9
Applications development

CALVIN WOODINGS

9.1 Artificial silk

The original cellulose nitrate yarns made by Chardonnet looked like silk and were naturally marketed at prices close to those of silk in traditional silk applications. As described in Chapter 1, the desire to emulate the silkworm had been the original driving force behind the technology, and at the end of the 19th century, the successful commercialisation of artificial silk was one of the great symbols of industrial progress. Chardonnet silk was thus assured an early success if only because of its novelty. Despite being less than half the strength of silk and much more prone to shrinkage, it could be converted into decorative trimmings, ribbon and lace, and its astonishing lustre made it ideal for embroidery. Poor wet performance made it more suitable for embellishing home furnishings than for apparel, and natural silk remained largely unchallenged in garments.

Cuprammonium rayon followed cellulose nitrate into the same markets, but having slightly less lustre it did so at a slightly lower price. The first viscose rayon yarns inevitably found applications in similar markets and, despite having been developed to make carbon lamp filaments for the new electric lights, it found a much larger market in braids for the old incandescent gas lighting. Clearly these applications were not really big enough to support a major industry, and the problems of weaving these products into broad, as opposed to narrow, fabrics had to be solved before the market could be expanded significantly.

While the new viscose rayon yarns proved easier to use as weft (across for example a cotton warp), the painstaking work carried out by Samuel Courtauld & Co at Bocking in Essex was a major contributor to both Courtauld's and the artificial fibre industry's rapid growth. In what was one of the early examples of the benefits of captive customers, Courtauld's Bocking weaving mill had to take the entire output of the Courtauld viscose factory in Coventry for the first year of operation. Little if any saleable fabric resulted, but the practical experimentation taught Courtauld's textile technologists how to modify the multitude of processes downstream of fibre making to suit the new yarns. Few if any independent weavers, as Courtauld's competitors who had to sell yarns on the open market discovered, could afford to stay the course.

Towards the end of 1906, the first broad woven viscose rayon fabric from Bocking started to sell and indeed, became fashionable. It was a striped fabric, the stripe being achieved by alternating bands of cotton and rayon across the warp and filling it with a 100% cotton weft. Viscose dyed darker than cotton, and this enhanced the great difference in lustre between the two fibres. A new market was thereby created, and for the next five years the new viscose yarns were used almost exclusively by Courtauld in the ornamentation of cotton fabrics. Not quite the market envisaged by Tetley when he sold the idea of manufacturing artificial silk to the Board of England's leading manufacturers of mourning crepe, but after years of difficult development, a welcome breakthrough. Stripes were in many ways an ideal opening gambit for the new fibres. The bulk fabric properties were largely unaffected by the original narrow stripes, dyeing differences became an effect rather than a problem, and as quality improved wider stripes could carry increased throughput. During the same period, Courtauld gained access, thanks to a curious patent judgment, to the German spin-bath technology that allowed the manufacture of stronger, more consistent yarns (see Chapter 1) and was in an ideal position to increase the use of them.

These new yarns made using the so-called Müller Bath, finally allowed satisfactory quality fabrics to be woven by Courtauld and others with viscose in the weft. A new series of applications resulted. Courtauld branded the new fabrics 'Luvisca' and developed outlets for the new fabrics in shirtings (cotton warp), blouses (silk warp), and, of course, the lining fabric (silk or cotton warps) that remains an important end-use to this day. As yarn quality improved further, viscose replaced the silk in the warp, and by 1914 Courtauld's Halstead Mill was using 100% viscose warps on 200 looms.

The problems of knitting viscose yarns were solved in 1912 by Wardle and Davenport of Leek, who had been Courtauld's first ever external customer, responsible for opening up the braid market to viscose. Silk hosiery had been an important target market since the early attempts to break out of the narrow fabrics niche, but most stocking manufacturers were fundamentally opposed to trying it, despite yarns being offered free of charge to encourage developments. Wardle and Davenport's eventual success owed much to a new knitting machine acquired from Wildt & Co in Leicester, said to be suitable for the new artificial silk yarns. This proved to be the case; others followed Wardle and Davenport's lead, and hosiery became one of the main outlets for viscose until nylon replaced it in the 1940s.

Table 9.1 T.V.C.: distribution of yarn sales by buyers expressed as sales by value, 1916–1918

Trade of buyers	Percentage of sale, by value		
	1916	1917	1918
Hosiery	52.7	40.8	40.3
Cotton	10.4	12.7	11.5
Silk	3.3	3.7	4.2
Woollens	0.9	0.2	..
Jobbers	20.1	31.2	32.7
Knitters	4.5	2.4	2.6
Plush	1.8	3.1	0.8
Tapestry	0.9	1.2	1.1
Underwear	0.6	0.4	0.5
Braid	2.2	1.8	3.5
Embroidery	1.9	2.3	2.8
Webbing	0.6	0.1	..
Lace	0.1	..	..
Exports	..	0.1	..
Total	100.0	100.0	100.0

T.V.C. is The Viscose Company, the US subsidiary of Courtauld.
Source: D.C. Coleman, *Courtaulds: an Economic and Social History*, Clarendon Press, Oxford, 1969.

In the USA, knitted hosiery was the first volume outlet for viscose yarn from the American Viscose Corporation's Marcus Hook (Pennsylvania) plant when it commenced production at the end of 1910. It is not clear whether the US knitting machines were superior to those in Europe, or whether the absence of 'captive' weavers prevented the development of woven fabrics until the viscose yarns were more dependable. By the outbreak of war in 1914, hosiery was the biggest single market for viscose on both sides of the Atlantic (see Table 9.1).

9.2 Artificial cotton

The period between the wars saw a dramatic expansion of rayon usage fuelled primarily by the expiry of the basic patents on the fundamental filament yarn technology. Despite the retarding effects of the Great Depression, every year for 20 years world rayon capacity (including acetate rayon) increased by 60000 tonnes on average.

This growth was fuelled mainly by the development of a whole range of new applications for what used to be the yarn process waste, staple fibre.

Between 1905 and 1910, the Coventry viscose plant produced thousands of tonnes of waste most of it looking not unlike dirty cotton wool, and most of it dumped on vacant land around the plant. As early as 1907 Tetley proposed extracting some value from this waste and had his chemists briefly investigate ways of making it suitable for the wool and cotton spinning systems. That this development was largely ignored speaks volumes about the preoccupation at that time with making a success of the technically more difficult continuous filament route in the then much more attractive silk market. So it fell to a Frenchman, Augustin Pellerin to patent the first staple process[1] and the first commercial process and applications were later developed in Germany.

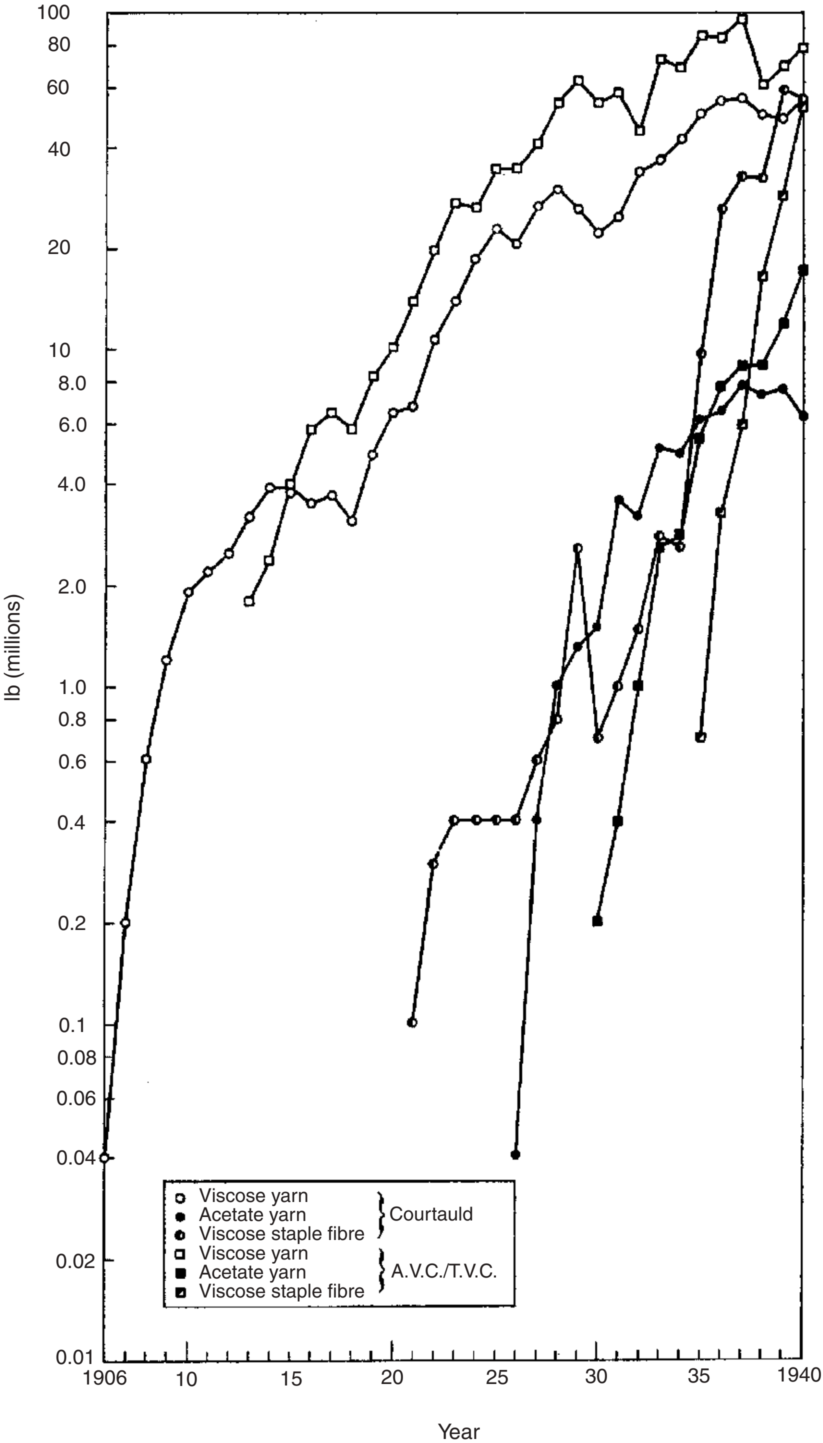
The success of this apparently bizarre step of adding value by improving the quality of waste is best illustrated by the fact that at the end of this 20-year period, half of world viscose production capacity was devoted to the waste product that had been largely exterminated two decades earlier. Further incongruity, of course, arose from the need to chop up an eminently weavable and knittable yarn in order to make a different type of yarn by a different type of spinning process. It is hardly surprising that the early proposals to exploit this route did not command the attention of those struggling to improve the quality of the filament route output.

However, in 1930, when the need to expand the application base for viscose into much larger, growth-sustaining markets was becoming evident, the logic for staple becomes clear. Seven million tonnes per year of the natural staple fibres, cotton and wool, were entering the textile market through a route closed to viscose, at a time when viscose filament sales proudly passed the 200 000 tonnes per year mark (see Fig. 9.1).

