all the jets on the spinning machine are combined into a few large tows and cut to length prior to washing. In filament yarn production, the yarns are kept separate and collected either as acid cakes for off-line cake washing, or wound onto bobbins after on-line washing and drying.

Again, irrespective of the hardware the chemistry is consistent. The partially regenerated fiber from the spinning machine is contaminated with sulfuric acid, zinc sulfate, sodium sulfate, carbon disulfide, and the numerous incompletely decomposed by-products of the xanthation reactions. The washing and drying systems must yield a pure cellulose fiber, suitably lubricated for the end use, and dried to a moisture level of around 10%.

The sequence of treatments is illustrated in Figure 4. Water consumption in washing is minimized by using a countercurrent liquor flow, clean water entering the system at the point where the fiber leaves, and dirty liquor leaving for chemical recovery at the point where the fiber enters.



**Fig. 4.** Staple fiber washing sequence: 1, a *hot acid wash* (2%  $\text{H}_2\text{SO}_4$  at  $90^\circ\text{C}$ ) decomposes and washes out most of the insoluble zinc salts. This wash completes the regeneration of xanthate and removes as much sulfur as possible in the form of recoverable  $\text{CS}_2$  and  $\text{H}_2\text{S}$ ; 2, an alkaline sodium sulfide *desulfurization bath* solubilizes sulfurous by-products and converts them into easily removed sulfides; 3, a *sulfide wash* to remove the sulfides created in bath 2; 4, a *bleach bath* (optional) uses very dilute hypochlorite or peroxide to improve fiber whiteness; 5, a dilute acid or *sour bath* removes any remaining traces of metal ions and guarantees that any residual bleaching chemicals are destroyed; 6, a controlled-pH freshwater *final wash* removes the last traces of acid and salt prior to drying; and 7, a *finish bath* gives the fiber a soft handle for easy drying and subsequent processing.

In the staple fiber system, the tows from spinning are cut to length and sluiced onto a 30–40-m-long wire-mesh conveyor that carries the blanket of fiber through cascades of the various wash liquors. Sluicing is a critical operation because the cut lengths need to be opened just enough to allow good washing and not so much that the individual fibers entangle. Sluicing must also lay a uniformly permeable blanket of fibers several centimeters thick and a meter or so wide because uneven laying results in uneven washing. Washing tows before cutting breaks out of the restrictions imposed by sluicing but results in the need to reoptimize processing conditions.

Cakes of textile yarn, collected in Topham boxes immediately after spinning, are processed on cake-wash machines. The cakes are wrapped in a porous paper and mounted in groups on stainless steel tubes through which the wash liquors can be forced. These tubes are mounted on a cake-wash box, which is a trolley on an overhead conveyor carrying the cakes to the different pumping stations on the machine. Each cake-wash box holds 100–200 cakes, and the permeability of each cake is critical to uniform washing. With permeability being determined largely by the degree of swelling of the fiber leaving spinning, very good control of all regeneration parameters is required to make yarn with consistent properties.

Yarn-drying procedures are far more critical than staple-drying procedures. All cellulosic fibers expand when wetted and contract on drying, the changes of size being greatest the first time the freshly made fiber is dried. If the contraction is hindered in any way, the yarn will possess a latent strain that will recover at a later stage, giving inferior weaving and dyeing. Furthermore, freshly formed regenerated cellulose undergoes a permanent change in molecular structure as it is heated, and this reduces its absorbency and hence its dye uptake.

Cakes are dried in low temperature, high humidity conditions for a long time in order to minimize strain and absorbency variability. The continuing

usage of the cake system almost a century after its invention owes much to the desirable strain-free yarn arising from its washing and drying operations.

Industrial yarn uses a continuous washing and drying process based on self-advancing reels. Whereas the processing of cake yarn can take many days to complete, the continuous process is over in minutes. The process is less labor-intensive and more productive than the cake system, but the engineering and maintenance requirements are easily underestimated. It is most used for industrial yarns—still the reinforcement of choice for radial tire carcasses. For these applications the strain built in by fast drying is no disadvantage because the yarns are expected to be at their best when bone dry. Dyeing is not required and an off-white color is tolerable. The main objective of the washing system is to remove acid and sulfur compounds that would affect the strength of the yarn during prolonged operation at high temperature.

**4.8. Modified Viscose Processes.** The need for ever stronger yarns resulted in the first important theme of modified rayon development and culminated—technically if not commercially—in the 0.88 N/tex (10 gf/den) high wet modulus industrial yarn process.

*Tire Yarns.* A method to increase the strength of viscose yarn from the 0.2 N/tex (2.2 gf/den) standard to levels needed in tires was first patented by Courtaulds in 1935 (18). By raising the zinc concentration in the spin bath to 4%, the thread could be stretched more by immersing it in a hot dilute acid bath during extension. Filament strengths increased to about 0.3 N/tex (3.3 gf/den), and the cross section became rounder, with a thicker skin than regular viscose. Pairs of these yarns were capable of being twisted into tire cords that outperformed traditional cotton cords.

The next significant strength improvement followed the 1950 Du Pont (19) discovery of monoamine and quaternary ammonium modifiers, which, when added to the viscose, prolonged the life of the zinc cellulose xanthate gel, and enabled even higher stretch levels to be used. Modifiers have proliferated since they were first patented and the list now includes many poly(alkylene oxide) derivatives (20), polyhydroxypolyamines (21–23), and dithiocarbamates (24).

Fully modified yarns had smooth, all-skin cross sections, a structure made up of numerous small crystallites of cellulose, and filament strengths around 0.4 N/tex (4.5 gf/den). They were generally known as the Super tire yarns. Improved Super yarns [0.44–0.53 N/tex (5–6 gf/den)] were made by mixing modifiers, and one of the best combinations was found to be dimethylamine with poly(oxyethylene glycol) of about 1500 mol wt (25). Ethoxylated fatty acid amines have now largely replaced dimethylamine because they are easier to handle and cost less.

The strongest fibers were made using formaldehyde additions to the spin bath while using a mixed modifier system (26–29) or using highly xanthated viscoses (50% + CS<sub>2</sub>). Formaldehyde forms an *S*-methylol derivative with xanthate, which decomposes slowly, permitting high levels of stretch. It also reacts with the cellulose backbone to form cross-links that render the fiber high in modulus and low in extension. Unfortunately, problems associated with formaldehyde side reactions made the processes more expensive than first thought, and the inevitable brittleness that results whenever regenerated cellulose is highly oriented restricted the fibers to nontextile markets. The commercial operations were closed down in the late 1960s.

The formaldehyde approach is still used by Futamura Chemical (Japan). They make spun-laid viscose nonwovens where the hydroxymethylcellulose xanthate derivative formed from formaldehyde in the spin bath allows the fibers to bond after laying. This process was originally developed by Mitsubishi Rayon (30), who later found that the derivative was thermoplastic, and the web could be calender-bonded (120°C) prior to regeneration (31).

**High Tenacity Staple Fibers.** When stronger staple fibers became marketable, the tire yarn processes were adapted to suit the high productivity staple fiber processes. Improved staple fibers use a variant of the mixed modifier approach to reach 0.26 N/tex (3 gf/den). The full 0.4 N/tex (4.5 gf/den) potential of the chemistry is unnecessary for the target end uses and difficult to achieve on the regular staple production systems.

The full potential of the mixed modifier tire yarn approach is, however, achieved in the modal or HWM (high wet modulus) staple processes using special viscose-making and -spinning systems. Courtaulds produced such fibers under the Vincel brand both in the United Kingdom and in Canada. Avtex made Avril (Fiber 40) until their closure in 1989. Lenzing still makes Modal staple in Austria. These fibers are most popular in ladies' apparel for their soft handle and easy dyeing to give rich coloration. They are made in finenesses down to 1 dtex (0.9 den) for fine yarns and hydroentangled nonwoven production (32).

