6
Fibres related to cellulose

JOHN W S HEARLE AND
CALVIN WOODINGS

This chapter is based on the accounts given by Moncrieff,[1] Coleman[2] and Raheel.[3] Other general references are by Cook[4] and Treiber.[5]

6.1 Cellulose acetate

6.1.1 Historical introduction

Paul Schützenberger, who heated cotton in a closed tube with acetic anhydride until it dissolved, first produced cellulose acetate in 1865.[6] When he diluted his solution with water, a white amorphous powder of highly degraded cellulose triacetate settled out. Over the next 25 years, important contributions to the science of cellulose acetylation were also made by Nadin,[7] Liebermann and Hoermann[8] and Franchimont,[9] but it was Cross and Bevan, of cellulose xanthate fame, who first described the industrial potential of the material in a series of patents and articles between 1889 and 1895.[10] The list of proposed uses, coming soon after their viscose patent, looks familiar: film, paints, varnishes, moulded articles, and when spun, filaments for electric lamps. Conversion of the cellulose ester into fibre was, however, a less straightforward proposition than the xanthate and it took a further 25 years before its fibre-making potential was realised on an industrial scale. Key developments of the fibre-making process were, in that period, made by George Miles, Arthur D. Little and the Dreyfus brothers, Camille and Henri.

In 1904 Miles discovered[11] that partially hydrolysing the cellulose acetate allowed it to be dissolved in relatively cheap and non-toxic solvents such as acetone, whereas the primary product of the acetylation reaction would only dissolve in 'difficult' solvents such as chloroform, nitrobenzene and epichlorhydrin. This conversion of the primary triacetate into the secondary diacetate was fundamentally important in allowing further development of practical fibre-making processes.

A D Little, working with W H Walker and H S Mork in Boston patented wet spinning of acetate fibres in 1905. Mork later became a Vice President of the Lustron Company of Boston, which, along with the Bayer Co in Germany pioneered small-scale commercial acetate fibre production. In 1907 the Bayer Co marketed cellulose acetate as 'Cellit' for the production of cinematograph film. The Swiss company Cellonite Co, run by the Dreyfus brothers, introduced a similar material a few years later. Count Donnersmark (see Chapter 1) had no more success with acetate than he had with viscose, and while the Chardonnet factory at Besançon (see Chapter 1) also experimented with dry spinning, none of the early developers succeeded in developing a commercial process. Overall, the acetate route looked more costly and more difficult than either the viscose process, or the nitrocellulose process that viscose was rapidly replacing. On top of this, acetate fibres had proved undyeable with those dyes commonly in use for viscose and cotton. Military interest in the use of the non-flam acetate dope to replace nitrocellulose dope nevertheless ensured developments continued.

The Dreyfus brothers also produced the fibre in a small way in Switzerland between 1910 and 1913, but during World War I their Cellonite company was the only company to respond to a British War Office tender for the UK manufacture of the acetate dopes used to coat the fabric skin of aeroplanes. They came to the UK, and with financial backing from Vickers Ltd and Pinchin Johnson & Co (Paints) Ltd, set up production in Spondon, near Derby as the British Cellulose Co Ltd.* As an interesting aside, they failed to deliver the product on time, and the War Office briefly encouraged Courtaulds to supply, before effectively granting exclusivity to the British Cellulose Co. Courtaulds nevertheless took what they learned about acetate seriously and convinced themselves that the problems of the fibre process would be solved. Acetate would then begin to threaten their dominant position in viscose.

The British Cellulose Co Ltd's unlisted shares rose from sixpence to £10 10s between 1916 and 1918 partly because they had the monopoly of aircraft dope and partly because they appeared able to enter the extremely lucrative artificial silk business. As war ended Camille Dreyfus set up the American Cellulose and Chemical Company to supply the US Army and Air Force with dope and both he and brother Henri, now running the British operation, successfully focussed on the artificial silk market. In 1921, when Spondon was capable of making about 1000 lb a day of acetate filament, Henri launched the product under the 'Celanese' brand. Camille commenced fibre production a year later in the USA. In 1923 the British

*They later changed the name to British Cellulose and Chemical Manufacturing Co Ltd.

company was renamed British Celanese Ltd, and the American operation later became The Celanese Corporation of America. Eastman Kodak produced acetate for films at about the same time, and their Tennessee Eastman subsidiary commenced fibre production as another outlet for the parent company's acetate in 1929. DuPont also started production of acetate fibre in 1929.

Meanwhile, in the UK, Courtaulds were becoming increasingly concerned by growing consumer interest in the new acetate yarns and decided to challenge the Celanese patents by setting up the Little Heath Works in Coventry to produce 'Seraceta' yarns. First deliveries were made in 1926, plans for US acetate production were laid, and a period of acrimonious relations between what were now the two leading rayon producers ensued. Briefly (for a full description see Coleman[12]), Celanese sued Courtaulds for infringements of their acetate patents in 1931, and in 1933 judgment favoured Courtaulds. Celanese appealed, lost again and took the case to the House of Lords where in 1935 they lost again and had their patents revoked. Amazingly in 1936 Dreyfus sued again (this time it was personal!) claiming that Glover at Courtaulds had given false evidence in a peripheral patent case, but in 1937 again lost and again appealed. The appeal was later withdrawn in what appeared to be the first move in talks leading to a merger of British Celanese and Courtaulds.*

The relative success of the upstart acetate against the established viscose can be judged by the fact that in 1930 the American Viscose Company (Courtaulds) commenced diacetate production and by 1940, 33% of all regenerated cellulosic filament output in the US was diacetate. In Japan, production commenced in 1919 in a joint venture between Snia Viscosa (see Chapter 1) and Teikoku, but it was the formation of Asahi with technology from VGF in 1925 that led to rapid expansion (see Fig. 6.1).