Filament yarns had proved to be very different, in many respects, to yarns spun on the cotton or woollen systems. Consumers proved reluctant to give up the aesthetic advantages of such yarns just because the new filament route was technically superior. Filament cellulose was leaner, weaker, and much softer and slipperier than staple cellulose as exemplified by spun cotton. Furthermore, cotton, being a partially collapsed tubular fibre was bulkier and warmer than the solid viscose fibres.* These were all good reasons why viscose would have to be converted on the cotton system to gain access to broader apparel markets.

It was during World War I, especially in Germany where cotton shortages were more acutely felt because of a successful Allied blockade of the

* The early attempts to use viscose filament in applications such as shirtings were probably only successful in the way that nylon filament was successful in shirtings in the 1960s. It was new and exciting and clever marketing people could persuade technically aware customers to buy it – for a time.



9.1 The introduction of viscose staple (and acetate yarn) by Courtauld's UK and US plants maintains total growth as viscose filament yarn growth rates decrease in the 1930s. (Reproduced from *Courtaulds: An Economic and Social History*, Clarendon Press, 1969.)

ports, that viscose yarn waste was deliberately cut up, cleaned and baled so that it could be blended with cotton and spun into yarns on the cotton system. The German government encouraged further developments by ordering 3000 tonnes from VGF, and the new staple was used instead of cotton in a variety of military textiles, and some apparel.

While this certainly accelerated the technical development of staple fibres and the processes to manufacture them, it did little for the market acceptance of what were, in reality, low quality cotton substitute fabrics with wartime economy connotations.

In the UK, Courtauld's interests in staple were confined to increasing the value of filament waste by making it more suitable for the wool combers. In 1921 they installed the first staple machine in Coventry, launched staple fibre under the 'Fibro' brand, and marketed at a price and quality that made it impossible to compete with the mainstream natural fibres. In this particular incarnation, Courtauld's staple fibre sales (excluding cut-filament waste) were to remain below 400 tonnes per year until 1928.

The Italian company, Snia developed the first efficient continuous precision cutter for large acid tows, launched their product as 'Sniafil' in Italy in 1925, and announced an intention to build a plant in Britain to make it. Snia (Società di Navigazione Italo-America), founded in 1917 as a trading company, acquired the Société Italienne de la Viscose and became Snia Viscosa in 1922 at the start of an Italian rayon boom. By the end of 1925, they controlled 60% of Italian rayon production, were the second largest rayon producer in the world, and thanks to aggressive pricing, were, after Courtauld, the leading supplier to the UK and USA markets. Courtauld had to react and began to produce, at the Aber Works* in Flint, a more economical filament yarn to meet this competition. In 1926 the Italian boom ended, Snia Viscosa weakened, and in 1927 Snia's founder, Riccardo Gualino, sold a controlling interest in the company to VGF and Courtauld jointly.

The Courtauld board, exposed in the course of the deal to the success of the Sniafil process, decided in 1928 to increase emphasis on staple fibre production, and concentrated its production at their more economical Aber Works. Success for Courtauld 'Fibro', however, still had to wait until a 'Sniafil' machine could be started up at Aber a few years later. Courtauld's first dedicated staple plants commenced production in 1936 at Greenfield near Flint in North Wales and at Nitro (an old cellulose nitrate explosives plant acquired by Courtauld in 1921 to process cotton linters) in West Virginia in 1937.

* Originally VGF's plant in the UK, and known as the British Glanzstoff Manufacturing Co., it was bought by Courtauld in 1917, with the encouragement of a UK government suspicious of 'enemy ownership'.

Despite the depression in world economies during the 1930s, the expansion of rayon staple production in Germany, Italy, Japan, Britain and the USA was phenomenal, especially after 1935. Over the 10-year period, sales of staple went from 3000 to 585 000 tonnes per year, overtaking 40 years development of filament (including acetate) which reached 542 000 tonnes per year in 1940.*

9.3 From speciality to commodity

If the development of staple fibre represented the ultimate move down-market for an artificial silk producer, there were many other changes needed to maintain the growth of filament sales. Costs had to be reduced and qualities of yarn had to be developed to suit a broader range of markets.

Cost reductions came initially from the economies of increasing production scale but by the late 1920s further progress was driven by falling market prices and technical solutions were required. The original labour-intensive hank-washing process was still being used to clean up the acid 'cakes' of yarn from the Topham boxes, but automatic 'cake-washing' machines were under development and were brought into use slowly† in the early 1930s. Process chemicals, especially the washing liquors, were routinely discarded, but as improved acid and caustic soda recovery processes were developed they were gradually adopted.

As the end-uses expanded beyond silk replacement, the harsh metallic lustre of the yarn proved disadvantageous and dull or matt fibres had to be developed. A French approach to the problem, patented in 1921[2] was to trap air in the yarn to give it a bulky wool-like texture and appearance. Dull yarn resulted naturally from the gas bubbles in the yarn, but the process was inherently harder to control than the bubble-free process. 'Oil-dulling' was invented by Walter Glover[3] of Courtauld who in 1926 patented the addition of petroleum jelly to the viscose. This development allowed Courtauld to establish the 'Dulesco' brand in hosiery where its opaque appearance met the fashion of the day, and its self-lubricating nature proved ideal for the knitting process. The American, James Singmaster developed an improved dulling method using titanium dioxide[4] in 1929. Courtauld eventually licensed the Singmaster patents from American Tubize, first in the USA (1936) and then in Europe where they had earlier regarded the Singmaster patent as invalid. (There is no record of how the abrasive titania-containing yarns fared on the knitting machines.)

* Source: CIRFS, Brussels.

† 40% of Courtauld's output in 1935 was cake washed, and this had risen to 70% by 1939.

The expansion of both filament and staple viscose rayon production, leading as it did to lower prices and a much broader range of textile applications, did much to improve the range of clothing available to working men and women. In retrospect it is unlikely that natural fibres alone could have met the demands created by increasing populations.

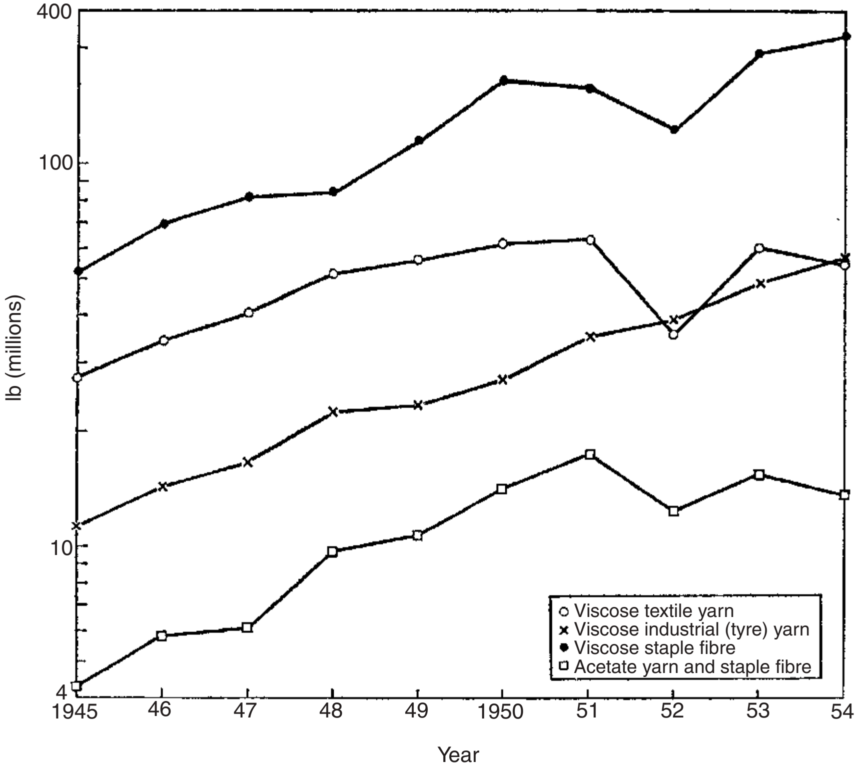
9.4 Industrial yarns

Courtauld's early 1920s attempts to use viscose yarn as a substitute for cotton reinforcement in Dunlop's pneumatic tyres failed because the strength of the filament yarns could not match the strength of spun cotton. Much research and development on the strength problem followed in most viscose companies, the first commercial fruit being the process,* developed in the late 1920s by Lilienfeld. VGF and a new British company The Nuera Artficial Silk Company, licensed it and set out to manufacture tyre yarns (1925). Courtauld acquired the Lilienfeld rights from Nuera in 1927 and commenced small-scale production both in the UK, and, as part of a collaborative venture with VGF, in a new factory in Cologne. They also sold the rights, in 1934, to their US subsidiary, AVC, as a defence against a new viscose tyre yarn emerging from DuPont.

However by then, Courtauld UK had dropped the Lilienfeld approach in favour of what was to become the most enduring solution to the strength problem. This came from the work of John Givens and Leslie Rose[5] who patented the use of hot water or steam to heat the incompletely regenerated yarn while stretching it. This gave strong yarns with much better resistance to abrasion than the Lilienfeld yarns. Cotton shortages and the military importance of tyres accelerated the pace of this line of development, and in 1939, about 20 years after the tyre yarn market had first been targeted by Courtauld research, large scale production commenced in the new factory at Preston in Lancashire. By 1945, 5000 tonnes per year of tyre yarn were being produced by Courtauld's alone. Ten years later this had increased by a factor of five. By the 1960s a significant part of the world's production of continuous filament viscose yarn went for tyre cord and other industrial applications (see Fig. 9.2).

The tyre yarn manufacturing process proved capable of improvement on several occasions as the demands of the tyre industry increased. The process which had first produced yarns with strengths above 2.5 g den^{-1} in the late 1930s was, by the end of the 1960s capable of producing high modulus industrial yarn at 10 g den^{-1}.

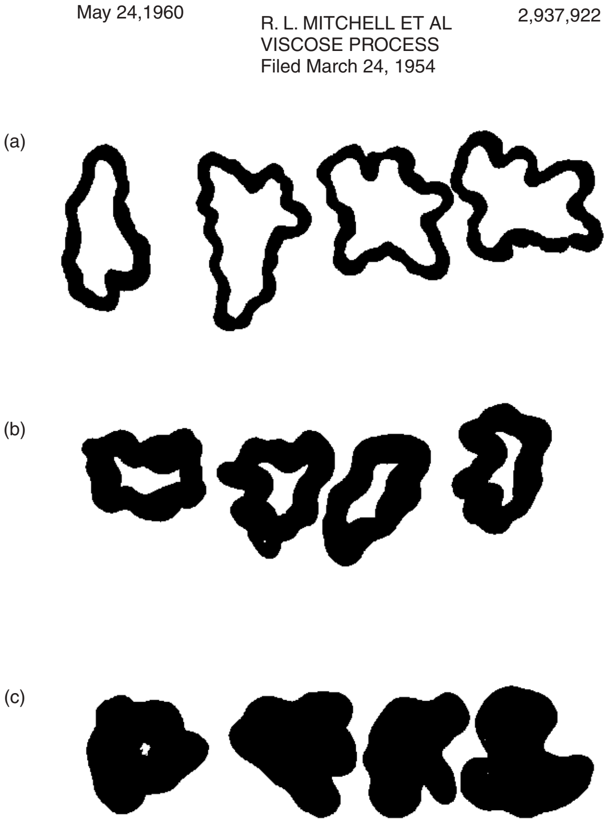
* Patented by Lilienfeld in June 1925. The patent revealed a way to make 5 g $denier^{-1}$ viscose fibres by spinning into strong sulphuric acid (~70%) and stretching at high tension before washing.