**Polynosic Rayons.** The foregoing viscose process variants depend on the presence of zinc in the spin bath and modifiers in the viscose for their efficacy. Another strand of development began in 1952 when Tachikawa (33) patented a method for making strong, high modulus fibers that needed neither zinc nor modifier. The process was in fact related to the Lilienfeld (34) route to high strength, high modulus yarns that had failed in the 1930s because of the need for a spin bath containing 50–85% sulfuric acid. Both processes depend (33,34) on the fact that minimally aged alk-cell can, after xanthation with an excess of carbon disulfide, be dissolved at a low cellulose concentration to give very viscous viscoses containing high molecular weight cellulose. These viscoses have sufficient structure to be spun into cold, very dilute spin baths containing no zinc and low levels of sodium sulfate. The resulting gel filaments can be stretched up to 300% to give strong, round-section, highly ordered fibers, which can then be regenerated.

Toyobo's Tufcel is an excellent example of a modern polynosic fiber process, probably the most difficult viscose process to run efficiently (35). On-line process control allows only four persons per shift to make 10,000 t/year of a variety of special fibers, including Flame Retardant, Deep Dyeing (two types), Activated Carbon Fiber, and Super Fine 0.55 dtex (0.5 denier). Alk-cell and mixing soda quality are maintained by pressings soda centrifugation, filtration, and dialysis to remove 90% of the hemicellulose. Ion-exchange membranes are used to give 50 times the life and twice the efficiency of the old dialyzer bags used in tire-yarn production. Dissolution of the 500 DP xanthate is augmented by crumb grinders on the churn outlets and by in-line homomixers, which together reduce the dissolution time from three hours to one. Spinnerets for the finer yarns have 40-mm holes, and these are protected by automatic backflush filters, removing gels down to 15-mm diameter.

The polynosic rayons enjoyed a revival of fortunes in the 1990s when the new lyocell fiber produced by Courtaulds (Tencel)—a solvent spun fiber with polynosic properties—became popular in ladies' apparel and denim. By 2001 however the Toyobo Tufcel plant in Japan had been closed and at the time of writing, it is likely to be transferred to China where lower labor costs would allow it to compete more effectively with lyocell (see below).

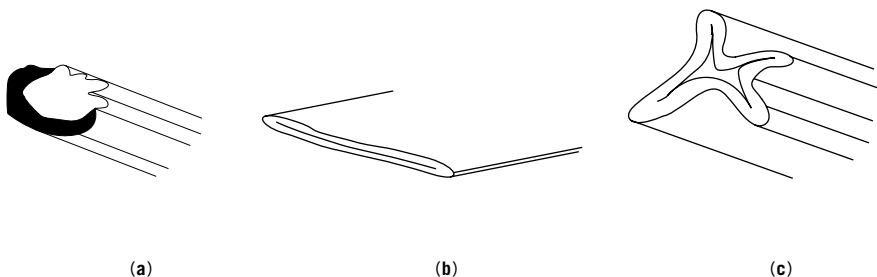
**Bulky Rayons.** Unlike the thermoplastic synthetic fibers, viscose rayon cannot be bulked by mechanical crimping processes. Crimpers impart crimp to a regenerated cellulose fiber, but it is not a permanent crimp and will not survive wetting out.

Permanent chemical crimp can be obtained by creating an asymmetric arrangement of the skin and the core parts of the fiber cross section. Skin cellulose is more highly ordered than core cellulose and shrinks more on drying. If, during filament formation in the spin bath, the skin can be forced to burst open to expose fresh viscose to the acid, a fiber with differing shrinkage potential from side to side is made, and crimp should be obtained (Fig. 5a).

Whether or not it is obtained depends on the washing mechanism allowing the shrinkage, and hence the crimp, to develop prior to the completion of regeneration. Crimp development occurs fully only in staple fiber processes, where the sluicing operation allows the cut tufts of acid tow to expand freely in ample volumes of hot liquor.

Even when crimp is fully developed it is easy to pull out (low energy) and difficult to translate into noticeably bulkier woven and knitted fabrics. It does however improve the absorbency and the cohesion of the staple (important in spun-yarn and nonwoven making) and gives a subtly different texture to woven fabrics. Coarse crimped rayon was the leading synthetic carpet fiber in Europe in the 1960s, but has since been replaced by the highly durable bulked continuous filament nylon yarns. Crimp is most important in rayon used for hygienic absorbent products.

Process conditions that favor chemical crimp formation are similar to those used for improved tenacity staple (zinc/modifier route). However, spin-bath temperature should be as high as possible (ca 60°C) and the spin-bath acidity as low as possible (ca 7%). Attempts have been made to overcome some of the leanness of high strength rayons by increasing the crimp levels. ITT Rayonier developed the Prima crimped HWM fiber (36) and made the process available to their customers. Avtex developed Avril III. Neither remain in production.



**Fig. 5.** Bulky rayons: (a) crimped rayon; (b) inflated–collapsed rayon; (c) super inflated rayon.



Cross-sectional modifications of a more extreme nature than skin-bursting, which nevertheless do not form crimp, have grown in importance since the early 1980s. These yield a permanent bulk increase, which can be translated into bulky fabrics without the need for special care. The first commercial staple fiber of this type was Courtaulds hollow Viloft, developed in the 1970s using a carbonate inflation technique (37).

Inflation had long been known as an intermittent problem of textile yarn manufacture. It was caused by the skin forming too quickly to allow the escape of gases liberated by the regeneration reactions, or as a result of air in the viscose at the jet. In the 1920s attempts were made to produce hollow naturally dull yarns by inclusion of gas (38) and by the addition of gas-generating agents to the viscose (39). It was also possible to cause inflation by capturing the regenerated gases when spinning a low soda viscose (40). In 1942–1943 Du Pont used air injection to produce Bublfil yarns as a kapok replacement for lifejackets, as thermal insulation for sleeping bags, and for aviators' uniforms.

All these early inflation processes (41) were difficult to control, and after World War II they were neglected until the 1960s. Companies in Japan, the United States, and Europe then started to develop inflated–collapsed rayons (Fig. 5b) for specialty papers (42) and wet-laid nonwovens.

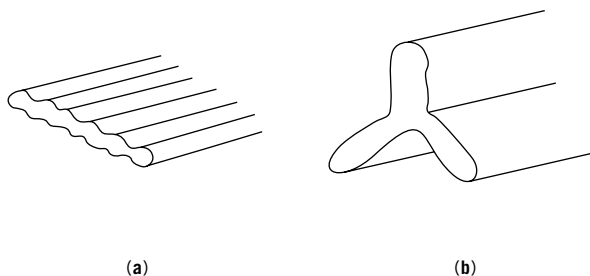
Although none of these survived commercially for more than a few years, their development led to an increased understanding of the inflation process and the identification of conditions that could yield a continuously hollow staple fiber in large-scale production (43).

The basis of this process was the injection of sodium carbonate solution into the viscose, although direct injection of carbon dioxide gas that reacts with the viscose soda to form sodium carbonate could also be used (44). The carbonate route yielded a family of inflated fibers culminating in the absorbent multilimbed super inflated (SI) fiber (Fig. 5c).

In its original form (45), the fiber was intended for use in toweling where the bulk, firm handle, and high rate of wetting made it one of the few fibers that would blend with cotton without spoiling the wet texture. An even higher absorbency version was developed (46) for use in nonwovens and tampons (47), where it comfortably outperformed cotton by reexpanding like a sponge on wetting.

By the mid-1980s a different approach to the production of fine fibers with novel cross sections became possible. Noncircular spinneret holes, eg, rectangular slots, allowed the large-scale production of flat fibers down to 2.2 dtex (2 den) (Fig. 6a). These I-shaped fibers were capable of replacing the inflated hollow fibers in textile applications, providing similar levels of bulk, warmth, and handle while having a much more regular shape. They were followed by the development of solid Y- and X-shaped multilimbed fibers (48) (Fig. 6b), which performed like SI fiber but had much lower levels of water imbibition than the inflated version. Their shape and relative stiffness enabled them to absorb more fluid between, as opposed to inside, the fibers. They were therefore as absorbent in use as the inflated versions (49,50) but did not require the extra process chemicals, and were easier to wash and dry in production and use. They are the most important bulky rayons now in production.

**Alloy Rayons.** It is possible to produce a wide variety of effects by adding materials to the viscose dope. The resulting fibers become mixtures or alloys of



**Fig. 6.** (a) I-section rayon; (b) Y-section rayon.

cellulose and the other material. The two most important types of alloy arise when superabsorbent or flame-retardant fibers are made.