World production of acetate fibres, all made in the more easily dissolved diacetate form, reached 90 000 tonnes in 1939. Fibre for textile uses peaked in 1971 at about 500 000 tonnes, this being the combined figure for diacetate and triacetate which had been reintroduced in the 1950s. As for viscose, the decline in textile uses of acetate was caused by the rapid expansion and price cutting of synthetic fibres, but unlike viscose the losses were more than compensated by the development of a massive new industrial market for

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* A deal which would have left Courtaulds in full control of the joint company was actually agreed with British Celanese in 1939. However war intervened, tax changes making the deal disadvantageous to both parties. Merger discussions were not renewed until Henry Dreyfus died in 1944. In 1947 they were again abandoned because of the risk of a combined company being nationalised by the Labour government. In 1957 Courtaulds finally acquired British Celanese in an agreed takeover.
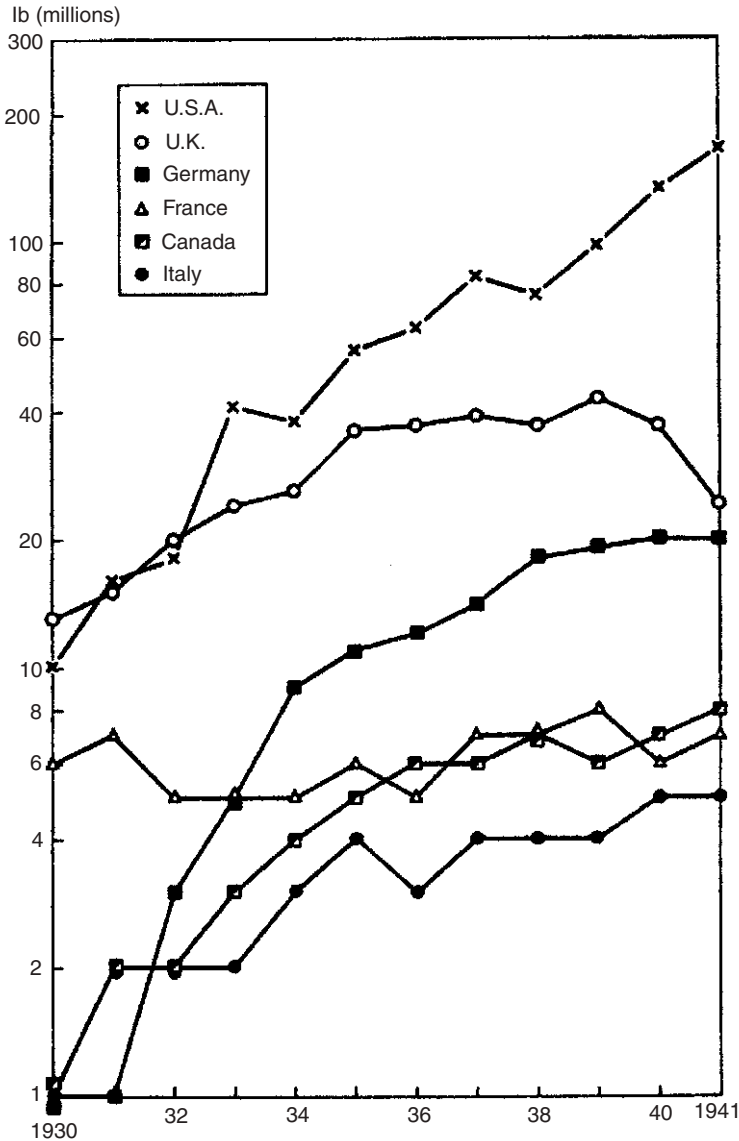
6.1 The growth of acetate rayon production 1930–1941. (Reproduced from *Courtaulds: An Economic and Social History*, Clarendon Press, 1969.)

the fibre: cigarette filter tips based on large crimped tows of diacetate. At the time of writing, despite many attempts by both synthetic and competitive cellulosic producers to displace it, diacetate tow reigns technically supreme in cigarette filters and worldwide production is now estimated to

exceed 700 000 tonnes (see below and Chapter 10). Surprisingly in view of Western attitudes to smoking, the market continues to grow as the majority of the worlds smokers (in Asia) are persuaded to change to tipped cigarettes.

During the 1939–1945 war, very strong cellulose fibres, known as *Fortisan*, were made by highly stretching secondary acetate yarns and then regenerating the cellulose. The converse of this has been the production of acetate fibres by acetylation of cotton or viscose rayon.

The Lustron Company, from 1914 to 1924, had spun cellulose triacetate fibres in small quantities from chloroform, but the toxic solvent hazard made this an unsatisfactory operation. In the 1950s, an alternative solvent, methylene dichloride, became available cheaply and triacetate fibre production started again. Celanese introduced 'Arnel' in the USA in 1952 and 'Tricel' from the Spondon plant in the UK. Courtaulds UK followed in 1955 with 'Courpleta' from the Little Heath plant but abandoned this in favour of Tricel after the takeover of British Celanese in 1957.

Low moisture absorption and heat settability gave triacetate fibres some of the easy-care properties of the synthetic fibres, though not the durability, and at that time, the fibre was cheaper than nylon or polyester. The reduction in the price of the synthetics caused the triacetate market to shrink, and problems with the health and safety aspects of the solvent once again led to the closures of the US and UK operations in the late 1980s.

Other fibres mentioned briefly in this chapter are alginate fibres, derived from alginic acid, which is closely related to cellulose, and sodium carboxymethyl cellulose fibres.