9.2 Courtauld's UK production 1945–1954: The growing importance of staple and tyre yarn developments. (Reproduced from *Courtaulds: An Economic and Social History*, Clarendon Press, 1969.)

After the development of hot stretching, further strength gains were achieved by adding amines to the spinbath. In 1947, Norman Cox of DuPont patented[6] the use of monoamines that have between 4 and 10 carbon atoms as 'modifiers', allowing the production of stronger yarns by permitting the spinning of unripe viscose. Extensive research on the effects of modifiers followed, and a further doubling of strength came from the use of mixed modifiers added to the viscose (developed by Mitchell *et al.*[7–9] for Rayonier). (see Fig. 9.3)

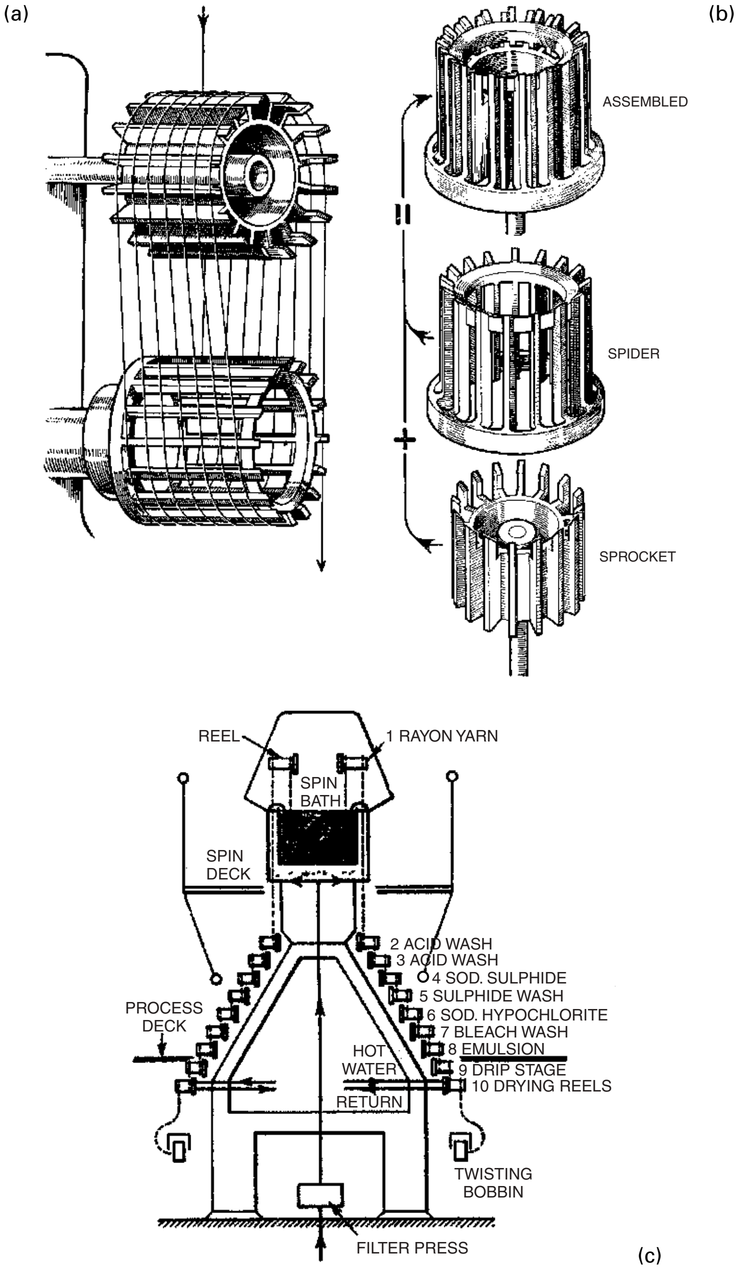
The development of continuous spinning and washing processes allowed the more economical production of yarns both for apparel and industrial use. These compact machines allowed the dried and finished yarn to be wound on bobbins within minutes of spinning. For industrial yarns they allowed higher tenacities to be achieved partly through their ability to strain dry the yarn. For apparel yarns, their inability to produce a yarn completely free of strain (and hence shrinkage potential) meant that the old cake



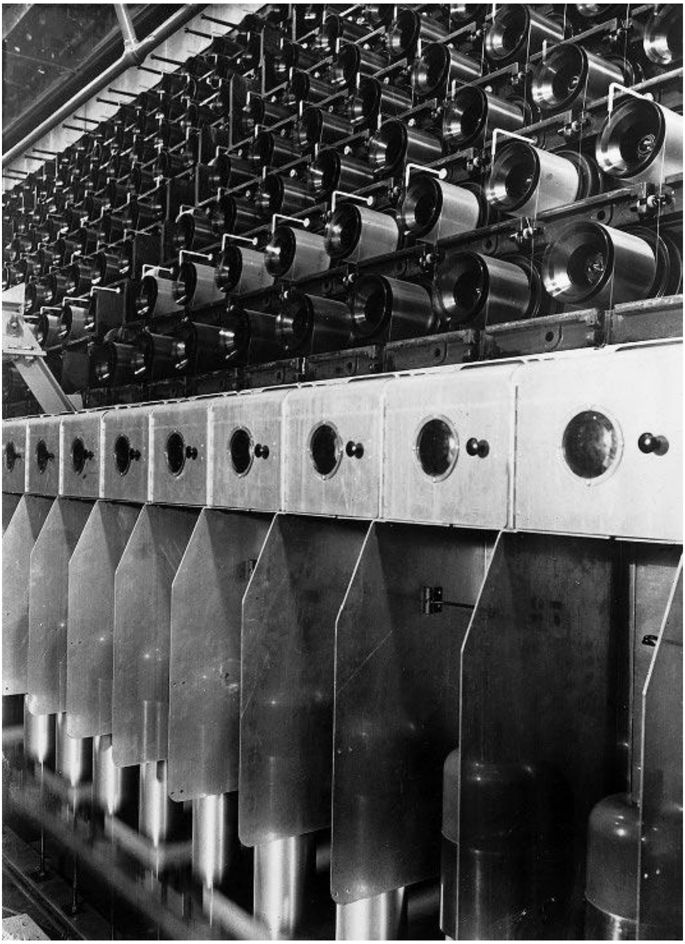
9.3 Development of stronger all-skin tyre yarns with modifiers: (a) textile yarn; (b) an early tyre yarn; (c) all-skin tyre yarn made by adding dimethylamine or dimethylformamide to the viscose and/or spinbath.[7]

process was often preferred for the highest quality materials. While the early continuous processes simply formed a 'warp' of all the yarns leaving the top godets of the spinning machines and then washed and dried this warp over rollers or drums, the invention of the self-advancing reel by the Industrial Rayon Corporation of America (c. 1937: see Fig. 9.4(a)–(c) and Fig. 9.5) provided the most elegant and compact of continuous processes. The reel design was licensed by Courtauld and others and machines based on it produced most of the world's viscose tyre yarn from the 1950s onwards.

The demand for such elegant cellulosics was however diminishing as the new synthetic industrial yarns came down in price. Furthermore the drive for improved modulus and tenacity had highlighted what appeared to be a fundamental weakness of regenerated cellulose technology: the more



9.4 The development of a continuous spinning process with self-advancing reels to convey the yarn at high speed through the washing liquors was necessary to make the improved tyre yarns. (a) and (b) illustrate how the self-advancing reel is constructed. (a) Two cages (a sprocket above and a spider below) set eccentrically advance the yarn. (b) The sprocket fits into the spider on an eccentric axis to form the complete thread advancing reel. (c) A machine cross-section diagram illustrating the washing stages each taking place on a single self-advancing reel. (Reproduced by courtesy of Courtaulds.)



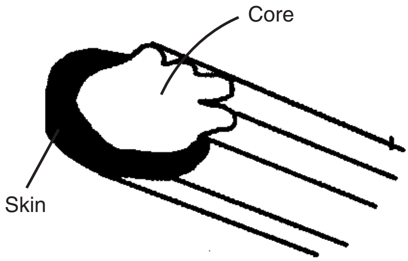
9.5 Viscose tyre yarn spinning-continuous process on self-advancing reels. (Reproduced by courtesy of Courtaulds.)

oriented and crystalline the cellulose became, the more the fibres fibrillated. Fibrillation brought with it poor lateral strength and hence poor abrasion resistance.

9.5 Modified staple fibres

9.5.1 For wool markets

If the filament process transferred easily to the new staple machines to make a product that could be used in blend with cotton without too much loss of cotton-like character, the same was not the case in wool markets.



9.6 Chemical crimp arises from the core bursting through the skin.

For success in wool outlets, where altogether bulkier, warmer fabrics were expected, coarser crimped staple fibres had to be developed.

Acetate rayon or the new synthetic fibres were easily crimped by mechanical devices that formed them into waves or spirals and set them into the new shape using heat. Viscose on the other hand had to be regenerated in such a way that the filaments became effectively bicomponent, one half having a more oriented structure and therefore shrinking more than the other half in subsequent washing and drying. This was achieved by using viscose and spinbath combinations that caused the rapid formation of a thick skin, which shrunk so fast that the filament burst open exposing fresh liquid viscose to the spinbath just before the filaments emerged onto the godet (Fig. 9.6). The difference in structure of the early and late fixed halves of the fibre could be amplified in stretching and as soon as the bundle of filaments were free to separate after cutting and sluicing (see Chapter 3) the wavy form developed and was finally set in place by the hot acid treatments on the wash machine.

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.

While crimped viscose fibres could be made at any denier, the finer crimped fibres were easily straightened in cotton-type yarn manufacture and they added little to the performance of fabrics. However, coarser fibres could be made with more durable crimp and these found applications as wool diluents in carpets, especially in the new tufted carpets that emerged in the late 1950s.

By the mid-1960s staple fibre use in dress fabrics was declining but crimped fibre for tufted carpets had become the single largest application for the cellulosic fibre. It was significantly cheaper and had a better texture than the new acrylic and nylon carpet fibres but was not as hard wearing. Some improvements in durability were achieved by applying tyre yarn process conditions to the staple machines, but the chemical conditions required for the highest durability were incompatible with crimp generation and vice-versa. As nylon, especially the bulked continuous filament version came down in price, the cellulosic fibre found it hard to compete.

9.5.2 For cotton replacement

To increase the marketability of viscose fibres in cotton outlets, two distinct lines of development were undertaken. These were to minimise the two most obvious deficiencies of viscose fibres when compared with the chemically identical cotton fibre in woven fabric form. Viscose fabrics were always leaner, limper, more prone to shrinkage and had a sleazier wet texture than identically constructed cotton fabrics.

The first approach was to boost the strength, modulus and stiffness of the fibre so that its durability and shrinkage could closely match that of cotton, and the second was to alter the shape of the fibre to give bulkier, more cotton-like textures than could be achieved by the chemical crimping process mentioned above. In an ideal world it would have been possible to combine both of these approaches in a single fibre with the strength and bulk properties of cotton. In reality, the chemical constraints of the viscose process means that the simultaneous achievement of high bulk and high modulus has yet to be achieved even in the laboratory.

