

3.1 Introduction

The first patent on the viscose process was granted to Cross and Bevan in England in 1893. By 1908 the fibre spun from viscose dope had been accepted as a key component of the burgeoning textile industry (see also Chapter 1). Viscose (or rayon) still enjoys the unique position of being the most versatile of all artificial fibres. This has resulted from an ability to engineer the fibre chemically and structurally in ways that take advantage of the properties of the cellulose from which it is made.

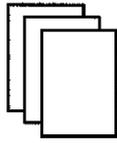
Over the past 100 or so years the viscose process has undergone many refinements. However, the basic chemistry is still the same. Through this route short-fibre cellulose (wood pulp) is converted in a series of controlled and coordinated steps to a spinnable solution (dope) and then into longer filaments which may be precisely controlled in terms of length, denier, physical properties and cross-sectional shape.

The pulp is first steeped in an aqueous solution of sodium hydroxide (17–19%) which causes the fibres to swell and converts the cellulose to sodium cellulosate, commonly called alkali cellulose or white crumb. After steeping, the swollen mass is pressed to obtain a precise ratio of alkali to cellulose, and then can be shredded to provide adequate surface areas for uniform reaction in subsequent process steps. The alkali cellulose is aged under controlled conditions of time and temperature to depolymerise the cellulose by oxidation to the desired degree of polymerisation (DP) prior to reacting with carbon disulphide to form sodium cellulose xanthate. The xanthate, which is a yellow to orange crumb, is dissolved in dilute sodium hydroxide to yield a viscous orange-coloured solution called viscose. The solution is filtered, deaerated, and ripened to the desired coagulation point (called salt index) appropriate for spinning (see Fig. 3.1).

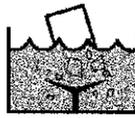
The rayon filaments are formed when the viscose solution is extruded through the very small holes of a spinneret into a spin bath consisting basically of sulphuric acid, sodium sulphate, zinc sulphate and water. The spin



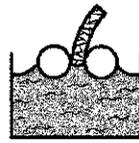
1. Viscose is made from cellulose, a constituent of all land-growing plant life. Spruce and eucalyptus yield much of the high-grade cellulose required for viscose.



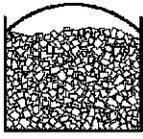
2. Cellulose. In the pulp mill the bark, lignin etc, are removed from the trees and the extracted cellulose is pressed and cut into sheets.



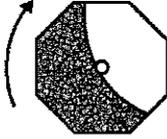
3. Slurrying. In the viscose factory the sheets of cellulose are slurried in caustic soda with which it combines to form alkali cellulose.



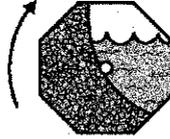
4. Pressing. The excess soda is then pressed out and drained off for recovery and re-use.



5. Pre-aging. The shredded alkali cellulose is stored to allow the oxygen in the air to oxidise it. This reduces the molecular size of the cellulose, which is necessary to obtain a spinning solution of the correct viscosity.



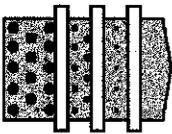
6. Xanthation. The alkali cellulose is combined with carbon disulphide (derived from carbon and sulphur) to produce sodium cellulose xanthate.



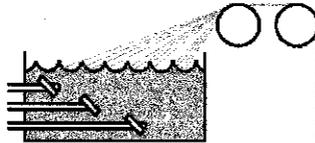
7. Dissolving. The sodium cellulose xanthate is dissolved in caustic soda to form the syrup-like spinning solution known as viscose.



8. Ripening. To improve its spinning qualities, the viscose is allowed to ripen. Meanwhile it is held under vacuum to remove air bubbles.



9. Filtration. The viscose is filtered to remove any particles and undissolved cellulose which might block holes in the spinning jet (spinneret), which could produce decitex variations.

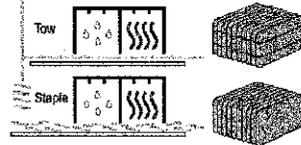


10. Spinning/Washing. The viscose is extruded through the fine holes of a spinneret into a coagulating bath of sulphuric acid and salts which neutralises the alkaline content of the viscose and regenerates the original cellulose as continuous filaments.

Filaments from a number of spinnerets are drawn together to form a continuous tow.

a) Tow. The tow is collected on a conveyor, washed and dried and plaited into bales.

b) Staple fibre. The tow, which consists of thousands of continuous filaments, is fed into a cutter which produces fibres of the desired staple length. The staple fibre is collected onto conveyor, washed and dried prior to baling.