American Enka (51,52) and Avtex (53) both produced superabsorbent alloy rayons by adding sodium polyacrylate, or copolymers of acrylic and methacrylic acids, or sodium carboxymethylcellulose to the viscose. The resulting alloys contained about 20% of the water-soluble polymer, giving water imbibitions up to double those of the unalloyed rayons. (See Superabsorbent Polymers). They performed particularly well in tampons, where the presence of the slippery polymer at the fiber surface encouraged wet-expansion of the compressed plug. Their use in this, the only real market that developed, declined after the Toxic Shock Syndrome outbreak (54,55) in the early 1980s. Other polymers that have formed the basis of absorbent alloys are starch (56), sodium alginate (57), poly(ethylene oxide) (58), poly(vinyl pyrrolidinone) (59), and sodium poly(acrylamido-2-methyl-2-propane sulfonic acid) (60).

Alloys of cellulose with up to 50% of synthetic polymers [polyethylene, poly(vinyl chloride), polystyrene, polytetrafluoroethylene] have also been made, but have never found commercial applications. In fact, any material that can survive the chemistry of the viscose process and can be obtained in particle sizes of less than 5  $\mu\text{m}$  can be alloyed with viscose.

Flame retardancy can be obtained by adding flame-retardant chemicals to make up about 20% of the fiber weight (61). The first commercial products used tris(2,3-dibromo-1-propyl) phosphate, but the P–O bonds made these susceptible to hydrolysis by strong alkali, and the bromine increased the rate of photodegradation. The chemical was found to cause cancer in laboratory tests and in the late 1970s fell from favor (62). Propoxyphosphazine (Ethyl Corp.) retardants were later used in Avtex's PFR fiber, and a bis(5,5-dimethyl-2-thiono-1,3,2-dioxaphosphorinanyl) oxide powder (Sandoz) was the basis of later European FR fiber developments. Alloys with inorganic salts such as silicates or aluminates are possible, the salts being converted to fibrous polyacids when the cellulose is burnt off (63). This latter approach is the basis of the Visil flame-retardant fiber introduced by Kemira Oy Saeteri (64).

## 5. Cuprammonium Rayon

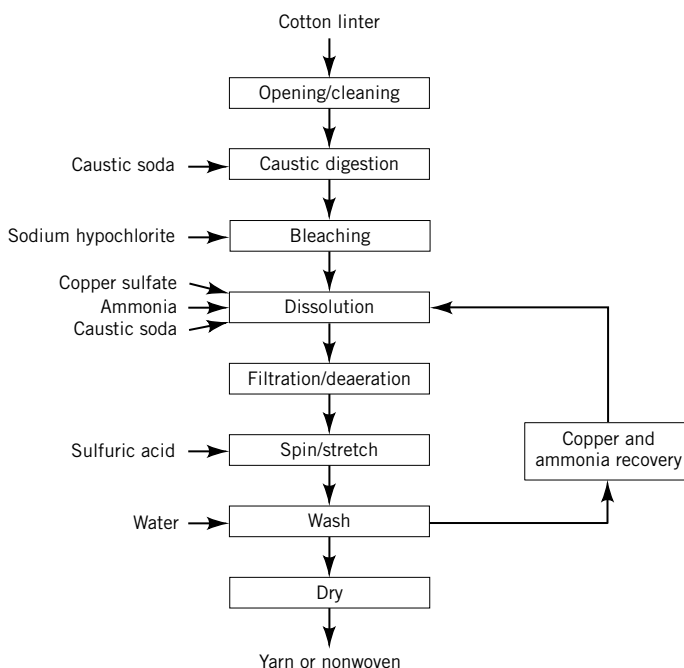
Asahi Chemical Industries (ACI, Japan) are now the leading producers of cuprammonium rayon. In 1990 they made 28,000 t/yr of filament and spunbond

nonwoven from cotton cellulose (65). Their continuing success with a process that has suffered intense competition from the cheaper viscose and synthetic fibers owes much to their developments of high speed spinning technology and of efficient copper recovery systems. Bemberg SpA in Italy, the only other producer of cuprammonium textile fibers, was making about 2000 t of filament yarn in 1990.

The process operated by ACI is outlined in Figure 7. Bales of cotton linter are opened, cooked in dilute caustic soda, and bleached with sodium hypochlorite. The resulting highly purified cellulose is mixed with pre-precipitated basic copper sulfate in the dissolver, and 24–28% ammonium hydroxide cooled to below 20°C is added. The mixture is agitated until dissolution is complete. If necessary, air is introduced to allow oxidative depolymerization and hence a lowering of the dope viscosity.

The dark blue solution containing 5–10% of cellulose with a DP of 1000–2000 is filtered through a series of plate-and-frame filter presses using fine-mesh metal screens to remove any particles that might block the spinneret holes. It is then deaerated under vacuum and stored ready for spinning. Unlike viscose dope, the cuprammonium cellulose [9050-09-3] solution is relatively stable.

In the old classical spinning technique developed by Bemberg, the deaerated and filtered dope is extruded into a funnel-shaped glass tube through which slightly alkaline water is forced. The water carries the regenerating cellulose gel while stretching it by about 10,000% as it accelerates to the exit. The yarn then passes through a bath containing about 5% sulfuric acid, which completes the regeneration of cellulose and converts the ammonia and copper residues into their sulfates.



**Fig. 7.** The cuprammonium process.

In the original batch process, the blue-colored yarn was collected on hanks for separate washing, lubrication, and drying treatments. The continuous process was first patented in the United States in 1934 (66) and 1935 (67), and operated by American Bemberg. This process (68) combined the batch process washing treatments in a series of tanks through which a warp of yarns (from hundreds of spinnerets) were pulled prior to drying and beaming.

The high speed continuous filament process (69) was first used for manufacturing in 1974, and this enabled the yarn production rates to be raised from 150 to 380 m/min. This system uses a pair of net conveyor belts to protect and transport an overfed warp of yarns through washing and drying. After spinning, excess bath is stripped from the yarns by a shaking mechanism that damages the yarn less than the old comb stripper guides. In 1987, Asahi commercialized their "mark 2" high speed spinning system, which operated at 1000 m/min, and are now working on systems that will exceed 2000 m/min.

Also in 1974, ACI started the direct spinning of Bemliese nonwoven fabrics using the same conveyor belt washing technique (70). This process uses wide spinnerets and spinning cells to produce a curtain of filaments, which fall in the spinning liquor onto the conveyor. The conveyor is oscillated from side to side in order to lay the continuous fibers down in sinusoidal waves. After washing, the webs, which have strength resulting from the self-bonding nature of the fibers as spun, can be further strengthened and finished by hydroentanglement.

Almost total copper recovery needs to be achieved to meet the economic and environmental criteria for a modern cellulosic fiber process. In the basic process (71), spent spin-bath liquor was passed through ion-exchange resins and the effluent from these resins was reused in the funnels. The copper washed out of the yarn was precipitated with sodium carbonate, forming the basic copper sulfate sludge, which was reused in cellulose dissolving. Only 95% copper recovery was possible using this system. Recovery efficiencies of up to 98% were claimed for the Russian Kustanai Plant in a document (72), which also records a 99.9% recovery achieved by Japan Organo Co., Ltd. Asahi claims to have perfected copper recovery to a point where it is no longer an issue.

A high percentage of the ammonia can be recovered from the spin-bath effluent and by washing prior to the final acid bath. During acidification, remaining ammonia is converted to the sulfate and recovered when the acid wash liquor is treated with carbonate to recover the copper. Ammonia residuals in the large volumes of washwater can only be removed by distillation. Overall about 75–80% of the ammonia required to dissolve the cellulose can be recovered.

Asahi's innovations have done much to transform the cuprammonium process from an uneconomic competitor for viscose and synthetics into the fastest wet-spinning system in the world. They now claim it to be competitive both economically and environmentally with the viscose filament process.

## 6. Direct Dissolution Processes

Regenerated fibers produced via the direct dissolution of cellulose in organic solvents are generically known as lyocell fibers.

The production routes already described cope with the difficulties of making a good solution by going through an easy-to-dissolve cellulose derivative, eg, xanthate or a cellulose complex, such as cuprammonium. The ideal process, one that could dissolve the cellulose directly from ground wood, is still some way off, but since the early 1980s significant progress has been made.