High wet modulus (HWM) rayons of two types were developed. *Modal fibres*, which were staple versions of the tougher tyre-yarn fibres, 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 fibres with even better wet stability and higher wet modulus were introduced to blend with and substitute for the better grades of cotton.

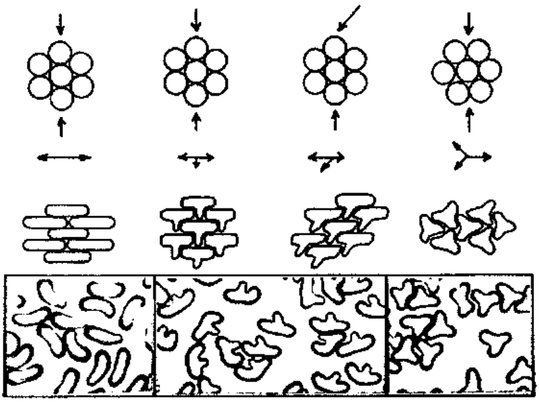
In fact, the polynosic fibres were developed first, and used radically different process technology from other forms of viscose. Whereas all the developments in viscose to this point appear as a more or less continuous evolution from the first use of the Müller spinbath, the polynosic process developed by Tachikawa[10] in 1952 was revolutionary. He abandoned the zinc and modifier route to higher strength in favour of a very short immersion in a cold low-acid low-salt zinc-free spinbath which did little more than coagulate the viscose. To make the viscose spinnable in such a bath and to get the desired strong high modulus fibres, he had to use cellulose with a high degree of polymerisation (minimal mercerising of the alkali-cellulose), xanthated to a high degree (in fact with an excess of carbon disulphide) and dissolved at an almost uneconomically low concentration in unusually dilute alkali to give a very viscous solution.

His process allowed filaments of cellulose xanthate to be drawn from the bath and stretched to three times their spun length before being regenerated in hot dilute acid. The high stretch oriented the cellulose molecules to a very high degree, giving the resulting fibres a high dry strength, an unusually high wet-to-dry strength ratio, a very high modulus and a characteristically high resistance to caustic soda. This latter point was regarded as important to allow the viscose fibre to be blended with cotton prior to the mercerising (caustic) treatment, regular viscose being almost completely destroyed by this treatment.

Polynosic staple fibres were produced in Japan, England, France and the USA during the 1960s but failed to gain the hoped-for share of the cotton-spinning market. One problem was the fact that they were more expensive than standard viscose, another related to the fact that being highly oriented, they fibrillated on wet-processing and could not easily be dyed to clean bright colours. Yet another problem arose from the almost perfectly circular cross-sectional shape: they made even leaner yarns than irregularly shaped standard viscose fibres. All producers therefore sought ways of reducing the orientation and perhaps surprisingly, with the exception of the Japanese, reverted to the older staple version of the high zinc tyre yarn process to make the above mentioned modal range of fibres.

Toyobo's 'Tufcel' provided an excellent example of how a modern polynosic fibre process, probably the most difficult viscose process to run efficiently, operated.[11] On-line process control allows only four persons per shift to make 10000 tonnes per year of a variety of special fibres including flame retardant, deep-dyeing (two types), activated carbon fibre, and super fine (0.5 denier). Alk-cell and mixing-soda quality are maintained by pressings soda centrifugation, filtration and dialysis to remove 90% of the hemi-cellulose. (Ion exchange membranes are used to give 50 times the life and twice the efficiency of the old dialyser bags used in tyre 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 deniers have 40 μm holes, and these are protected by automatic backflush filters removing gels down to 15 μm diameter.

Avtex went further than most in trying to make cotton-like modal fibres from a variant of the tyre yarn process. Using a process developed by ITT Rayonier, they attempted to address the leanness problem, and made a lobed-section, crimped high wet modulus fibre. Rayonier also licensed it to Saeteri, Sniace, Sniafi and Snia Viscosa. Only Avtex introduced the process commercially as Avril Prima® and for its launch ITT Rayonier mounted what was probably the first and last TV advertising campaign in support of a rayon fibre. Avtex also developed a novel way of modifying the cross-section of their standard 'Avril' modal fibre by deforming the incompletely regenerated fibres on the godet. The simple mechanical forces of pressure and shear allowed the production of fibres with a



9.7 Bulky high modulus fibres are very hard to make using viscose technology, but this approach deformed the fibres while still in the gel state. Diagram shows flat and three-lobed rayon cross-sections. (Reproduced from chapter by J Dyer and C Daul in *Fibre Chemistry*, ed. M Lewin and E M Pearce, Marcel Dekker, 1985, Volume IV *Handbook of Fibre Science and Technology*.)

roughly trilobal shape and reasonably high modulus (see Fig. 9.7). When dulled with titania pigment, these fibres were said to give a handle and appearance very similar to cotton. They did not, however, have the same high modulus.

As mentioned above, the really high moduli were appropriate for cotton blends, and to start with, the intermediate wet-modulus rayon's targeted polyester blends. However, with the exception of some industrial end-uses such as sewing threads and hose reinforcement, the intermediate wet modulus rayons were easily replaced by cheaper regular rayon simply by increasing the proportion of polyester in the blend.

Courtaulds therefore approached the problem of attacking the rapidly growing polyester/cotton market by getting the bulk right and sacrificing the high modulus. The resulting inflated viscose fibres, introduced in the late 1970s were in fact a spin-off of earlier attempts to replace cotton in a completely different market sector, speciality papermaking. Inflating the fibre allows simultaneous increases of bulk and absorbency but at the expense of fibre strength and processability. Flat fibres are self-bonding and only usable in wet lay or papermaking processes (see Table 9.2).

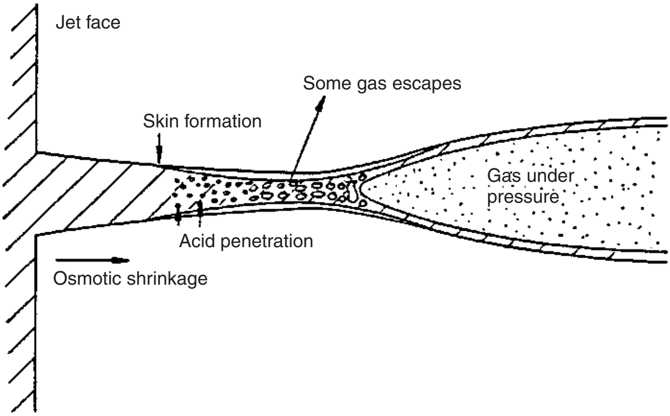
In the 1960s and 1970s, viscose producers in Europe, the USA and Japan made various attempts to make rayon behave more like cotton in speciality papers. Avtex (USA) and Courtaulds (UK) commercialised inflated/collapsed papermaking fibres under the codenames 'RD101' (Avtex) and 'PM1' (Courtaulds). Kurashiki Rayon (Japan) also entered the market.

Table 9.2 Inflated viscose rayons and their properties

Cross section	Name	Water imbibition (%)	Dry tenacity $(\mathrm{g\,den^{-1}})$	Dry extension (%)	Comments
	Standard rayon	90–100	1.9–2.5	18–30	Uninflated rayon for comparison
	—	110	—	—	Not commercial
	Viloft	120–140	2.2–2.5	13–15	High bulk cotton-like textile fibre
	PM2 fibre	150–160	1.8–2.0	20–25	Self-bonding fibre for wet laid nonwovens
	PM1 fibre	160–180	1.4–1.8	20–25	Self-bonding fibre for quality papers
	Super inflated fibre	190–350	1.0–1.4	30–50	Highly absorbent, opaque and bulky fibre for nonwovens

Courtaulds fibre met the technical specifications to replace cotton in banknote papers and the rayon technology enabled some useful new security features to be incorporated. However, also for security reasons, the currency manufacturers required total exclusivity for such a fibre and because Courtaulds had identified a major new market for the same fibre in disposable diapers, restriction of sales of this fibre type to the smaller currency market was not acceptable.

Inflated fibres (Fig. 9.8) were made by injecting a gas or gas-forming compound such as sodium carbonate into the viscose.[12] When the regeneration conditions had been adjusted to form an impervious skin on the fibre as it emerged from the spinneret, the gas was retained in the forming fibre and the resulting bubbles would coalesce into a tube. To make fibres suitable for papermaking, the tube had to be sufficiently thin walled to allow it to collapse across a diameter in washing and drying. The resulting smooth-surfaced flat filaments were highly self-bonding simply because they were deformable enough to come into intimate contact with one another as they dried, and when in contact hydrogen bonding locked them together. As with



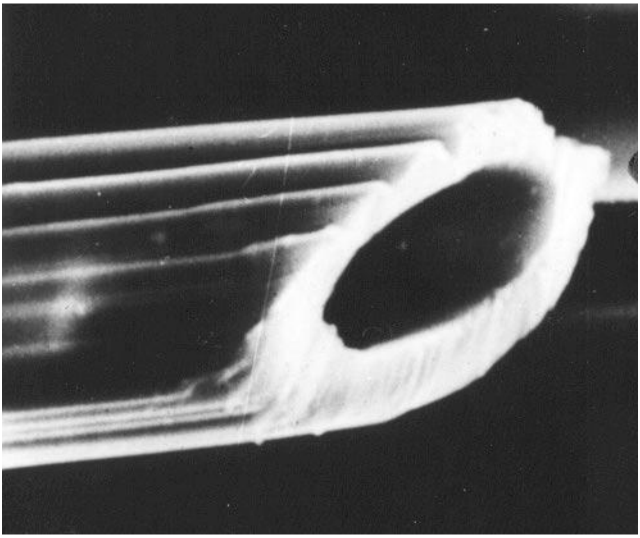
9.8 Inflation levels can be controlled by adjusting the stationary bubble diameter, which in turn depends on the rates of gas evolution and gas escape through the forming filament.

cotton and woodpulp, wet strength could only be achieved by adding resins such as melamine–formaldehyde, but without these resins the inflated rayon papers had an even greater tendency to disintegrate in water.

It was this 'flushability' that attracted the attention of the embryonic disposable diaper makers at a time when the consumers were reluctant to dispose of soiled diapers in the dustbin. The flat fibres could be made into an absorbent cover tissue that could be reinforced to just the right degree to allow coherence in use yet disintegrate in the much higher turbulence of the toilet bowl.

Courtaulds (UK) were alone in commercialising two other inflated fibres targeting cotton markets. The first, an uncollapsed tube (see Fig. 9.9), was not self-bonding, but had the bulk and handle of cotton. While the initial justification for developing and launching this fibre was indeed cotton replacement, the marketing and pricing policy positioned it as a premium product with unique aesthetics for high fashion applications. As with all fashion applications, success can be short-lived and dependent on the size and creativity of the marketing effort. It ultimately found worthwhile and continuing application in thermal underwear until the only factory capable of making it, Greenfield Works in the UK, was closed in 1984. Courtaulds then developed a solid flat cross-section fibre (see Fig. 9.10) that had similar bulk and could be sold under the same brandname ('Viloft').