6.1.2 Secondary acetate fibres

6.1.2.1 *Manufacture*

The starting material for acetate fibres was formerly cotton linters, the short fibres attached to the cotton seed, but wood pulp is now used. Thorough purification is necessary as a first step. The purified fibres are steeped in glacial acetic acid, so that they become more reactive, and are then thoroughly mixed with an excess of glacial acetic acid and acetic anhydride. In these conditions, acetylation would be slow, but it is speeded up by the addition of sulphuric acid, which forms sulpho-acetic acid as a fast acetylating agent. The reaction is strongly exothermic, and in order to avoid degradation of the polymer molecules, it is necessary to cool the vessels. After an hour at 20°C and about seven hours at 25–30°C the reaction is complete, and the fibre/liquid dispersion has turned into a viscous gelatinous mass. The cellulose has been converted to cellulose triaceate, which has the chemical formula shown in Fig. 6.2:
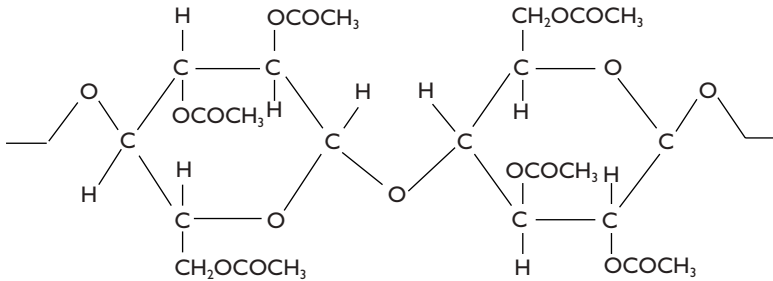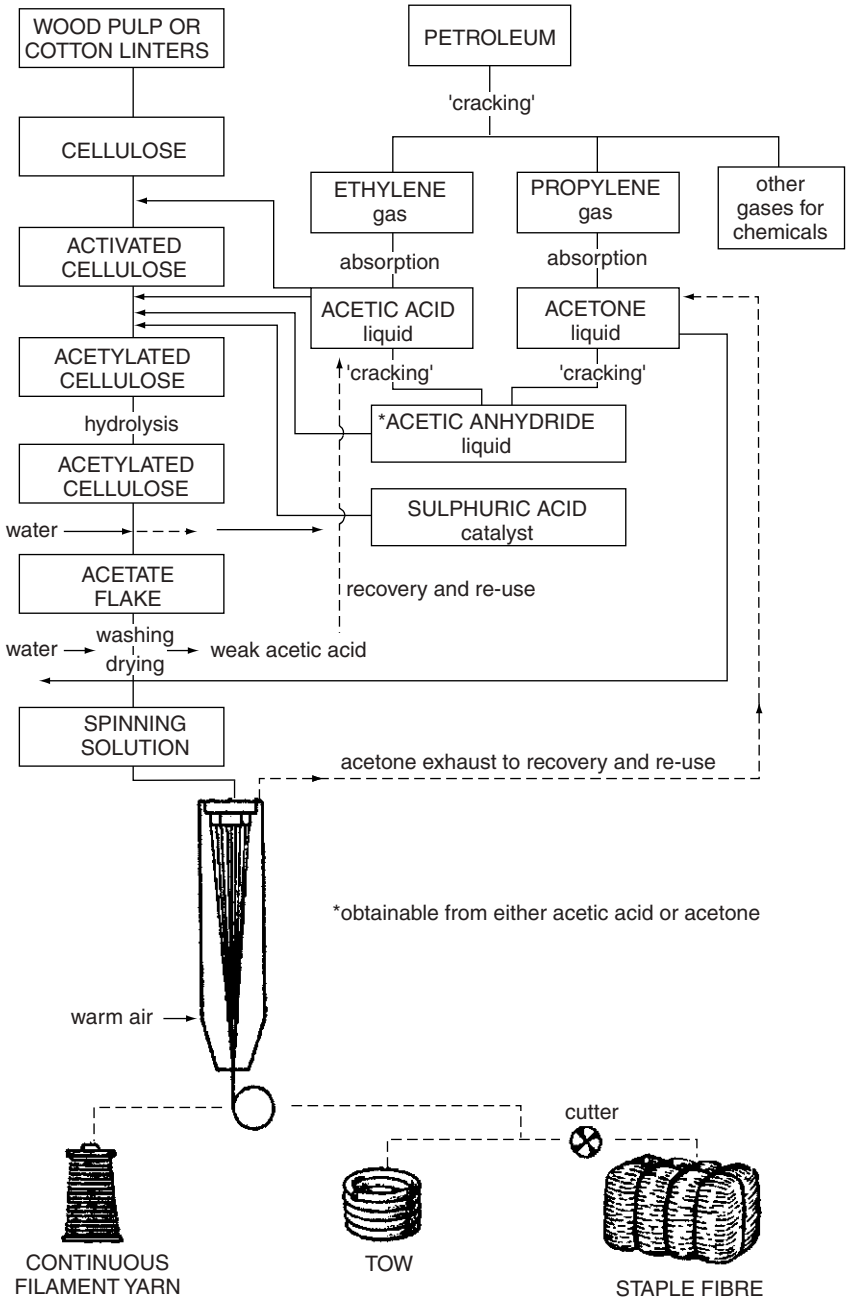
6.2 Fully acetylated cellulose. This primary product of the acetylation reaction, cellulose triacetate, is partially hydrolysed to the diacetate before fibre is produced.