There have been reviews of the early work on direct dissolution (73,74). The efforts to dissolve cellulose directly as a *base* using phosphoric, sulfuric, and nitric protonic acids, or zinc chloride, thiocyanates, iodides, and bromides as Lewis acids are recorded (73,74). With regard to cellulose acting as an *acid*, sodium zincate, hydrazine, and sodium hydroxide are listed as inorganic solvents, and quaternary ammonium hydroxides, amines, dimethylamine–DMSO mixtures, and amine oxides as organic bases. Cellulose solutions of 16% have been achieved in lithium chloride–dimethylacetamide systems (75), and 14% solutions in dinitrogen tetroxide–dimethylformamide systems (76). Solutions of up to 14% cellulose were achieved in an extensive study of the ammonia–ammonium thiocyanate solvent system (77). The dimethylsulfoxide–paraformaldehyde system (78) is capable of dissolving a wide range of DPs without causing degradation. However, despite early promise, the problems of developing fiber production routes using these systems have, with the exception of the amine oxide route, proved insurmountable.

The cellulose-dissolving potential of the amine oxide family was first realized (79) in 1939, but it was not until 1969 that Eastman Kodak described the use of cyclic mono(*N*-methylamine-*n*-oxide) compounds, eg, *N*-methylmorpholine-*n*-oxide [7529-22-8] (NMMO), as a solvent size for strengthening paper (80) by partially dissolving the cellulose fibers.

Other patents (81,82) covered the preparation of cellulose solutions using NMMO and speculated about their use as dialysis membranes, food casings (sausage skins), fibers, films, paper coatings, and nonwoven binders. NMMO emerged as the best of the amine oxides, and its commercial potential was demonstrated by American Enka (83,84). Others (85) have studied the cellulose–NMMO system in depth; one paper indicates that further strength increases can be obtained by adding ammonium chloride or calcium chloride to the dope (86).

Both American Enka (87) and Courtaulds set up pilot-plant work in the early 1980s with the objectives of developing fiber spinning and solvent-recovery operations. The Austrian viscose producer Lenzing studied various systems (88) and commenced pilot operations on an NMMO system at the end of the 1980s. At the time of writing, only Courtaulds and Lenzing have proceeded to a commercial scale.

American Enka decided not to commercialize 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) reentered 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. However, Akzo–Nobel had earlier granted a lyocell license to Lenzing, the Austrian viscose fiber 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.

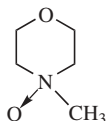
Lenzing obtained a patent in the U.S.A. for a process, some aspects of which had been operated by Courtaulds for many years, and indeed were used in production at Courtaulds Tencel plant in Alabama. Courtaulds naturally objected, and applied for summary dismissal of both the U.S. and the subsequent European 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 U.S.A., the Lenzing patent was summarily dismissed, but Lenzing appealed successfully. 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. The settlement only covered patented technology; there was to be no sharing of "knowhow" gained in the operation of the process, which at the time had only been commercialized by Courtaulds.

Akzo–Nobel acquired Courtaulds in 1998, and formed Acordis Fibers, bringing together in one company all the key lyocell technologies.

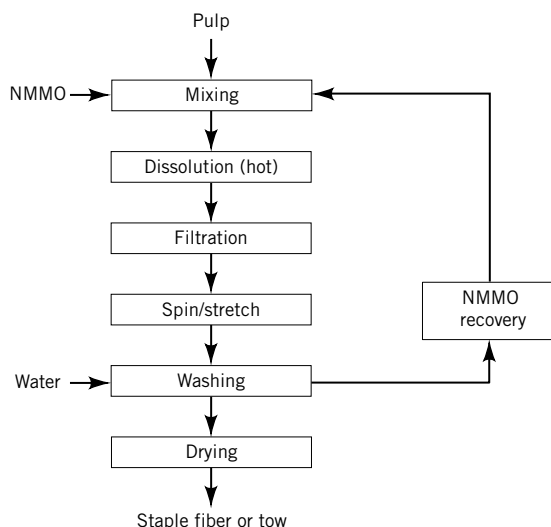
**6.1. The Courtaulds Lyocell Process.** The increasing costs of reducing the environmental impact of the viscose process coupled with the increasing likelihood that the newer cellulose solvents would be capable of yielding a commercially viable fiber process led Courtaulds Research to embark on a systematic search for a new cellulosic fiber process in the late 1970s.

The project, code-named Genesis, did not involve basic research into new solvents for cellulose so much as screening the known solvents against criteria felt to be important for the cellulosic fiber process of the future. The solvent chosen had to be recyclable at a very high level of efficiency, and hence as near to totally containable in the process as possible. It had to be safe to work with and safe in the environment in the event of any losses. It had to be able to dissolve cellulose completely without reacting with it or degrading it, and the resulting process had to be less energy-intensive than the viscose route, which was already proven to be less energy-intensive than the synthetics in an independent study (89). It was especially important to choose a system that, like the melt-spun synthetics, would not require costly gaseous- or liquid-effluent treatment systems. Finally, the process would be capable of making good textile fibers to maintain, or even extend, the cellulose's share of the global market against fierce competition from melt-spun synthetics based on cheap but nonrenewable oil reserves.

By 1980, *N*-methyl morpholine-*n*-oxide (NMMO) was shown to be the best solvent, provided well-known difficulties associated with its thermal stability could be avoided by appropriate chemical engineering.



*N*-Methyl morpholine-*n*-oxide (NMMO)



**Fig. 8.** Direct dissolution: Acordis Tencel process.

Filaments obtained from the first single-hole extrusion experiments had promising properties, so Courtaulds committed the resources in 1982 to build a small pilot plant to test the feasibility of overcoming the solvent handling and recovery problems that had prevented earlier commercial exploitation. This system, capable of making up to 100 kg of fiber per week, met its objectives and allowed the first serious end use development to begin. Scale-up to 1000 kg/week pilot line was possible in 1984, and in 1988 a 25,000 kg/week semicommercial line was commissioned in Grimsby, United Kingdom, to allow a thorough test of the engineering and end-use development aspects. Commercialization of the fiber as Tencel followed in 1990 and rapid sales buildup, especially in Japan, led to a 16,000-t plant being built and started up in Mobile, Alabama, in 1992. A second 20,000-t factory followed in Mobile in 1995 and a third 40,000-t plant was commissioned in Grimsby in 1998.

The Acordis system is illustrated in block, diagram form in Figure 8. Dissolving-grade woodpulp is mixed into a paste with NMMO and passes through a high temperature dissolving unit to yield a clear viscous solution. This is filtered and spun into dilute NMMO, whereupon the cellulose fibers precipitate. These are washed and dried, and finally baled as staple or tow products as required by the market. The spin-bath and wash liquors are passed to solvent recovery systems that concentrate the NMMO to the level required for reuse in dissolution.

Figure 9 is an outline flow sheet illustrating the layout of the key process steps provided courtesy of Acordis. Unlike both the viscose process and the later Lenzing Lyocell process, the fiber is washed, dried, and crimped in tow form prior to cutting. Unlike the viscose spinning process, the cellulose solution is extruded into warm air prior to immersion in the aqueous NMMO spinning solution. (This is known as dry-jet wet-spinning to distinguish it from the totally dry acetate spinning process and the totally wet viscose spinning.)