The other inflated fibre arose from the uneven collapse of a very thin-walled tubular fibre and had a very high absorbency. This fibre briefly enjoyed large and profitable sales as a replacement for cotton in tampons in the 1980s under the brandname 'SI Fibre' (see Fig. 9.11). This fibre was



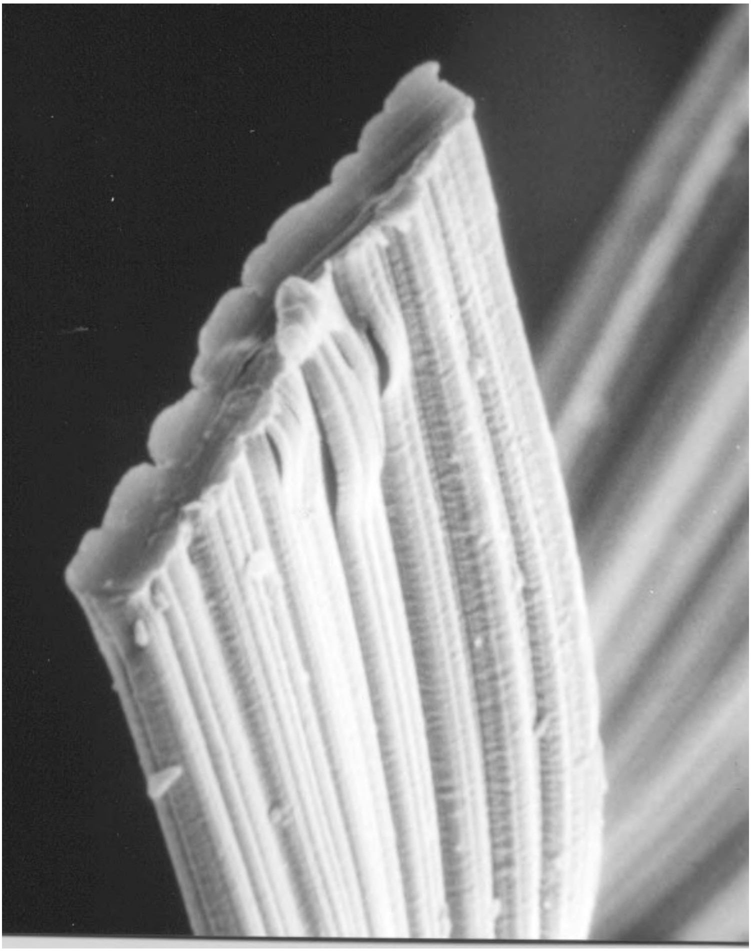
9.9 Courtaulds Viloft®: the first commercial inflated rayon staple. (Reproduced by courtesy of Acordis.)

also adversely affected by the decision to close the versatile Greenfield Works, and after a short period of production in France and Canada, it too was replaced by a solid Y-shaped fibre, 'Galaxy' (see Fig. 9.12). Galaxy, made on ordinary staple machines from Y-shaped spinneret holes of a size impossible to make a decade earlier, provided many of the unique attributes of the collapsed tube fibre while being easier to produce and process. In Japan, the Daiwabo company still manufactures a range of inflated fibres for special paper and hygienic applications.

At the time of writing, both Courtaulds' unusually shaped cotton replacement fibres remain in production. The development of applications for these and their inflated precursors allowed Courtaulds in particular to begin to appreciate the merits of non-traditional, non-textile markets for their rayon fibres. Collectively known as the Unspun or Nonwoven markets for fibre, these markets, unheard of in the first half of the century, became increasingly large users of rayon fibre during its third quarter. Attempts by regenerated cellulose fibre producers to develop further products to suit this new range of applications was a natural consequence.

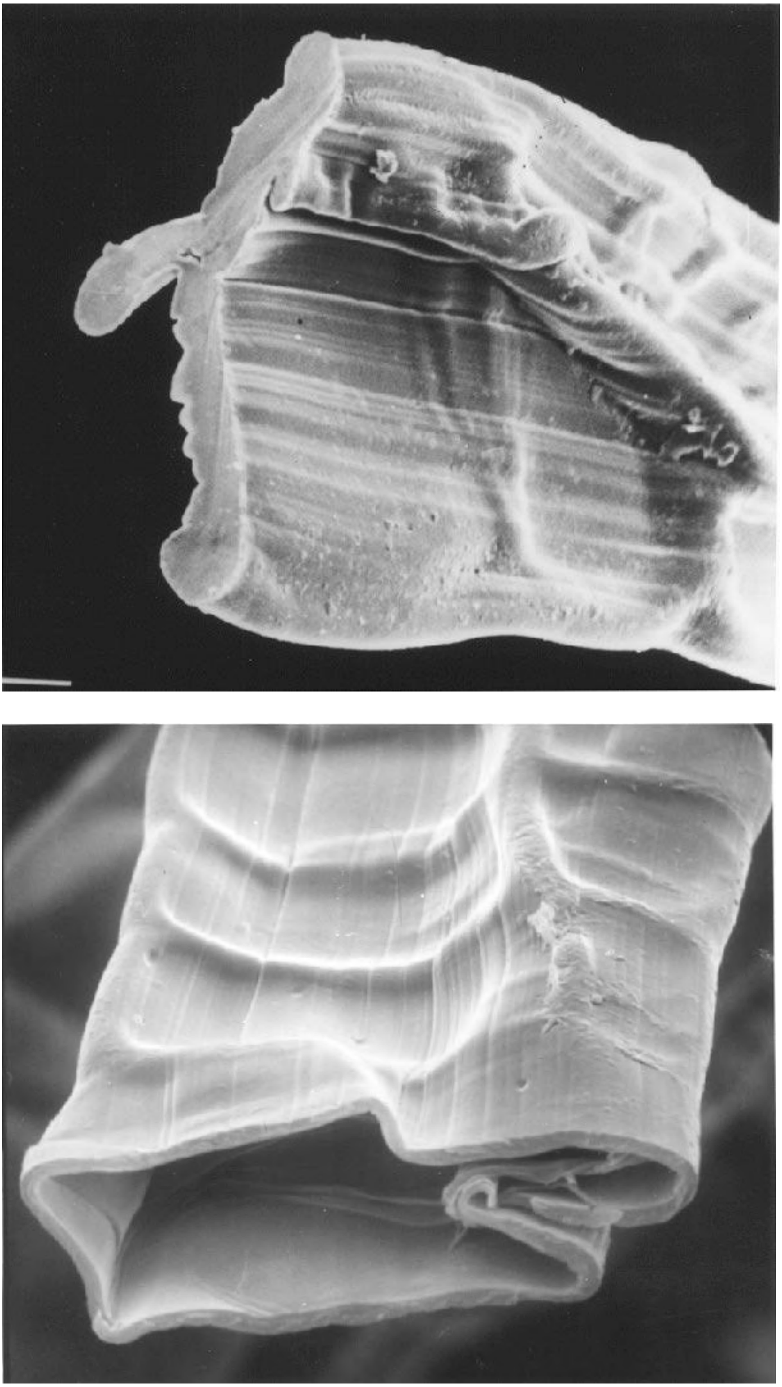
9.5.3 Flame-retardant rayons

Rayon, like cotton, will burn if ignited, and this characteristic has prevented the fibre being used alone and untreated in nightwear and some workwear applications.



9.10 Solid flat fibres are easier to make and give similar bulk to the hollow Viloft®. (Reproduced by courtesy of Acordis.)

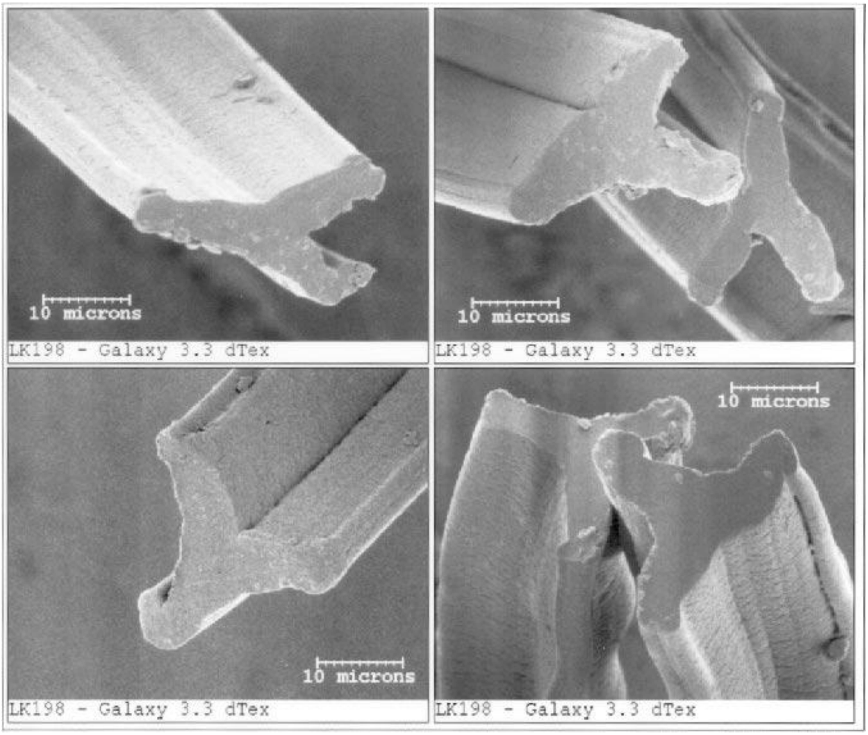
Flame retardancy can be obtained by adding flame-retardant (FR) chemicals to make up about 20% of the fibre weight.[13] The first commercial products used tris(2,3-dibromo-1-propyl) phosphate, but the P—O bonds made these susceptible to hydrolysis by strong alkali, and the bromine increased the rate of photodegradation. The chemical was found to cause cancer in laboratory tests and, in the late 1970s, fell from favour.[14] Propoxyphosphazine (Ethyl Corp) retardants were later used in Avtex's 'PFR' fibre, and a bis(5,5-dimethyl-2-thiono-1,3,2-dioxaphosphorinanyl) oxide powder (Sandoz) was the basis of later European FR fibre developments. Alloys with inorganic salts such as silicates or aluminates are possible, the salts



(a)

(b)

9.11 (a) Dry ‘SI Fibre’®: superinflated fibres give maximum bulk, absorbency and opacity but at the expense of processability.
(b) Wet ‘SI Fibre’®: some of the high absorbency of the superinflated fibres arises from the collapsed tube opening up on wetting. (Reproduced by courtesy of Acordis.)



9.12 Galaxy®: the same shape and bulk as dry SI fibre® but easier to process and lower water imbibition.

being converted to fibrous polyacids when the cellulose is burnt off.[15] This latter approach seems to be the basis of the 'Visil' flame-retardant fibre introduced by the Finnish viscose fibre manufacturer, Kemira Oy Saeteri.[16]

9.5.4 Alloy rayons

It is possible to produce a wide variety of different effects by adding materials to the viscose dope. The resulting fibres become mixtures or *alloys* of cellulose and the other material. The two most important types of alloy arise when superabsorbent or flame retardant fibres are made.