It is necessary to sample the mixture in order to determine when this point has been reached, as indicated by the disappearance of swollen but undissolved fibres from microscopic observation and by solubility in chloroform. Degradation is monitored by viscosity measurement.
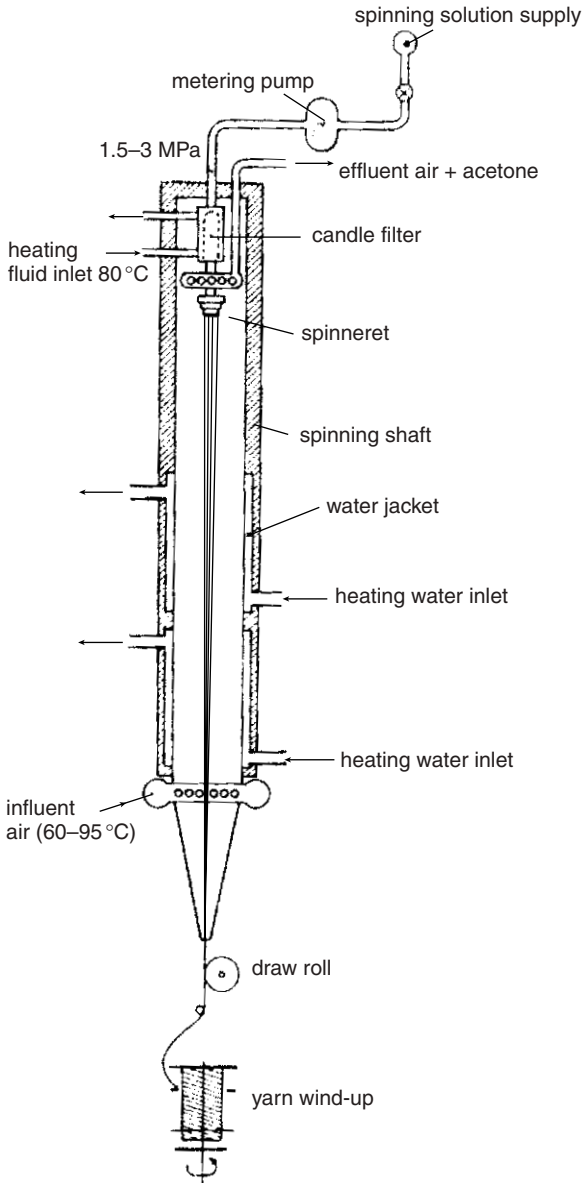
In order to make the secondary acetate, sufficient water is added to the mixture, which contains excess acetic acid and acetic anhydride, to give a 95% solution of acetic acid. Acid hydrolysis takes place over a period up to 20 hours at a higher temperature. The reaction is stopped when 1/6th of the acetate ($CH_3.COO-$) groups have been randomly changed to hydroxyl (–OH) groups. It is essential that any sulphate radicals are removed during hydrolysis. Excess water is added and the secondary acetate is precipitated. The liquor is removed to a recovery plant to extract the residual acetic acid. The polymer flakes are thoroughly washed, centrifuged and dried. Each batch is analysed and mixed with other batches in order to ensure a uniform product and avoid later troubles caused by differential dyeing or lustre.

It takes about 24 hours, with powerful stirring, to dissolve the secondary acetate in about three times its weight of acetone mixed with some water or alcohol. Titanium dioxide is added when dull yarns are being made. Black or other coloured pigments may also be added. After more blending, the spinning dope, which will be clear and colourless (unless pigments have been added), is filtered, de-aerated and passed to a feed tank (see Fig. 6.3).

Figure 6.4 illustrates the essential arrangement of dry-spinning equipment used to produce acetate fibres. The viscous dope, which contains 25–30% of secondary acetate, is pumped from the feed tank at a metered rate and through another filter to the spinneret, where the solution is extruded into the spinning cabinet. The spinneret is a metal plate, in which holes have been drilled typically between 50 and 100 μm in diameter. The

WOOD PULP OR COTTON LINTERS

PETROLEUM

'cracking'

CELLULOSE

ETHYLENE gas

PROPYLENE gas

other gases for chemicals

absorption

absorption

ACTIVATED CELLULOSE

ACETIC ACID liquid

ACETONE liquid

ACETYLATED CELLULOSE

'cracking'

'cracking'

hydrolysis

*ACETIC ANHYDRIDE liquid

ACETYLATED CELLULOSE

water

SULPHURIC ACID catalyst

ACETATE FLAKE

recovery and re-use

water → washing drying → weak acetic acid

SPINNING SOLUTION

acetone exhaust to recovery and re-use

*obtainable from either acetic acid or acetone

warm air →

cutter

CONTINUOUS FILAMENT YARN

TOW

STAPLE FIBRE

6.3 Diacetate fibre production flow chart. (Reproduced from Cook[4]).

spinning solution supply

metering pump

1.5–3 MPa

effluent air + acetone

candle filter

heating
fluid inlet 80 °C

spinneret

spinning shaft

water jacket

heating water inlet

heating water inlet

influent
air (60–95 °C)

draw roll

yarn wind-up

6.4 Diagrammatic representation of a spinning plant.

emerging dope descends vertically for 2–5 m against a countercurrent of hot air which enters the bottom of the tube. The temperature, moisture content and velocity of the air are important parameters. A guide roll at the bottom of the cabinet directs the fibres out to a collection device. For yarns,

a take-up bobbin is arranged to insert a small amount of twist. Take-up speeds are typically between 200 and 400 m min^{-1}, but may be as high as 1000 m min^{-1}. A small amount of finishing oil may be applied to the yarn before wind-up. A stretch of around 100% is imposed on the yarn as it is drawn down from the spinneret. This stretch causes molecular orientation to develop in the plastic filaments in the upper part of the tube and provides the comparatively low strength needed for the textile applications. An additional drawing step is not required.