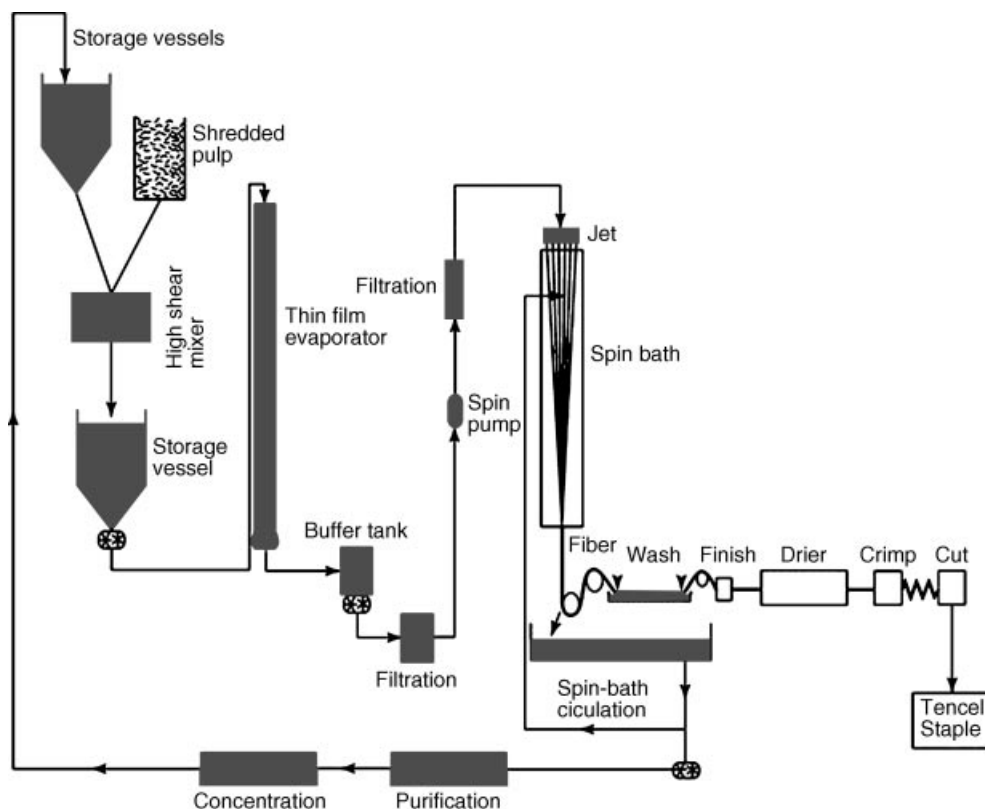


Fig. 9. Direct dissolution: Acordis Tencel Flow Diagram.








## 7. Lyocell Applications

Dry-jet wet-spinning of lyocell fiber has been described (90) as being similar to the extrusion of lyotropic rigid-rods, giving rise to a highly microfibrillar structure that is consistent across the entire cross section of the fiber—ie, differing from the skin-core structure observed in viscose rayon. Wide-angle X-ray diffraction data shows lyocell to have a crystallinity of 60% (cf 40% for viscose), the cellulose crystals having a lateral dimension of about 4 nm. However, micro-focus small-angle X-ray scattering (91) has recently shown a definite skin-core structure, with the thin skin having better-oriented voids than the core. This observation is more in keeping with the macro observations of fibrillation in paper-making—the surface appearing to fibrillate easily—whereas breaking up the core region of the fiber proves very difficult.

The new fiber thus had physical properties (Table 1) sufficiently different from regular rayon to allow an initial market development strategy that did not erode the position of the traditional viscose fiber. The unique strength, texture, and coloration potential of the fiber enabled it to command premium prices



Table 1. Properties of Selected Commercial Rayon Fibers

Property	Cuprammonium	Regular rayon	Improved rayon	Modal	Polynosic	Y-Shaped rayon <sup>a</sup>	Solvent spun rayon <sup>b</sup>
fiber cross section							
dry tenacity, cN/tex <sup>c</sup>	15–20	20–24	24–30	34–36	40–65	18–22	40–44
extensibility at break (dry), %	7–23	20–25	20–25	13–15	8–12	17–22	14–16
wet tenacity, cN/tex <sup>c</sup>	9–12	10–15	12–16	19–21	30–40	9–12	34–38
extensibility at break (wet), %	16–43	25–30	25–35	13–15	10–15	23–30	16–18
water imbibition, %	100	90–100	90–100	75–80	55–70	100–110	65–70
cellulose DP <sup>d</sup>	450–550	250–350	250–350	300–500	550–700	250–350	550–600
initial wet modulus <sup>e</sup>	30–50	40–50	40–50	100–120	140–180	35–45	250–270

<sup>a</sup> The Y-shaped rayon data are based on Courtaulds Galaxy fiber.<sup>b</sup> The solvent-spun rayon data are based on Courtaulds Tencel fiber.<sup>c</sup> To convert cN/tex to gf/den, divide by 8.82.<sup>d</sup> DP = degree of polymerization.<sup>e</sup> The load required to extend the wet fiber by 5%  $\times$  20.

in upmarket mens' and ladies' outerwear, largely due to the fibrillation tendency being harnessed by creative finishing processes to produce "soft-touch" or "peach-skin" textures. However while premium pricing allowed the process to expand rapidly, it was only achievable while the special characteristics of lyocell were in fashion, and before the soft-touch characteristics had been developed using other celluloseics such as polynosic rayon and cotton. Furthermore the uncontrolled fibrillation that occurred when textiles made from early lyocell fibers were conventionally dyed, finished, or washed led to unacceptable fabric appearance and texture. The fibrils splitting away from the fiber surface became apparent as a frosty-looking surface that prevented the true dyed color from emerging. In extreme cases, and especially on knitted fabrics where the fibers were less tightly bound to the structure, the fibrils caused these looser fibers to entangle and form pills. Thus early lyocell had restricted potential in mass-market textiles, being confined to woven products dyed and finished by gentle processes to lighter shades for dry-clean-only garments.

This unacceptable situation was addressed by developing production processes to allow the manufacture of lyocell fiber with minimal fibrillation tendency—even if this meant increasing process cost. This was achieved in part by altering the spinning conditions, and in part by the use of cross-linking agents in washing, to bond the fibrillar fiber structure more strongly. It was also addressed by investigating nonwoven applications for lyocell, thereby avoiding wet processing except in areas (eg paper-making and hydroentanglement) where fibrillation could be an advantage.

Several studies of its performance in nonwovens had shown it capable of yielding fabric strengths 2–3 times higher than hitherto possible with regenerated celluloseics (92,93). It appeared particularly suitable for the latest hydroentanglement systems, where its basic strength and an ability to develop a microfiber surface under the action of high pressure water jets enabled it to make very strong nonwoven fabrics having textile-like properties. The effect of high pressure water jets on lyocell fiber was first described publicly in 1989 (94). In addition to the higher fabric strengths, extensive fibrillation had occurred, making the fabrics stiffer (bonding between the fibrils). The fiber took on a chalky white appearance as bonding proceeded (light scattering from the fibrils), and absorbent capacity and wicking rates were higher than that for the higher water-imbibition viscose rayon controls: this too being an effect of the microfiber content. However the most significant alteration in properties caused by fibrillation was in the dry and wet texture of the fabrics.

Dried conventionally after hydroentanglement, hydrogen bonding between the fibrils of the highly fibrillated fibers stiffened up the fabrics, giving them an unattractive papery handle. Once rewetted, however, the material took on a suede or chamois-leather-like texture, which proved interesting to makers of durable wipes for car and window cleaning and for artificial leather, especially for shoe construction, where the inherent absorbency of the fiber could improve the comfort of leather substitutes made from, for example, splittable synthetic/lyocell blends.

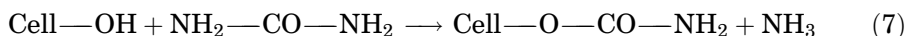
Current lyocell, like the almost identical polynosic viscose rayons developed half a century ago (33), has so far proved to have similarly limited and variable potential in the fashion textile markets for which it, and the process for making

it, was designed. Whether a cheaper, high-fibrillation version would improve lyocell's prospects in nonwovens is still open to debate.

## 8. Other Solvent Routes

Work on other routes to cellulosic fibers continues, some driven by a desire to identify an environmentally benign route to cellulosic fibers that can utilize the large capital investment in the viscose process equipment and hence cost less than a completely new fiber process such as lyocell.

The Finnish viscose producer Kemira Oy Saeteri collaborated with Neste Oy on the development of a carbamate derivative route. This system is based on work (95) that showed that the reaction between cellulose and urea gives a derivative easily dissolved in dilute sodium hydroxide:



Neste patented an industrial route to a cellulose carbamate pulp (96) that was stable enough to be shipped into rayon plants for dissolution as if it were xanthate. The carbamate solution could be spun into sulfuric acid or sodium carbonate solutions, to give that when completely regenerated had similar properties to viscose rayon's. When incompletely regenerated they were sufficiently self-bonding for use in paper-making. The process was said to be cheaper than the viscose route and to have a lower environmental impact (97). It has not been commercialized, so no confirmation of its potential is yet available.