American Enka[17,18] and Avtex[19] both produced superabsorbent alloy rayons by adding sodium polyacrylate, or copolymers of acrylic and methacrylic acids, or sodium carboxymethyl cellulose to the viscose. The resulting alloys contained up to about 20% of the water-soluble polymer giving water imbibitions up to double those of the unalloyed rayons. They performed particularly well in tampons (see below) where the presence of the slippery polymer at the fibre surface encouraged wet-expansion of the compressed plug. Their use in this, the only real market which developed, declined after the 'toxic shock syndrome' outbreak[20,21] in the early 1980s. Other polymers which have formed the basis of absorbent alloys are starch,[22] sodium alginate,[23] polyethylene oxide,[24] polyvinyl pyrrolidone[25] and sodium polyacrylamido-2-methyl-2-propane sulphonic acid.[26]

Alloys of cellulose with up to 50% of synthetic polymers (polyethylene, polyvinylchloride, polystyrene, polytetrafluoroethylene), have also been made, but have never found commercial applications.

In fact any material which can survive the chemistry of the viscose process and can be obtained in particle sizes of less than 5 μm can be alloyed with viscose. An X-ray detectable yarn loaded with barium sulphate (30% cellulose/70% barium sulphate) was an extreme but profitable example of the type, developed and commercialised for medical applications.

9.6 Nonwoven applications

By the end of the 1960s the apparel and home furnishings markets for rayon were highly cyclical and gradually declining, rayon had relatively easily achieved a dominant position in the fast growing nonwovens industry. Since the mid-1970s significantly more effort has been spent on developing new applications for regenerated cellulose fibres in nonwovens than in conventional textiles. A more detailed look at applications development in this sector is therefore appropriate.

9.6.1 Dry-laid nonwovens

The first stage of traditional cotton or woollen textile manufacture involved opening and carding fibres to parallelise them prior to condensing them into slivers for drawing and spinning into yarns. The early cotton cards produced thin, 40 inch wide webs of fibres with just enough coherence to be handled by the sliver-making machinery.

In the late 1930s, the first lightweight* nonwoven fabrics were made by taking this card web and gluing the fibres together with natural latex emulsions or with phenol– or urea–formaldehyde resins. Cotton proved less satisfactory than rayon in these early absorbent disposables because unbleached cotton had a waxy hydrophobic surface layer, and absorbent cotton, made by bleaching, was both too expensive and too difficult to card

* Wool has been felted into what could be regarded as the first nonwovens for millennia. Heavyweight needlepunched 'felts' made from jute and sisal have been made since the 1890s in both the UK and USA. Wet-laid nonwovens from long natural cellulosic fibres were first produced by Dexter Corp. in 1934 in the USA.

into thin even webs. Rayon, especially second-grade staple fibre that would make uneven yarns or unevenly dyed fabrics thus became the fibre of choice for the embryonic nonwoven industry. The so-called 'dry-laid, latex-bonded rayon' nonwovens, were of course far too weak to replace conventional textiles in all but the flimsiest of applications, but they were stronger, more durable and more textile-like than many papers. As cheap new materials with unusual properties they allowed the development of a new range of 'disposable' consumer products for an apparent gap between markets normally served by textiles and those served by paper.

Single-use nappies, sanitary towels, incontinence pads, wipes, and medical swabs were among the early products made possible by the new disposable latex-bonded rayon nonwovens. For wiping applications the absorbent latex-bonded rayon formed the entire product (e.g 'J-Cloth' from Johnson and Johnson in the UK and 'Handiwipes' from Colgate in the USA). As the market grew and consumers demanded higher performance, these disposable wipes could be made to survive 10 washes, further increasing their cost effectiveness compared with paper, while maintaining some hygiene advantages over dishcloths. Interlinings, those out-of-sight textiles used to give stiffness and body to garments could also be made from the new nonwovens, but other 'durable' products required different system of bonding.

Needlepunching and stitchbonding allowed thicker card webs to be consolidated without recourse to latex and such products had a significantly better softness/strength balance that the albeit much lighter latex-bonded varieties. These nonwovens required coarser rayon fibres but achieved significant success in a variety of home-furnishing applications, especially curtains and blinds (for stitchbonded), blankets (for needlepunched) and floor/wall coverings (i.e. carpet tiles, also for needlepunched).

Unbonded absorbent rayon wadding became a common diluent of, or substitute for, the more expensive bleached cotton in sanitary and medical applications. In these and other sensitive wadding applications such as tampons, the rayon fibres had to be produced to meet the purity requirements laid down by the various national pharmacopoeias. Nevertheless some early successes in these more critical applications led to the development of new varieties of rayon staple having better whiteness retention on sterilising and higher absorbency (see above).

Tampons had been developed in the 1930s and by the early 1960s were an established but still growing market for bleached cotton, especially the shorter and hence cheaper varieties based on linters or comber waste. Replacing cotton in such a conservative yet technically sophisticated end-use proved difficult, but occasional shortages of the desired grades of cotton led to 'windows of opportunity' that allowed special versions of crimped viscose to break in. Once established, despite offering no perceivable benefits for the user over cotton, the new rayon fibres were preferred by the tampon producers for their consistency in both processability and price. For the fibre producer, the tampon application offered a large market for special fibres with a modest price premium over regular rayon. At the risk of stating the obvious, the market also required its fibres to be inherently absorbent, biodegradable, and to have a long history of safe use in contact with skin; in other words it was relatively invulnerable to competition from the synthetic fibres.

There were, of course, times when high demand for regular rayon in the more cyclical textile markets made the tampon and other nonwoven markets appear unattractive but over the longer term the very non-cyclicality and recession-proof nature of the nonwoven sector meant most rayon producers were willing to commit a significant proportion of their output to it.

All the US staple producers and several European and Japanese producers also committed many years of serious development effort to producing new fibres specifically for the market. In addition to the inflated and modified cross-section fibres mentioned above, highly absorbent rayons were manufactured by adding water-soluble polymers to the viscose dope prior to spinning. Two varieties were commercialised in tampons, one using sodium polyacrylate as the additive and the other using carboxymethyl cellulose, both at around the 15% level on fibre. These inclusions* increased the fibre water imbibition by about 50%, but perhaps more importantly they made the fibres more resilient and slippery when wet, a feature that allowed good recovery (and hence absorbency) from the highly compressed dry state of the tampon.

9.6.2 Wet-laid nonwovens

Wet-laid nonwovens were manufactured using papermaking machinery adapted to make webs containing synthetic fibres and to bond them using either latex or (if the webs had a synthetic component) thermal means. Less versatile and often more costly to operate than the slower dry-laid route based on textile cards, wet-lay technology was also limited to fibres short enough to be handled in aqueous dispersion: in practise less than 2.5 cm long and typically less than 1 cm in length for 1.7 dtex fibres. Nevertheless rayon fibres, which are very similar to the wood and cotton fibres normally

* Before their use in these alloy rayon fibres, both carboxymethyl cellulose and sodium polyacrylate had, in their crosslinked powder form, been sold as superabsorbents for use in diapers and sanitary products. After they had proved satisfactory in tampons, processes were developed, especially in Courtaulds UK, to convert them into highly absorbent staple fibres.

used in papermaking proved well suited to the technique, provided they could be precision-cut to the short lengths needed.

Unlike the related speciality papermaking sector (see above) wet-laid nonwovens did not require fibres to be self-bonding and hence regular rayons simply cut to the right length were usable. Wet-lay technology was thus not only able to enter some of the markets already penetrated by dry-lay technology, but also to take rayon into new highly technical markets such as tea bags, vacuum cleaner bags, milk filters, and food casings (i.e. salami skins). Wet-laid nonwovens have, however, failed to live up to their early promise and totally failed to justify the late 1960s hype about their prospects in 'paper dresses'. The rayon producers have been blamed at least in part for the disappointing wet-laid market growth. Because during the crucial early years no rayon producer would commit full-scale manufacturing facilities to allow short-cut fibre to be produced at the same low price as staple-fibre for dry-laid nonwovens, the wet-laid industry was unable to compete in the large and fast growing coverstock* and wipes markets. The problem for the rayon producers was that precision short-cut fibre was hard to make on staple fibre machines and the wet-laid market was too small to allow several suppliers to install the large-scale machinery needed to bring the costs down.

9.6.3 Spun-laid nonwovens

Spun-laid nonwoven processes developed in the late 1950s by Freudenberg (Germany) and DuPont (USA) proved much more significant than wet-laid processes. These processes converted synthetic polymers directly into fabrics on a single large machine, the entire fibre and 'textile' manufacturing processes being compressed to the ultimate conceivable degree in both time and space. Polymer chips were fed into an extruder, fibres were spun vertically downwards, oriented in high-pressure airjets, randomly laid on a conveyor and the resulting web bonded and reeled up within seconds of the fibres being spun.

The relevance of a synthetic fibre nonwovens technology to this chapter probably needs some explanation. The direct relevance is that at the time of writing there are two producers of spun-laid regenerated cellulose nonwovens in the world, both in Japan, and the origins of these are dealt with below. The indirect relevance is that the inability of regenerated cellulose to maintain its leading position in the nonwovens market through the last quarter century of dramatic growth can be traced to a progressive deterio-

* Coverstock is the very lightweight nonwoven used to cover the absorbent wadding of disposable diapers, sanitary towels and incontinence pads.

ration in its cost/performance ratio. Producing nonwovens on-line at the rayon plant was a natural evolution from staple fibre production technology to improve the cost/performance of a cellulosic nonwoven.

9.6.3.1 Spun-laid regenerated cellulose nonwovens

Several cellulosic fibre producers did however attempt to improve this performance/cost ratio by making nonwovens themselves.

9.6.3.2 Viscose process based

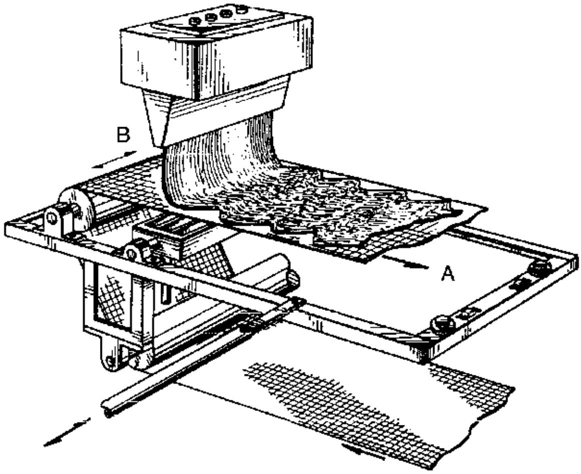
In Europe Courtaulds, Rhone-Poulenc and Enka Glanzstoff AG (now, like Courtaulds, part of Acordis) developed spun-laid rayon nonwovens on a pilot scale in the late 1960s and early 1970s.

In Japan, Kanebo and Daiwabo researched similar techniques, Asahi worked with viscose and cuprammonium pilot lines, but Mitsubishi Rayon developed a process based on hydroxymethyl cellulose xanthate in which the webs were point bonded in a hot calender before regeneration. Also in Japan Kosabura Miura spun viscose vertically downwards from oscillating spinnerets onto a conveyor, and oversprayed the liquid filaments with acid. The Tachikawa Research Institute developed a polynosic viscose spun-laid process.

Courtaulds introduced the first spun-laid regenerated cellulose nonwoven at the first International Disposables Exhibition in the USA in 1971, but closed the development two years later for reasons associated with the undesirability of competing with its then rapidly growing rayon staple business in nonwovens, and the small size of the available market at that time.