The linear density (tex or denier) of the filaments produced depends on the rate of mass flow through the spinneret holes, which is controlled by the metering pump, and the speed of take-up. The extent of drawdown is influenced by the hole diameter, since it depends on the linear flow rate through the spinneret and the take-up speed. The yarn linear density is given by the filament linear density, determined as stated, multiplied by the number of holes in the spinneret. Celanese Acetate, the world's largest producer of acetate yarns, produces about 16 different combinations of filament and yarn sizes in variants adapted to different applications. The yarns range from 55 to 600 denier (60.5–660 dtex). The commonest filament sizes are around 3.7 denier (4.1 dtex), but go down to 1.67 denier (1.84 dtex) in the 100/60 yarn and up to 6.25 denier (6.9 dtex) in the 200/32 yarn.

Tows, for cigarette filters or for cutting into staple fibres, are obtained by combining the output from a number of spinning positions.

Generally, dry spinning is a cleaner and faster process than wet spinning and requires less labour. Each kilogram of acetate fibre produced needs about 0.65 kg of cellulose, 1.5 kg of acetic anhydride and 4 kg of acetic acid, of which about 0.4 kg of the cellulose and 0.6 kg of the acetic compounds make up the fibres. In addition, 0.05 kg of sulphuric acid, 3 kg of acetone and 45 kg of water are used. Economy dictates efficient recovery of the acetone evaporated from the solution and of excess acetic acid from the earlier stages.

6.1.2.2   Properties and processing

Secondary acetate fibres, which do not show any evidence of crystallinity in X-ray diffraction, have a density of 1.32 g cm^{-3} and a lobed cross-section. Different-shaped fibres can be made by using shaped spinneret holes. The fibres are comparatively weak, extensible, and have low stiffness, with poor elastic recovery above about 5% extension. Melting, which is accompanied by decomposition, is at about 230°C, but sticking occurs at lower temperatures, so that care must be taken in ironing. Because of the thermoplastic nature of the fibres, it is easy to emboss acetate fabrics. Moisture absorption is much lower than in viscose rayon, but the rate of change of moisture content is about the same as for cotton in the middle range of

humidities. Cellulose acetate is an excellent insulator, which was one of the reasons for making acetylated cotton. Secondary acetate is soluble in a number of organic solvents and swollen by others, but is unaffected by ether; it is ultimately biodegradable, but much more resistant to biological attack than viscose rayon and moderately resistant to degradation by light. Acetate is attacked by some concentrated acids and is saponified by alkalis. Alkaline scours should be avoided.

Because of the lack of reactive groups, dyeing was initially a problem. However, new dyestuffs, notably disperse dyes, suitable for acetate were developed and a wide range of colours can be produced. Boiling water impairs the lustre of acetate fibres, so that dyeing temperatures must be kept below 85°C.

6.1.3 Cigarette filter tow

Filter tow was introduced in the mid-1950s, initially as a better looking, better tasting and more wet-collapse resistant alternative to the semi-crêpe filter paper used on the few brands sold with filter tips at that time. It has since become the preferred filter material for most of the world's cigarette producers and, thanks to changes in smoking habits, tipped cigarettes are now by far the most important sector of the world tobacco market.

The tow is produced in much the same way as diacetate textile yarns, with the output from many spinnerets being combined to form the tow rather than being wound individually on bobbins. There are, however, some key differences. Most cigarette tow filaments now have a Y-shaped cross-section achieved by spinning the dope through jets with triangular orifices. As the acetone solvent evaporates in dry spinning, the sides of the triangular dope stream collapse inwards to give the shape illustrated in Fig. 6.5.


6.5 Typical Y cross-section tow.

This shape increases the bulk of the tow and increases the surface area available for intercepting smoke particles. Of even greater importance to the overall performance of the filter tow is the crimping and baling process. After the individual yarns have been lubricated with a mineral oil/surfactant mixture, they are 'dried' to remove most of the acetone solvent and combined into tow form for crimping in a stuffer box. The precise nature of the crimp has a significant effect on both the ability to make filter tips at the high speeds required by the tobacco industry and on the filtration and hardness characteristics of the filter tips. After crimping, the tow goes through a further drying stage to remove any residual acetone and to arrive at a precisely controlled moisture level in the region of 6%.

Filter tows are produced in sizes ranging from 18000 to 50000 total denier but most cigarette makers specify between 30000 and 40000 denier. The individual filaments can be as fine as 1.6 denier or as coarse as 7 denier, and while, as mentioned above, fibre cross-sections are mainly Y-shaped, I-shaped filaments and roundish filaments are also made. The tows are very carefully laid and packed into cardboard cartons which can contain up to a tonne of fibre. Precise presentation of long lengths of highly consistent tow is essential for the rod-making stage of the process of making filter tips. In this process the tows are 'bloomed' to deregister the crimp, sprayed with a partial solvent such as triacetin, wrapped in cigarette paper, and heated to fuse the filaments together at speeds that allow the production of some 6000 rods per minute. Each of these rods will have to be cut to form tips for 4 or 5 cigarettes at the next stage in the process, and each of these tips must meet exacting standards of diameter, porosity, hardness and pressure drop. They must also be capable of removing precise amounts of tar and nicotine from the smoke to allow the current wide range of advertised target tar and nicotine levels to be achieved with great consistency.