It has been claimed that solutions containing 10–15% cellulose in 55–80% aqueous zinc chloride can be spun into alcohol or acetone baths to give fibers with strengths of 0.13–0.18 N/tex (1.5–2 gf/den). However, if these fibers were strain-dried (ie, stretched) and rewetted while under strain, strengths of 0.46 N/tex (5.2 gf/den) were achieved (98).

Asahi has been applying the steam explosion (99) treatment to dissolving pulp to make it dissolve directly in sodium hydroxide (100), and they claim (101,102) a solution of 5% of steam-exploded cellulose in 9.1% NaOH at 4°C being spun into 20% H<sub>2</sub>SO<sub>4</sub> at 5°C. The apparently poor fiber properties [best results being 0.16 N/tex (1.8 gf/den) tenacity dry, with 7.3% extension] probably arise because the fibers were syringe-extruded at 8.3 tex/filament (75 den/fil). Asahi feels that this could be the ultimate process for large-scale production of regenerated cellulose fibers.

Patents (103,104) published in February 1996 describe anisotropic cellulose solutions at concentrations up to 40% in a "solvent containing from 72 to 79 wt% of phosphorous pentoxide." Claiming a highly economical route for the production of tire yarns, the process described therein appears to be simple and elegant.

A twin-screw extruder is fed with dry fluff-pulp and the phosphoric acid solvent. The first cooled zone mixes the cellulose into the solvent and reduces the particle size, the second hotter zone starts the dissolution, and the third zone provides further blending and dissolution time, its temperature being controlled to achieve the desired reduction in cellulose DP. A final low pressure

zone allows deaeration and dewatering (or the injection of additives) as necessary, and filters remove particles before spinning.

While "all available types of cellulose" can be used, dissolving pulps are preferred for best spinning and fiber properties. The solvent preparation involves mixing orthophosphoric acid with polyphosphoric acid, in a 80:20 ratio at around 50°C and then cooling and storing for several hours to arrive at the desired concentration of anhydride.

After less than 15 min in the extruder, the cellulose solution, typically containing 20% cellulose, is spun, like lyocell, through a similar-sized air gap, but into cold acetone, followed by water washing, sodium carbonate or soda neutralization, and a final water washing. Tire yarn with a breaking tenacity of 76 cN/tex, an elongation at break of 6.5%, capable of sustaining a load of 20 N/tex without extending by more than 2%, was obtained at 120 m/min spinning speed.

Michelin Research had earlier developed a process using a mixture of phosphoric and formic acids, also for tire yarns. The Akzo–Nobel process, based on phosphoric acid alone, was felt to give easier solvent recovery. A process using phosphoric acid alone (105) emerged from Michelin Research in March 1996.

Further work at Akzo–Nobel (106) showed that if extra water is injected with the solvent, or added to the anisotropic solutions described above, isotropic solutions of cellulose could be obtained at concentrations of 7–20%. A 7.6% cellulose solution could be spun to give fibers with tenacities of 18–38 cN/tex (extension at break declining from 17.4 to 8.4%) as draw ratios were increased from 60 to 150%.

One of the key requirements for making high quality high modulus fibers using the phosphoric acid approach is to keep the level of phosphorus bound to cellulose at a minimum. Allowing it to rise from the <0.5% level preferred in the above process to more than 3% by increasing the phosphorus pentoxide level in the solvent, or by increasing the storage temperature of the solvent prior to introduction of the cellulose, resulted in weaker, hard-to-handle gel fibers with very high absorbency. Akzo–Nobel therefore postulated the production of superabsorbent fibers using a variation of the phosphoric acid route (107). While the resulting patent covers conventional fiber production, perhaps in recognition of the difficulties of cleaning up such fibers, it also covers the production of fibrils by extrusion into a high shear mixer to obtain a fibrous slurry. Water absorbencies of up to 100 g/g are claimed if the fibers containing more than 6% bound phosphorus are cross-linked with ethylene glycol diglycidyl ether in a 70:30 ethanol/water mixture.

Centrifugal spinning of phosphoric acid solutions of cellulose was also explored (108), and found capable of producing mixtures of filaments with linear densities ranging from 1 to 23, and tenacities of 4 to 90 cN/tex and extensions at breakup from 1 to 15%.

In an attempt to remove the problems associated with the acetone coagulation bath, fibers were air-gap spun into aqueous salt solutions, eg up to 25% of diammonium hydrogen phosphate or potassium phosphate or 5% zinc sulphate (109). This patent also makes it clear that the corrosive nature of the solution is an issue in spinneret design.

None of the above patents address the crucial solvent recovery issues. While recovery of acetone is possible, re-creating concentrated phosphoric acid from either dilute solutions or phosphates appears as difficult as the recovery of sulfuric acid from sulfates in the viscose process. The viscose approach is of course to extract and sell the neutralization product and use fresh concentrated sulfuric acid to make up the recovery shortfall—an option that is apparently unattractive in phosphate systems.

## 9. Fiber Properties

The bulk properties of regenerated cellulose are the properties of Cellulose II, which is created from Cellulose I by alkaline expansion of the crystal structure (110,111) (see CELLULOSE). The key textile fiber properties for the most important current varieties of regenerated cellulose are shown in Table 1. Fiber densities vary between 1.53 and 1.50.

A discussion of the fiber properties is complicated by the versatility of cellulose and its conversion routes. Many of the properties can be varied over wide ranges, depending on the objectives of the producer. For instance, dry fiber strengths from less than 1 but up to 10 g/den have been made commercially, and at a given dry strength it has proved possible to vary the elongation and wet properties independently. The water imbibition of pure cellulose fibers has been varied from 45 to 450%, and the cross-sectional shape altered from circular all-skin, to multilobal collapsed tubes that reopen on wetting. Alloying adds further scope for adding properties unachievable with pure cellulose. Chemically, cellulose fibers are well endowed with reactive hydroxyl groups that render them amenable to modification by grafting, which, more so than alloying, allows the properties to be moved in the direction of synthetic polymers if the need arises. The same reactivity makes the fibers more degradable than synthetics, both chemically and biologically, although it must be said that biological degradability is easily halted by inclusion of suitable biocides.

**9.1. Thermal Properties.** Fibers are not thermoplastic and are stable at temperatures below 150°C, with the possible exception of slight yellowing. They begin to lose strength gradually above 170°C, and decompose more rapidly above 300°C. They ignite at 420°C and have a heat of combustion of 14,732 J/g (3.5 kcal/g).

**9.2. Moisture Regain.** The fibers are all highly hydrophilic, with moisture regains at 65% rh, ranging from 11 for the polynosics to 13 for regular rayon. Wetting of cellulose is exothermic, with the regenerated forms giving out 170 J/g (41 cal/g) between 40 and 70% rh, compared with 84 J/g (20 cal/g) for cotton. The fiber structure swells as fluid is imbibed, and fiber strength and stiffness falls. The contact angle for unfinished fiber is greater than 150°.

**9.3. Chemical Properties.** The fibers degrade hydrolytically when contacted with hot dilute or cold concentrated mineral acids. Alkalies cause swelling (maximum with 9% NaOH at 25°C) and ultimately disintegration. They are unaffected by most common organic solvents and dry-cleaning agents. They are degraded by strong bleaches such as hypochlorite or peroxide.

Table 2. 2000 World Capacity for Regenerated Cellulose Fibers

Fiber type	Production, 10 <sup>3</sup> t
industrial filament yarns	105
textile filament yarns	390
regular staple fiber and tow	2300
high wet modulus staple	100
Lyocell staple	100
Total	2995

**9.4. Optical Properties.** The fibers are birefringent. The refractive index parallel to the fiber length ranges from 1.529 for regular rayon to 1.570 for the polynosics. Refractive indexes perpendicular to the fiber length range from 1.512 (regular) to 1.531 (polynosic). Basic fibers are naturally lustrous, but can be made dull by adding opacifiers or by changing the cross-sectional shape.

**9.5. Electrical.** The electrical properties of the fiber vary with moisture content. The specific resistance of the fibers is around  $3 \times 10^6$  W/cm at 75% rh and 30°C compared with  $1 \times 10^{18}$  W/cm for pure dry cellulose. The dielectric constant (100 kHz) is 5.3 at 65% rh and 3.5 at 0% rh. The zeta potential in water is -25 mV.