This early cellulosic filament nonwoven was not a true spunbond. It was a wet-laid continuous filament web made from a fully washed viscose tow, laid on-line on an inclined wire former, dried and print-bonded with latex. It nevertheless made an excellent wiping cloth, demonstrably outperforming the market leader (at that time 'J-Cloth' from Johnson and Johnson's Chicopee Division.) However, also at that time the European market for nonwoven wipes of all types was at best 10 000 tonnes, and the minimum economic process scale-up would have produced 25% of this.

In 1974, Asahi introduced 'Bemliese', the cuprammonium version of Courtaulds' process (see Fig. 9.13). With cuprammonium the continuous filaments could be laid in the incompletely regenerated state to give a true spunbond of pure cellulose. Because the cupro-based process[27] was significantly more costly to operate than the Courtaulds' viscose-based approach, they targeted higher value medical nonwovens and made much capital in Japan of the fact that they dissolved cotton linters rather than wood pulp.



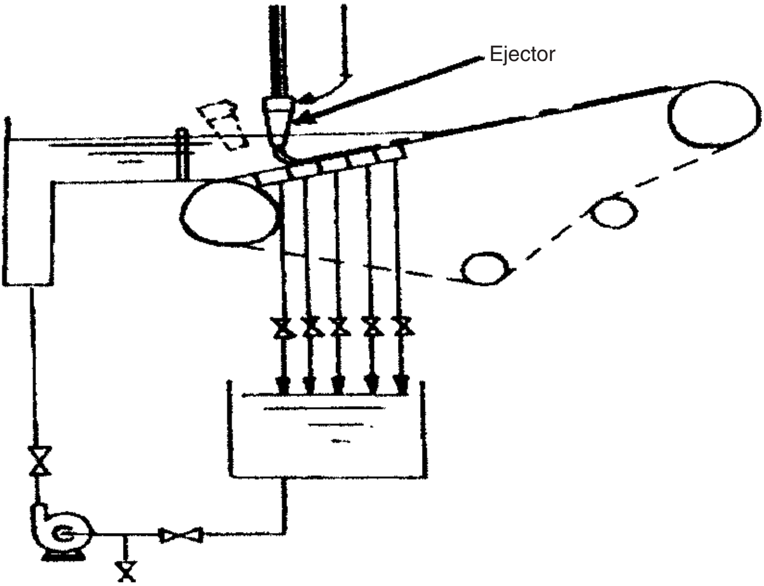
9.13 Asahi's Bemliese® cuprammonium rayon spun-laid process. Filaments are spun vertically downwards onto the wash conveyor and overfed to create lateral interactions prior to washing, bonding and drying as a nonwoven fabric.

This allowed them to describe the resulting nonwoven as made from cotton, just like the woven products they planned to replace.

In 1976, the Mitsubishi Rayon Company introduced nonwovens from their methyol cellulose process[28] as 'TCF' (Textiles Continuously Formed) (see Fig. 9.14). This was made on-line in a viscose plant, and while it looked and felt similar to the Bemliese fabrics it was in fact wet-laid from 10 mm to 15 mm fibres prior to washing and bonding using a hot calender. Today, both of these Japanese processes use the latest hydroentanglement bonding techniques to arrive at softer materials than true spunbonding allows.

Also in 1976, Courtaulds and their in-house nonwoven producer Bonded Fibre Fabrics (now the BFF Nonwovens division of Lamont Holdings) decided to reopen the development of spun-laid viscose. A second large pilot plant was built in the Coventry Research Laboratories, this time along lines more similar to the Asahi approach, with tow-laying preceding washing. This gave the benefit of higher web uniformity from the perfectly parallel filaments laid straight from the special spinning heads, and the ability to use different bonding methods, before or after washing, or both.

Unlike Asahi and Mitsubishi, the Courtaulds route involved either spinning regular fibres and viscose bonding them immediately after laying, or aperturing and hydroentangling the acid tow web using a very early in-house version of the hydroentanglement technology which began to grow



9.14 Mitsubishi Rayon's TCF® spun-laid process uses a conventional wet-lay former and introduces hydroxymethyl cellulose fibres 'ejected' straight from the spinning machine into the headbox.

so rapidly 10 years later. Surgical swabs and binder-free, lint-free wipes were among the main target markets. The development met its technical objectives but plans to install a large commercial line in a UK viscose plant were shelved.*

At Courtaulds the spun-laid viscose equipment had also produced calcium alginate nonwoven, partly to investigate medical applications of alginate and partly because alginate was an easy spinning proposition which allowed the design of the laying section to be finalised. By the time spun-laid viscose was shelved, these alginate spun-laid nonwovens were in demand as advanced wound dressings. The spun-laid pilot plant was therefore converted to alginate and became the foundation of the current Speciality Fibres business of Acordis. The reason for this apparent digression into alginate nonwovens is to note that their development led to an understanding of gel dressings for advanced wound care, which in turn led to the development of an advanced regenerated cellulose nonwoven made by

* In 1982 Courtaulds took the view that the new hydroentangled nonwoven process would allow the manufacture of all-cellulose nonwovens from regular staple fibre, and the new lyocell process would be much more amenable to spunbond manufacture, if ever the market grew enough to justify it.

carboxymethylation of viscose and latterly, lyocell fibres (see Chapter 6). However, one of the first commercially produced carboxymethyl cellulose nonwovens was made by Asahi, and the product, based on carboxymethylation of their Bemliese cuprammonium rayon spunbond was marketed as 'Super AB' superabsorbent nonwoven in the 1980s.

9.6.4 Lyocell nonwovens

Lyocell makes excellent nonwovens, especially in those processes that allow its superior aesthetics to shine through, like needlepunching and hydroentanglement. Its high strength is of little intrinsic value in disposables, but it enables the nonwoven producer to reduce basis weight while meeting strength targets. Its freedom from shrinkage and high wet stability allows higher area yields in hydroentanglement processes, and its high modulus prevents it from collapsing in the wet to the same extent as viscose rayon. Fibrillation, the development of surface microfibres on wet abrasion or in high-pressure entanglement, adds an additional dimension for the nonwoven developer. Unfortunately, while to date it has established itself in several profitable niches, its premium positioning as a fashion apparel fibre has so far prevented its use in mainstream disposables. The Appendix contains a full set of technical data on lyocell in nonwovens.

9.6.5 Spun-laid lyocell nonwovens?

Most fibre-forming polymers or polymer solutions can also be converted into continuous yarns, films, sponges or indeed nonwoven fabrics. Lyocell dope is no exception and many of the characteristics of the lyocell process make it a better basis for spun-laid nonwovens than the viscose process ever was. Technically speaking, the challenges are not great. Economically and commercially speaking, they are enormous.

In the nonwovens market the leading products are nearly always those with the lowest cost, and justification of spun-laid cellulosics on added-value alone has failed several times already. The ultimate in economy arises from inherently low cost raw materials converted on state of the art machinery at the largest possible scale. The nonwoven industry enjoys the economies of (say) polypropylene (PP) because PP is a by-product of the world's largest industry, energy. Viscose rayon, a premium product of the timber industry, requires the most costly grades of wood pulp. Lyocell is currently similar, but its simple production process has the so far unexplored potential to use cheaper pulps. It also has the potential to achieve very high levels of sales in textiles, and hence the economies of scale that may ultimately attract the major nonwoven converters.

9.6.6 From commodity to speciality

Prior to 1960, regenerated cellulosic fibres enjoyed 50 years of rapid expansion. Since then, synthetics have grown to dominate the market. Cotton, for centuries the most important of all fibres is taking second place to the combined weight of synthetics and viscose rayon. But rayon now appears relegated to little more than a niche in a global fibre market driven by the ready availability of cheap fossil fuels and the demand for commodity textiles and nonwovens.

Nonwoven production was founded on the ready availability of low-cost viscose rayon fibres and these continued to dominate the industry until the mid-1970s. Since then the reducing cost of synthetics, coupled with their easy conversion into binder-free spun-laid and melt-blown fabrics, caused a steady decline in rayon's nonwoven market share.

Is the relative decline in use of cellulose, both natural and regenerated, in nonwovens and textiles just another example of the last stage of the inevitable growth/maturity/decline life cycle of most markets? Or is there any suggestion that, on a longer time scale, the biopolymers will prove to be a serious rival to the synthetics?

This section reviews how rayon arrived at its current position in the nonwovens market, records the technology-based attempts to reverse the decline, and examines possible futures.

9.6.6.1 Current positioning of cellulosic fibres

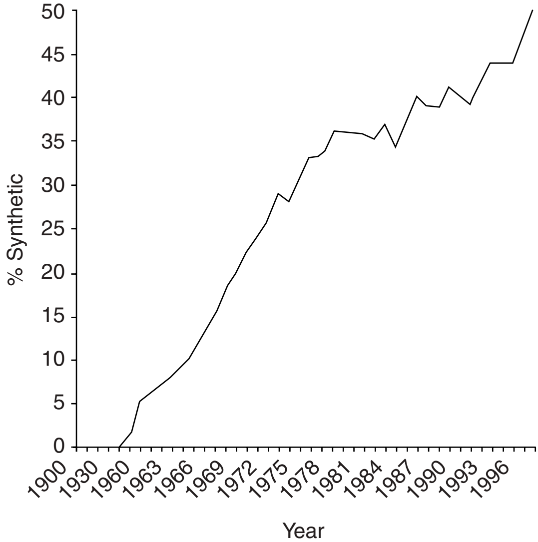
Figure 9.15 illustrates how fibres based on fossil fuels have replaced fibres based on biopolymers over the 20th century according to the CIRFS statistics on world fibre usage in all markets.

Roughly half of the 45 million tonnes of fibre consumed annually in the world are now made from synthetic polymers. The only perturbations in an impressively smooth growth curve appear in the 1973–1974 period, the 1978–1984 period and the 1990–1991 period and are explained later.

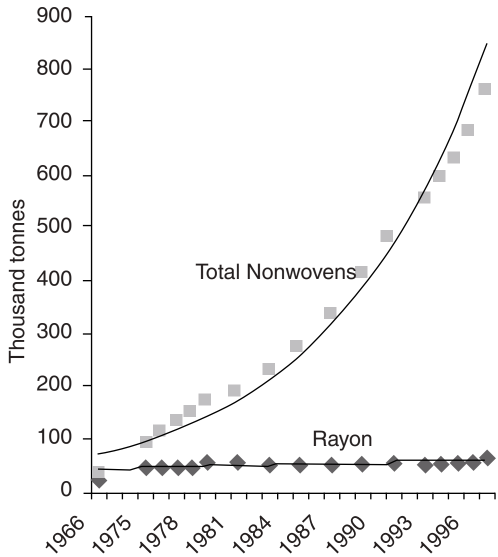
On a more local level, fibre usage in the European nonwovens industry is illustrated in Figs. 9.16 and 9.17.

While the tonnage of viscose rayon sold has held remarkably constant for 30 or more years, rayon has not participated at all in the massive growth of the industry and its market share is now one tenth of the 1970 figure.

The enormous expansion of the synthetics in the 1960s and 1970s put the viscose rayon industry on the defensive. Despite having taken almost 25% of a 14 million tonne cellulosic fibre market without ever promoting rayon strongly against 'King Cotton', and despite having the potential to double this share, the viscose producers felt the future of manufactured fibres to be synthetic.