As mentioned earlier, the cigarette filtration market for diacetate tows has proved to be a 'fortress' that legions of attempts on behalf of polypropylene and other cheaper fibres including viscose and lyocell have failed to storm. It owes its continuing success to the fact that because it has been driven for the best part of 50 years by the demands of the tobacco industry, the process has evolved a quality and consistency of tow production that eludes those dealing mainly with the requirements of textiles. Its success is also a matter of taste. Diacetate, especially when bonded with triacetin, appears to have a beneficial effect on the perceived taste of filtered smoke: other fibres can perform just as well on the smoking machines, but human expert smokers always seem to prefer diacetate.

One possible future vulnerability of diacetate filter tips is their inability to filter down to the ultra-low tar levels now being introduced in response to consumer demands for 'safer' cigarettes. Tar levels below about 4 mg
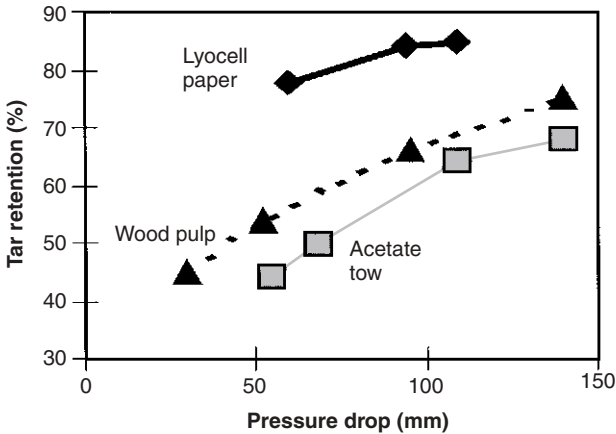
6.6 Filtrona Crest™ filter tips. Tar retention levels achieved by acetate tow, wood pulp paper and lyocell paper.

require filtration efficiencies that cannot be achieved with diacetate tow while maintaining acceptable pressure drops (draw resistance). Current commercial products therefore use laser perforation of the wrapping paper at the tobacco end of the tip which allow fresh air to dilute the smokestream entering the test equipment on the smoking machines used to test tar and nicotine yield. Ultra-low tar perforated diacetate cigarette tips can dilute the smoke with up to 70% of fresh air, a fact which human expert smokers detect very easily, and, allegedly, counteract easily by subconsciously or otherwise covering the perforations with their fingers. New 'Crest' tips have been developed by Filtrona using fibrillated lyocell fibres, and these, with numerous fine cellulosic hairs in the spaces between the filaments, allow ultra-low tar yields to be achieved without recourse to smoke dilution, and with acceptable pressure drops (see Fig. 6.6).

Hoechst Celanese addressed the need for ultrafine diacetate fibres that can intercept more tar and nicotine in cigarette filters with their 'Fibrets' product. These acetate fibrids* were manufactured by precipitating an acetate dope in water under conditions of high shear such that the precipitate was fibrous in nature. These fibrids could be made with very high specific surface area and could be made into papers, or attached to acetate tows for incorporation in filter tips.

*Fibrid: a term coined apparently by DuPont, which in the late 1960s developed the Fibrid–Textril approach to producing synthetic fibres (including viscose rayon) with paper-making properties. Fibrids were the pulp-like fibrillar microfibres that could be mixed with the short-cut regular fibres (Textrils), the combination being self-bonding enough to be converted on paper machines.

6.1.4   Cellulose triacetate

The advent of the synthetic fibres showed that there was a market for hydrophobic fibres, which could be heat set. This stimulated the production of triacetate fibres from solutions in methylene dichloride, which was easy and safe to handle and had become cheaply available by 1930. Acetylation of purified cotton linters or wood pulp may be carried out as described above for secondary acetate, but precipitated into water without hydrolyis of acetate groups, though it is necessary to remove sulphuric ester groups. In an alternative process, acetic anhydride acts directly on the cellulose in the presence of a non-solvent such as benzene, which has a slight swelling action, and an acid such as sulphuric acid, which speeds up the reaction. The solid cellulose triacetate is dissolved in methylene dichloride, mixed with some alcohol, and then dry spun into fibres in a similar way to secondary acetate.

Because of the regularity of the polymer molecules, triacetate fibres are partially crystalline with a melting point of 290–300°C. Many properties are similar to those of secondary acetate, but fabrics have a crisper handle. The moisture regain is lower and is further reduced by heat setting. There are two methods for heat setting: either dry heat at 170–200°C or steaming under pressure at 110–130°C.

6.2   Alginate fibres

Unlike other plants, the fibrous parts of seaweed are not based on cellulose but on the closely related polymers, alginic acid or its salts. The acid exists in two forms and has the chemical formula shown in Fig. 6.7.

Alginates, chain-forming heteropolysaccharides made up of blocks of mannuronic and guluronic acids, occur in the cell walls of the brown algae (*Phaeophycota*). They are present in sufficient concentrations for commercial exploitation (30–45% weight of dry seaweed) in the larger kelps and wracks (*Laminariales* and *Fucales*).

Alginic acid was first isolated by E C C Stanford in 1860 as jelly precipitated when a sodium carbonate solution of the abundant brown (not red or green) seaweed was acidified. He commercialized his process in the western highlands of Scotland and developed a range of alginates, mainly for thickening food, drinks and printing pastes. Scotland remains a leading producer, along with Norway, China and the USA. Some 25 000 tonnes of alginic acid are extracted from seaweed per annum worldwide, but the total is declining slowly.