## 10. Economic Aspects

**10.1. Production and Consumption.** Approximately 3 million metric tons of regenerated cellulose fibers production capacity existed in 2000 (Table 2). The leading producers of filament yarns were the Chinese state-owned factories (118,000-t capacity), Acordis in Europe (69,000 t), and the Russian plants (with 44,000 t). The leading producers of staple fiber and tow were the Chinese with 480,000 t, the Birla Group (India) with 408,000 t, Lenzing (Austria, U.S.A., and Indonesia) with 315,000 t and Acordis with 170,000-t capacity split between the United Kingdom and North America, Formosa Chemicals and Fibers Co. with 162,000 t (in Taiwan). Acordis was formed in 1998 from the fiber businesses of Courtaulds and Akzo–Nobel following the takeover of Courtaulds by Akzo, who later sold Acordis to a consortium of CVC Partners and Acordis management. (Note: since these statistics were compiled, 100,000 ton of Acordis's viscose staple fiber capacity has closed.)

Actual staple fiber consumption figures for 2001 were estimated (118) to be ca 1.6 million tons because of a sharp decline in Eastern Europe masking slight growth elsewhere (Table 3). Asian countries now account for 75% of the consumption of viscose staple in textiles, with Western Europe leading the consumption in nonwovens.

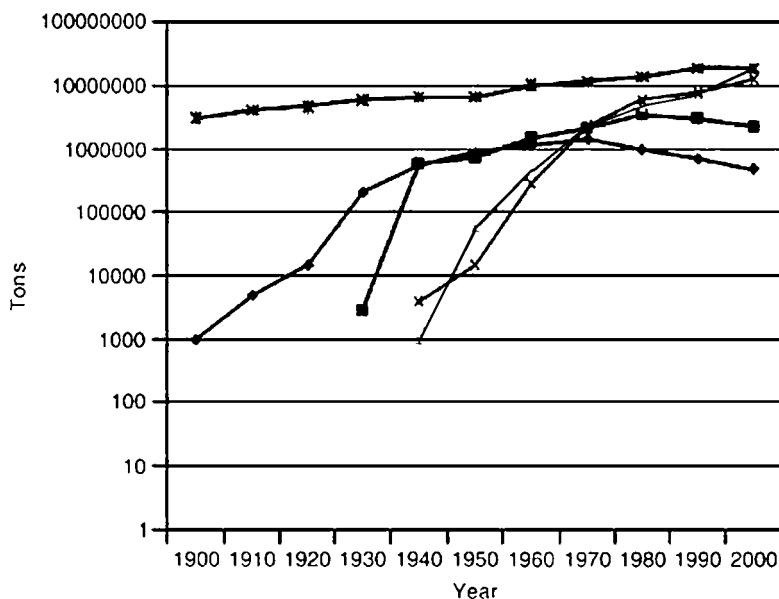
**10.2. Commercial Aspects.** Since the early 1980s, the viscose-based staple fibers have, like the cuprammonium and viscose filament yarns in the 1970s, ceased to be commodities. They have been repositioned from the low cost textile fibers that were used in a myriad of applications regardless of suitability, to premium priced fashion fibers delivering comfort, texture, and attractive colors in ways hard to achieve with other synthetics. They are still widely

Table 3. The Top 10 Consuming Countries in 2000

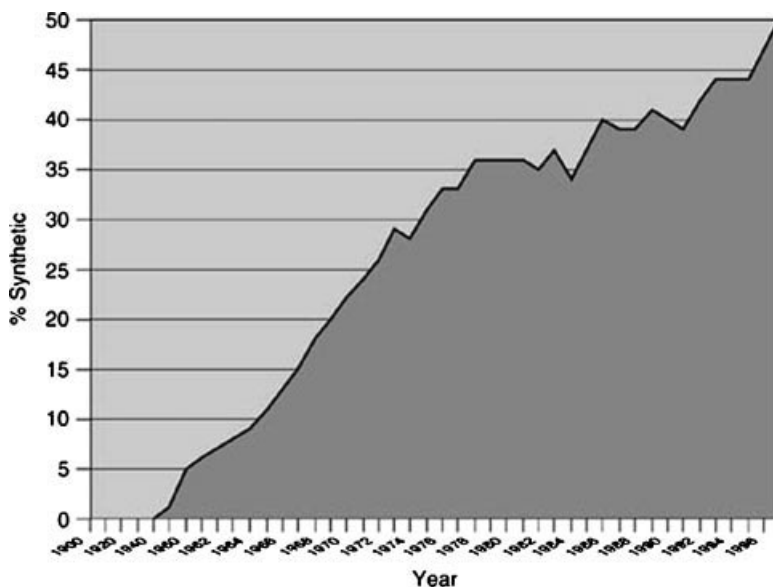
Country	Consumption, ton
China	400,000
Western Europe	280,000
India	225,000
Indonesia	175,000
U.S.A	85,000
Taiwan	80,000
Turkey	60,000
Japan	55,000
Thailand	30,000
Korea	25,000

used in blends with polyester and cotton to add value, where in the 1980s they would have been added to reduce costs.

Such repositioning inevitably means reduced production volume, and this is illustrated using CIRFS data ([www.cirfs.org](http://www.cirfs.org)) in Figure 10. Most capacity reductions have been in North America and especially eastern Europe. This has been offset in part by capacity increases in the Far East. Rayon is no longer a significant component of carpets, and has lost the disposable-diaper coverstock business to cheaper and more easily processed polypropylene. It has, however, gained share in health and hygiene products and is now a principal component of tampons worldwide.



**Fig. 10.** World fiber production in 20th century of Cotton Usage—Log Scale. —◆— Cellulosic filament; —■— cellulosic staple; —×— synthetic filament; —▲— synthetic staple, —\*— cotton.



**Fig. 11.** Synthetics vs biopolymers in the 20th century.

Figure 11 illustrates the major share changes over the last century, this time combining the natural (mainly cotton) and regenerated cellulosics as “biopolymers”.

Roughly half of the ca 50 million tons of fiber consumed annually is now made from polymers synthesized from fossil fuels.

The aesthetic, absorbency, and comfort advantages still enjoyed by the biopolymer fibers has unquestionably slowed synthetic penetration of the apparel sector. Synthetics are used mainly for their low-cost, easy-care and durability characteristics. In the absence of fibers combining all these properties, polyester/cellulosic blends have been a most popular combination. Ratios varying between 35% cellulosic and 35% synthetic depending on the market positioning of the fabric and the relative prices of the fibers are typical.

Within the cellulosic part of the blend, rayon has to compete with cotton and can do this only

1. when rayon prices (esp. modal or polynosic) are below cotton prices,
2. when a fashion in a particular sector values the softness, leanness, and drape of rayon above the crisper, fuller, stiffer handle of cotton, and
3. when the enhanced absorbency, uniformity, and processability of rayon (in this case compared with overbleached cotton at a higher price) is technically desirable, for instance in disposable nonwovens.

The lyocell process offers an environmentally acceptable way of converting natural cellulose into a premium quality rayon fiber with tensile properties approaching those of polyester. Furthermore the technology offers the potential



for converting pulp to fiber on a scale and at a cost to give polyester and cotton some serious competition. The high levels of investment in the first lyocell plants necessitated launching the fiber at a premium price and therefore into the quality fashion-apparel market. This proved highly successful and led to rapid expansion up to the current capacity of around 100,000 ton. However this represents about one half of one percent of the current cellulosic fibers market, and lyocell fiber is still only available from two sources, Acordis and Lenzing.

At the time of writing, demand for lyocell has yet to increase to absorb the latest expansions, and some repositioning of the fiber in the market appears necessary.

## 11. Environmental Issues

**11.1. Viscose Process.** As noted in the introduction, rayon is unique among manufactured fibers because it is the only one to use a natural polymer (cellulose) directly. Polyesters, nylons, polyolefins, and acrylics all come indirectly from vegetation; they come from the polymerization of monomers obtained from reserves of fossil fuels, which in turn were formed by the incomplete biodegradation of vegetation that grew millions of years ago. The extraction of these nonrenewable reserves and the resulting return to the atmosphere of the carbon dioxide from which they were made is one of the most important environmental issues of current times. Cellulosic fibers therefore have much to recommend them provided that the processes used to make them have minimal environmental impact.