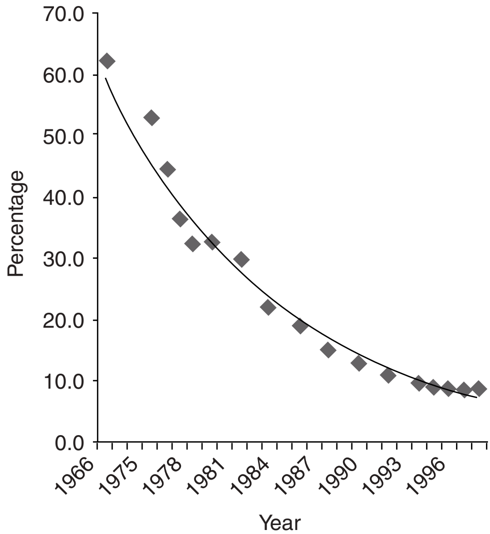


9.15 Synthetics versus polymers in the 20th century.



9.16 Rayon in European nonwovens (EDANA).

With hindsight, the viscose industry entered an end-game strategy at this time. Profits that had been substantial during the upside of the textile cycle, were spent on synthetic fibres or in diversification ventures rather than in marketing rayon against cotton or in building efficient new plants.



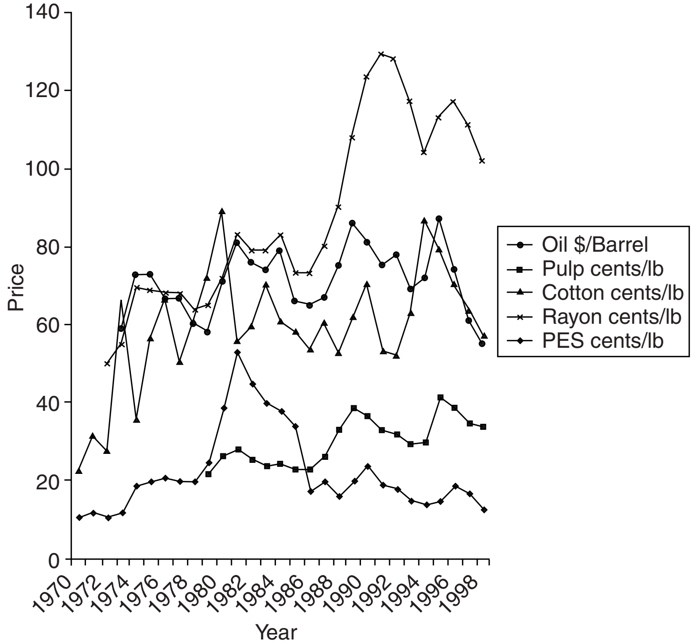
9.17 Rayon share of EDANA tonnage.

What rebuilding and expansion there was became largely confined to replicating existing production technology in parts of the world where cheap labour allowed more competitive manufacturing costs. A progressive tightening of the regulations governing the release of gaseous and liquid effluents from the viscose process compounded the problem and adversely affected the older plants. Effluent control projects and 'modernisation' took whatever funds were available. During the downside of the textile cycle, the higher cost viscose capacity was simply closed down. By the end of the 1970s nobody expected to see a new viscose plant being built anywhere.

In the absence of substantial reinvestment in new plants, the repositioning of viscose rayon became inevitable, and from 1985, the fibre was successfully transmogrified from a commodity to a premium-priced speciality fibre for the more lucrative niches in apparel and nonwoven markets. The reasons for the decline are obviously related to relative fibre price and performance, but a more detailed analysis is needed to decide if a simple extrapolation of the graphs correctly identifies the most likely future.

9.6.6.2 Price

The graph shown in Fig. 9.18 brings together fibre, oil and pulp prices from a variety of sources to throw some light on the competitive positioning of



9.18 US price indications from various sources.

the key fibres in the period from 1970. They are not all on the same basis and the more readily available US figures are used in preference to less complete and more volatile European data.

They nevertheless illustrate the following:

- A doubling of oil price was caused by the oil embargo during the 1973 Yom Kippur War.
- The oil price controls during the Iranian revolution/Iran–Iraq war and aftermath (1978–1986) caused a massive disturbance in oil price.
- A return to 'normal' oil pricing was interrupted by the Gulf War in 1990.
- Cotton price increased from the 20 cents/lb to the 60 cents/lb region during the 1970s, opening the door to polyester.
- Ignoring the political perturbations in oil price, the pulp/oil price ratio is increasing.
- A quadrupling of oil price (1972–1982) hardly affected the relative price of polyester.
- Polyester and cotton prices appear to be linked.
- Rayon prices remained broadly in line with polyester and cotton until 1986 when they moved rapidly ahead of both the competitive fibres and of reasonable price expectations based on pulp prices.

- By 1990 the repositioning of rayon at prices 50–100% higher than cotton was complete.

9.6.6.3 Performance

The aesthetic, absorbency and comfort advantages still enjoyed by cellulosic fibres has slowed synthetic penetration of the apparel sector, and has extended their life at premium prices in the hygiene sectors of the nonwovens industry. Synthetics are used for their low-cost, thermal bondability, resilience, dryness, and durability characteristics. In the absence of fibres combining all these properties, synthetic/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 fibres have been typical.

Within the cellulosic part of a nonwoven fabric, however, rayon now has to compete with wood pulp and to a much lesser extent, cotton.

9.6.6.4 Key markets

While the versatility of rayon has ensured its continued use in a wide range of absorbent disposables, its fortunes appear to have been dominated by events in a few key markets. Development aimed at responding to the needs of these markets extended the boundaries of rayon technology and identified ways of significantly altering its performance. These are worth reviewing, but it goes without saying that none were capable of reversing the market share decline.

The first major market share loss occurred in coverstock, a market where the skin-friendly absorbent nature of cellulose was felt to be a major advantage.

During the late 1960s when disposable nappies came in two pieces (reusable plastic pant with rectangular absorbent pad), latex bonded rayon was the cover of choice. At this time 'flushability' was becoming a key development issue. The rectangular inserts with their heat-sealed latex-bonded rayon covers were too stable to be disposed of in the toilet even after tearing in half. New wet-laid nonwovens made from the specially developed self-bonding collapsed-tube rayon fibres had no wet-strength at all and dispersed easily in flowing water. However, when treated with the standard wet-strength agents used in the paper industry it became strong enough in use and remained disintegratable in toilet turbulence. Rayon producers in Europe, Japan and the USA developed such fibres and a small market developed in the USA. The introduction of the more convenient one-piece happy pushed mothers' concerns about flushability into the background.

Latex-bonded 100% rayon continued as the leading cover on one-piece nappies, but in 1974 coverstocks containing 50% polyester were market tested for the first time. Consumers found they could not really spot the difference from the 100% rayon fibre versions, so in a second test the latex bonded rayon/polyester blend was put through a point embossing calender to give it a textured surface. This time the mothers could express a preference for the patterned over the plain and a 'unique' new product was born. This first use of synthetic fibre in what had been regarded as an absorbent fibre 'fortress' appeared to be driven by nothing more than the concern over the escalating price of rayon. Technically, however, the success of polyester was put down to its easy embossability.

In the course of the introduction of polyester to coverstock, the nappy industry discovered a major new marketing angle to support a move up to 100% polyester. Coverstocks containing polyester were found to be drier to the touch than the rayon versions. This was initially explained as a consequence of the fact that the synthetics did not absorb water, and so the rayon industry was asked to develop hydrophobic embossable fibres to stay in the game.

Embossability, achievable through alloying rayon with polyethylene emulsions, proved difficult to scale up, but hydrophobic rayons made simply by using hydrophobic finishes, were nevertheless commercialised in both the USA and Europe.

One other feature of the new synthetic coverstocks was proving to be at least as important to surface dryness as their hydrophobicity. Resilience when wet, coupled with much greater dry-bulk associated with their low-collapse in latex bonding allowed them to provide a greater mechanical barrier to urine wetback than a water-plasticised viscose fibre ever could.

Solutions to cellulose's wet collapse problem have been many and various. Dry crosslinking technology had been used on-line in rayon plants in the 1960s to improve the resiliency of fibres used in carpets. Wet crosslinking had been possible since the early 1970s but was rejected as compromising the chemical simplicity of rayon. Hollow and multilimbed fibres gave benefits that allowed them to become major products, but only in markets where the premium prices allowed them to be considered.

Despite their advantages, 100% polyester latex-bonded coverstocks had a short life span. Concerns over latex chemistry (e.g. formaldehyde) led to reformulation of the binders, but the progress in making thermal-bonded polypropylene nonwovens allowed the nappy producers to move swiftly on to this even cheaper, even cleaner technology.

Several attempts were made to develop a thermally bonded rayon nonwoven: Acetylation of the surface of rayon and the use of a solvent bonding process perfected for stabilising acetate in cigarette filters was one obvious approach. Like the surface grafting of thermoplastic materials, this was felt to add more cost than value. Alloying with polyethylene, a technique developed to improve embossability, gave insufficient strength in calendering.

Through-air bonding of 70/30 rayon/bicomponent fibres to lock the rayon into a high volume configuration allowed the manufacture of coverstocks that had attractive softness and a good balance of strikethrough and surface dryness. The former was achieved without recourse to the high levels of surface finish necessary for polypropylene (PP). However the rapid expansion of point-thermal bonding on wide high-speed calender lines allowed 100% PP coverstock to be made at prices that could not be matched on any less dedicated hardware using more costly fibres. The rayon industry quickly decided that this was a wave of nonwoven expansion that held no opportunity.

The rayon tonnage that was lost in the coverstock market was largely regained in new latex-bonded fabric softeners for use in tumble driers. These were lightweight latex-bonded rayon nonwovens produced from rather coarser fibres than had been possible in coverstock. They were made on purpose-built wide lines at speeds well in excess of those possible on coverstock lines a few years earlier. Rayon gave better thermal stability than polypropylene and more strength than latex-bonded polyester. As this market matured, the fact that rayon absorbed too much softener was identified as a technical disadvantage because it allowed the sheets to be used in more than one drying cycle. Technical solutions were, of course, possible, and one involved harnessing the technical advantages of the new lyocell fibre (high strength, less absorbent rayon which could be converted into very light nonwovens – see Chapter 4 on lyocell). However spun-laid polyester emerged as a lower cost alternative.

With fabric softeners as with coverstock, the absorbency of rayon appeared to have changed from a fundamental advantage at the outset, to a fundamental disadvantage as the converters' experience in the marketplace grew. Rayon's absorbency advantage has been less transient in the wiping and hygiene markets, and it is here that ingress of cheaper synthetics has been resisted best. This has been aided by the rapid growth of the hydroentanglement (HE) bonding method that allowed the true character of pure cellulose to be realised in major nonwovens markets for the first time. The silky softness of rayon had, until the development of HE, always been masked by the need to use external bonding agents. Here again though, the poor wet resilience of cellulose has been disadvantageous, and many wipe producers now use up to 50% of synthetic fibres to prevent wet-collapse.

Coming right up to date, the growth of HE bonding has led to a turnaround in rayon's fortunes and in 1998 and 1999 tonnages consumed in nonwovens have reached their highest ever levels in Europe. World HE capacity now exceeds 350 000 tonnes and an estimated 40% of this remains to be utilised. One of the major new products made possible by HE bonding of rayon is the ultra soft baby wipe as exemplified by the European 'Pampers' product from Procter & Gamble. Many other companies are now imitating this and it may be just a matter of time before similar products appear in the US market.

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