Alginate's fibre-forming potential was explored by Speakman at Leeds University and first exploited during World War II when green monofilament yarns of chromium alginate were spun, on viscose machinery, to make
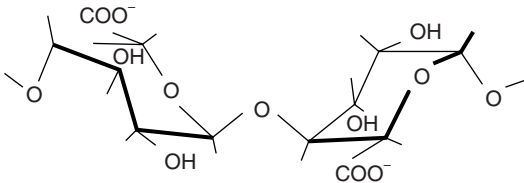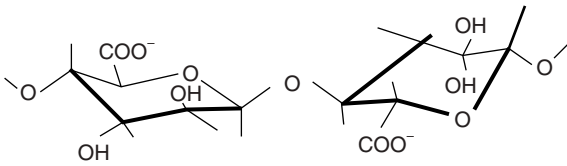
6.7 Two forms of alginic acid: guluronic and mannuronic acids.

camouflage netting. In order to make fibres, powdered and dried seaweed, usually the *Laminariae*, are treated with sodium carbonate and caustic soda to obtain a brown solution of sodium alginate. A series of purification steps, including conversion to alginic acid and back to sodium alginate, yield a dry white powder that can be dissolved in water to form a spinning solution. The fibres are formed by viscose-style wet spinning into a coagulating bath of 1 N calcium chloride solution and 0.02 N hydrochloric acid with a surface active agent. The filaments of calcium alginate are drawn, washed, lubricated, dried and wound up.

The non-flammability of calcium alginate fibres led to some applications. However, the main use found for alginate fibres derived from a property which rendered them useless for most purposes. They are soluble in hot soapy water and were used as 'disappearing threads' when fibres were required to be present in an intermediate stage of production but removed later. One example was to provide a scaffolding thread for the production of very lightweight fabrics. The commonest use was, however, as a linking thread during continuous knitting of socks, a market that the leading producer, Courtaulds, appears to have got into in order to help major customers to use viscose yarns in hosiery manufacture.

Polyvinyl alcohol, synthesized from acetic acid and acetylene via saponification of the polyvinyl acetate intermediate, became cheaper and more available than alginate during the 1970s and has now replaced alginate fibre in these markets. However, there was one small volume but very high value

alginate product for which polyvinyl alcohol was not suitable: a knitted algi-
nate gauze used as a haemostat – a dressing used to encourage blood to
clot, for example a nasal cavity packing for treating otherwise unstoppable
nose bleeds.* Collaboration between the fibre maker and the dressing man-
ufacturer led to the development of alginate nonwoven dressings that were
not only able to replace the old knitted product, but also capable of being
used in a wider range of medical applications. In numerous clinical trials
since 1990 it has been confirmed that alginate allows wounds to heal more
quickly and less painfully than traditional cotton dressings.

The multimillion pound business now enjoyed by alginate fibres in
advanced wound-care nonwovens is based on the special properties of
mixtures of sodium and calcium alginate in fibre form. Whereas sodium
alginate will dissolve in water, the calcium form is insoluble. A mixture
of the two shows intermediate behaviour and swells in water to form a
gel. Calcium alginate will also form a gel in fluids containing sodium ions –
wound exudates for example – and as we learnt above will dissolve
completely in alkaline soapy water. These properties have allowed
Courtaulds, Innovative Technologies Ltd and others to engineer dressings
that can provide the ideal healing environment for hard to heal wounds.
When these dressings need to be changed they can be removed without
trauma simply by dissolving the dressing in water containing sodium
ions.

The differing response to sodium and calcium ions arises because algi-
nate polymer is in fact a mixture of two monomers, mannuronic (M) and
guluronic (G) acids, and in the polymer these tend to be arranged in blocks.
Depending on the types of seaweed from which the alginate is extracted,
fibre can be made rich in one monomer or the other and those with more
of the mannuronic form (high in M units) exchange calcium for sodium
more readily. High-M fibres form gels more rapidly than high-G fibres. In
fact when any mixed fibre swells, it does so because the calcium crosslink-
ing in the M units is exchanged first and the gel is prevented from dissolv-
ing by the links between the G units (see Fig. 6.8).

Alginate fibres have dry properties similar to viscose and can be con-
verted into a variety of dry-laid nonwovens with ease. They are typically
bonded by needlepunching, but can also be produced in the spun-laid form
and as such can be self-bonded or bonded after drying using water as the
solvent. The nonwovens will absorb up to 20 times their own weight of test
fluid when tested according to the Pharmacopoeia procedure.[13] High-M
products, for example Sorbsan®, can be distinguished from High-G prod-
ucts such as Kaltostat® by this test (see Fig. 6.9).

*The wound-healing properties of seaweed have apparently been appreciated by
sailors for centuries.
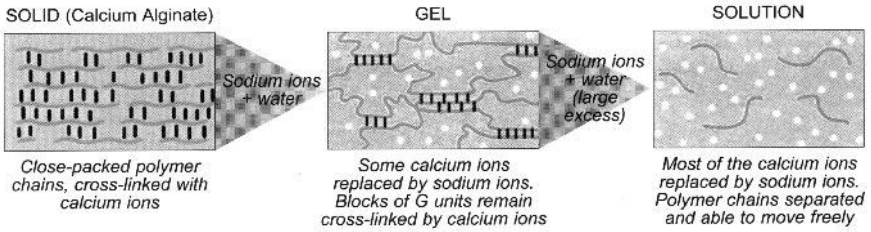
6.8 Principles of gel dressings based on alginates. (Reproduced by courtesy of Acordis Speciality Fibres.)
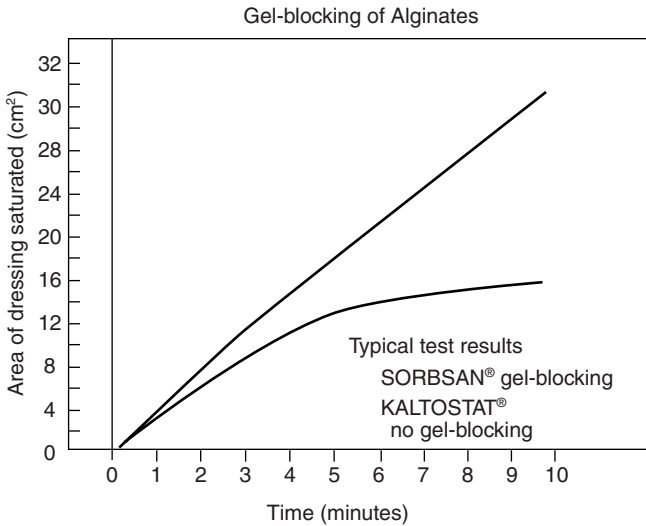
6.9 High-M dressings such as Sorbsan® (lower curve) resist the spreading of wound exudates better than high-G dressings such as Kaltostat® (upper curve). (Reproduced by courtesy of Acordis Speciality Fibres.)