**Fossil Reserves.** Renewable resources will become increasingly important as the planet's stocks of fossilized reserves are depleted and as governments realize that biomass can provide a truly sustainable, cost-effective source of energy and materials. The viscose route currently needs fossil reserves for energy generation but for little else.

**Liquid Effluents.** Recycling of acid, soda, and zinc have long been necessary economically, and the acid-soda reaction product, sodium sulfate, is extracted and sold into other sectors of the chemical industry. Acid recovery usually involves the degassing, filtering, and evaporative concentration of the spent acid leaving the spinning machines. Excess sodium sulfate is removed by crystallization and then dehydrated before sale. Traces of zinc that escape recovery are removable from the main liquid effluent stream to the extent that practically all the zinc can now be retained in the process.

**Gaseous Effluents.** Twenty percent of the carbon disulfide used in xanthation is converted into hydrogen sulfide (or equivalents) by the regeneration reactions. Ninety to 95% of this hydrogen sulfide is recoverable by scrubbers that yield sodium hydrogen sulfide for the tanning or pulp industries, or for conversion back to sulfur. Up to 60% of the carbon disulfide is recyclable by condensation from rich streams, but costly carbon-bed absorption from lean streams is necessary to recover the remaining 20 + %. The technology to deal with this is becoming available, but there remains the danger that cost increases resulting from the necessary investments will make the fibers unattractively expensive compared with synthetics based on cheap nonrenewable fossil fuels.

**Energy Use.** Energy consumption in the xanthate process compares favorably with the synthetics. The methodology of assessing the energy usage of products and processes is currently the subject of much debate, and a standardized approach has yet to emerge. Not surprisingly, most of the published work on fibers was carried out during the last energy crises in the 1973–1981 period.

The early attempts to assess the total energy required to make baled staple fiber from naturally occurring raw materials—wood in the case of cellulosics and oil in the case of synthetics—used differing approaches and were insufficiently rigorous to allow hard conclusions to be drawn. In general, the fiber production sequence is broken into monomer making, polymer making, and fiber production, and although a variety of fibers are covered, only viscose rayon and polyester are mentioned in all of them (113–117). Tons of fuel oil equivalent per ton of fiber (TFOE/T) is the most popular unit, with rayon requiring from 1.7 to 2.4 TFOE/T and polyester requiring 2.6 to 4.2 TFOE/T.

The studies all concluded that rayon required less energy to make than polyester but there was little agreement on the magnitude of the difference. The wet-spun cellulosic fibers required more energy than melt-spun polyester for the fiber-making step, but they had no monomer energy requirement. The polymerization requirement was therefore minimal. In the case of the 1.7 TFOE/T figure for rayon, full credit was being given for the fact that the pulp mills energy needs were renewable and not dependent on fossil fuels. Pulp could be fed directly into the viscose process without incurring any transport or drying cost, and the pulp mill could be driven entirely by energy obtained from burning the parts of the tree that were not needed in the final product. This free and renewable energy was not counted.

**Fiber Disposal.** Cellulosic fibers, like the vegetation from which they arise, can become food for microorganisms and higher life forms; ie, they biodegrade. If necessary they burn with a rather greater yield of energy than natural vegetation. In complete biodegradation or incineration, the final breakdown products are carbon dioxide and water; these disposal methods simply recycle the cellulose to the atmospheric components from which it was made.

It is also possible to liberate and use some of the free solar energy that powered the manufacture of sugars and cellulose during photosynthesis. This can be achieved by burning or by anaerobic digestion. Slow anaerobic biodegradation occurs in all landfill sites dealing with municipal solid waste. This process generates methane from cellulose, which can be burnt to drive gas turbines. If future landfills are lined and operated with moisture addition and leachate recycling, then energy generation and the return of landfill sites to normal use can be accelerated (118).

**11.2. Lyocell Process.** The solvent route to rayon reinforces the inherent environmental benefits of regenerated cellulosic fibers by using a modern fiber production process which, being physical rather than chemical, reduces environmental impacts to a minimum.

*N*-Methylmorpholine *n*-oxide (NMMO), the solvent used, is manufactured by methylation and oxidation of morpholine, which comes from a reaction between diethylene glycol and ammonia.

Apart from woodpulp (as used to make viscose rayon) it is the only significant raw material used. It does not react with the cellulose and >99% of the

solvent in the dope is recovered in spinning and washing, reconcentrated and reused. It is considered to be practically nontoxic by oral or dermal route and would not be considered harmful by EEC labeling criteria. Similarly it is considered to be minimally irritating to skin and eyes by EEC criteria.

**Energy Use.** From an energy viewpoint, the solvent route to cellulosic fibers is identical to the viscose route up to the point where the cellulose enters the solvent. The energy content of the noncellulosic raw materials is significantly lower in the case of the solvent route, but the solvent route requires similar energy levels in dope handling, spinning, washing, and recycling. The lower water imbibition of the solvent fiber (65 vs 95%) yields savings in fiber drying and in any subsequent end-product washing and drying operations. Overall, the solvent route is capable of showing a useful economy in this important resource when compared with viscose production on the same scale.

**Fossil Reserves.** The ethylene glycol for NMMO manufacture currently comes via ethylene from oil refineries. However, as indicated above, the solvent recycling rate is so high that solvent usage is kept down to a few kilos per tone of fiber, and hence fossil reserve dependence is minimal.

**Gaseous Emissions.** The solvent process produces very little atmospheric emission. There are traces of volatile organic compounds associated with the solvent and the soft finish, which will leave the plant in the normal course of ventilation.

**Liquid Effluents.** The solvent route uses much less water than viscose, and the process effluent needs significantly less treatment.

## 12. Future Considerations

Johnson (119) argued that continued population growth and increased per capita fiber use will result in a demand for a further 70 million tons of fibers by 2050. With the potential for further cotton yield or hectareage increases now limited, and with the synthetics still looking unlikely to provide the comfort element of future textiles, Johnson postulates a "Cellulosics Gap" of up to 20 million tons.

He points out that for 60 years, cotton production has grown almost entirely because of increased fiber yield per hectare. Land area under cotton cultivation has been constant for that period, and pressure for the same top quality agricultural land will increase because of the need to feed increased population. Better irrigation, higher pesticide use, higher chemical fertilizer use, and genetic improvements achieved the cotton yield increase. In fact cotton cultivation in Russia became so intensive that despite its benign environmental image it has been the origin of environmental degradation on a massive scale (120). In the 1980s, a ton of Central Asian cotton required approximately 800 kg of fertilizers, 100 kg of pesticides, and an aggregate of 1.5-m depth of water per square meter of growing area. In recent years cotton yield per acre has leveled off.

It is taken for granted that the implied need for an additional 50 million tons of synthetics could be readily provided. The predicted 20 million tons shortfall in absorbent or "comfort" fibers is likely to be filled by a combination of a variety of technologies:

1. Development of more comfortable blends containing progressively less cellulosic fiber.
2. Some increased yield of cotton per hectare from genetic engineering advances yet to be achieved.
3. Some increased use of prime agricultural land for cotton growing.
4. Development of low cost viscose and lyocell fibers.
5. Development of soft flax fibers encouraged by agricultural subsidies and improved fiber-separation methods.
6. Development of truly hydrophilic synthetics.
7. The direct use of wood fiber in textiles.

In order for rayon to benefit from the opportunity offered by this increasing demand for fibers, the price differential between cellulose and polyester must be reduced. The technology to achieve this does exist, but the justification for the necessary long-term investment becomes increasingly difficult as research into ever more comfortable synthetics pays off. Existing rayon plants will be unable to compete with polyester plants unless the relative costs of woodpulp and oil change dramatically in woodpulp's favour. The sustainability of cellulose and the transience of fossil reserves means that this change is likely, but not in the timeframe beloved of today's investors. In the meantime 350,000 ton/annum lyocell plants linked to a major source of low cost pulp and using a modified process to make fiber with properties similar to current viscose rayon would appear to be one of the few options for further growth of the regenerated cellulosic class of fibers.

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