In a wound-care context, gel blocking, as the restriction in lateral transfer of fluid is known, prevents healthy tissue surrounding the wound from being damaged by maceration.

6.3   Sodium carboxymethyl cellulose (CMC) fibres

The carboxymethylation of cotton and wood cellulose has been practised for many years to produce thickening agents for food, drinks and drilling lubricants. Alkaline cellulose is reacted with monochloracetic acid, Equation [6.1]:

$$(C_6H_9O_4 \cdot O^-Na^+)_n + nCH_2ClCOOH$$
$$\rightarrow (C_6H_9O_4 \cdot OCH_2COOH)_n + nHCl$$

[6.1]
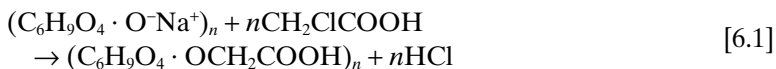
While these products were usually more powdery than fibrous, short-fibre versions could be produced from cotton linters and these could be blended with rayon fibres to enhance the absorbency of hygienic disposables, especially tampons. (Hercules in the USA produced 'Aqualon' for such end-uses.) Normally water soluble, these products could be crosslinked to limit the extent of swelling in water and as such they were early examples of superabsorbent fibres. Buckeye Cellulose produced 'CLD2' (Cross-Linked Derivative) in the USA for Procter and Gamble and the 'Rely' tampon. In Japan, Asahi developed and commercialized a superabsorbent version of their cuprammonium rayon spun-bond nonwoven fabric as 'Super AB' for use in medical dressings.

Viscose rayon can be carboxymethylated to give products ranging from highly absorbent to water soluble depending on the degree of substitution and crosslinking, but the fibres are generally too harsh and brittle to be used as textile or nonwoven fibres. Less costly products with useful absorbency benefits were however commercialized by Avtex and Enka in the USA, based on dissolving CMC in sodium hydroxide and injecting it into the viscose dope just prior to spinning. These so-called 'alloy fibres' were not true CMC fibres but a practical way of bringing the functionality of CMC into regenerated cellulose fibres.

Lyocell fibres (see Chapter 4) are much stronger than viscose, a feature which led Courtaulds (now Acordis) to investigate continuous carboxymethylation processes on lyocell tows and batch processes on both tow and staple fibres. Like the alginate products mentioned above, nonwoven dressings made from these true CMC fibres provided the ideal healing environment for difficult wounds, and the product has now been commercialized by the Speciality Fibres division of Acordis Fibres.

For a fibre that gels instantly in water, imbibing over six times its own weight while remaining coherent enough in the wet state to be handled, the physical properties of this CMC fibre are outstanding. Air dry (i.e. at 12% moisture content) 2 decitex fibres have a tenacity of 29 cN tex^{-1} and an extensibility of 13%. Needlepunched nonwovens are easily manufactured and freely absorb 58 g g^{-1} of water, or 35 g g^{-1} of 0.9% saline. Furthermore they absorb 22 g g^{-1} of 0.9% saline under loads of 3 kPa (0.45 psi).

References

1 R W Moncrieff, *Man-made Fibres*, 6th edition, London, Newnes-Butterworth, 1975 Chapters 11, 12, 16.
2 D C Coleman, *Courtaulds: an Economic and Social History*, Oxford, Clarendon Press, 1980.

 3 M Raheel, History of cellulose acetate fibers, *Man-Made Fibers: Their origins and development*, eds R G Seymour and R S Porter, Oxford, Elsevier, 1991, pp 142–168.

 4 J G Cook, *Handbook of Textile Fibres. II Man-made Fibres*, 5th edition, Shildon, Co. Durham, Merrow, 1984, Chapters 2, 4.

 5 E E Treiber, Formation of fibers from cellulose solutions, *Cellulose Chemistry and its Applications*, eds T P Nevell and S H Zeronian, Chichester, Ellis Horwood, 1985, Chapter 18.

 6 P Schützenberger, *Comp. Rend* 1865 **61** 485–486.

 7 L Nadin and P Schützenberger, *Comp Rend* 1869 **68** 814.

 8 C Liebermann, and O Hoermann, *Berichte* 1878 **11** 1618.

 9 A Franchimont, *Rec Trav Chim* 1889 **18**(2) 465, 472.

10 C Cross, E Bevan and C Beadle, *Proc Chem Soc* 1895 **31**.

11 G Miles, German Patent M-28289, Sept 30th 1905.

12 D C Coleman, *Courtaulds: an Economic and Social History*, Oxford, Clarendon Press, 1969, Vol. II.

13 Thomas and Loveless, *Pharm J* 1992 **248** 850–851.