3.1 The viscose process. (Reproduced by courtesy of Acordis.)

bath often also contains a low level of surfactant. Coagulation of the filaments occurs immediately upon neutralising and acidifying the cellulose xanthate followed by controlled stretching and decomposition of the cellulose xanthate to cellulose. These latter steps are important for obtaining the desired tenacity and other properties of the fibre. Finally, the newly formed

Table 3.1 Common grades of dissolving pulp

Pulp manufacturer	Wood type	Cooking process
IP	Southern hardwood/northern softwood blends	Kraft
Tembec	Mixed softwoods	Sulphite
Riocell	Eucalyptus	Kraft
Borregaard	Spruce	Suphite
Modo	Spruce	Sulphite
Lenzing	Beech	Sulphite
Saiccor	Eucalyptus/acacia	Sulphite
Bacell	Eucalyptus	Kraft

filaments are washed free of acid, chemically treated (desulphurised), and bleached prior to final washing and applying a processing finish. This is done either in the form of continuous filament (yarns or tow) or as cut staple, prior to drying and packaging.

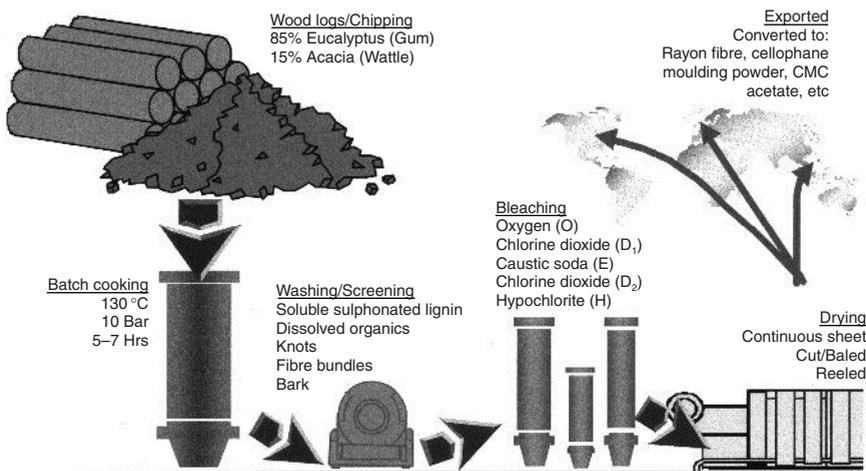
3.2 Viscose making

3.2.1 Pulp

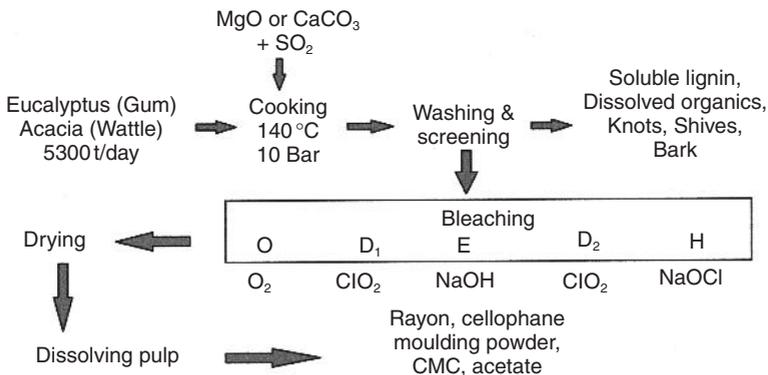
A variety of dissolving-grade wood pulps can be used as the cellulose source in viscose rayon processes, as shown in Table 3.1. A minority of viscose is also made from cotton linters.

For commercial reasons, many viscose plants have optimised their process conditions for pulp furnishes containing predominantly one or two types of pulp. This may be a combination of short and long fibre grades. Wood pulp is usually supplied as either bales of pulp sheets or flock (compressed bales of pulp fibres).

A typical pulp used for viscose manufacture is made by SAPPI Saiccor. This is predominantly a eucalyptus pulp (short fibre hardwood), with perhaps some acacia (Wattle) also present in the blend. SAPPI Saiccor (Fig. 3.2–3.4) use the acid sulphite process for manufacturing pulp, and bleach with an elemental chlorine-free (ECF) sequence, having replaced their chlorine gas delignification stage first with oxygen, and then with chlorine dioxide treatments. The replacement of chlorine bleaching has been a recent trend in the pulp industry brought about by environmental pressures (see also Chapter 2). Other market pulp manufacturers use a range of wood types, and some also employ the alkaline Kraft process. For dissolving pulp,



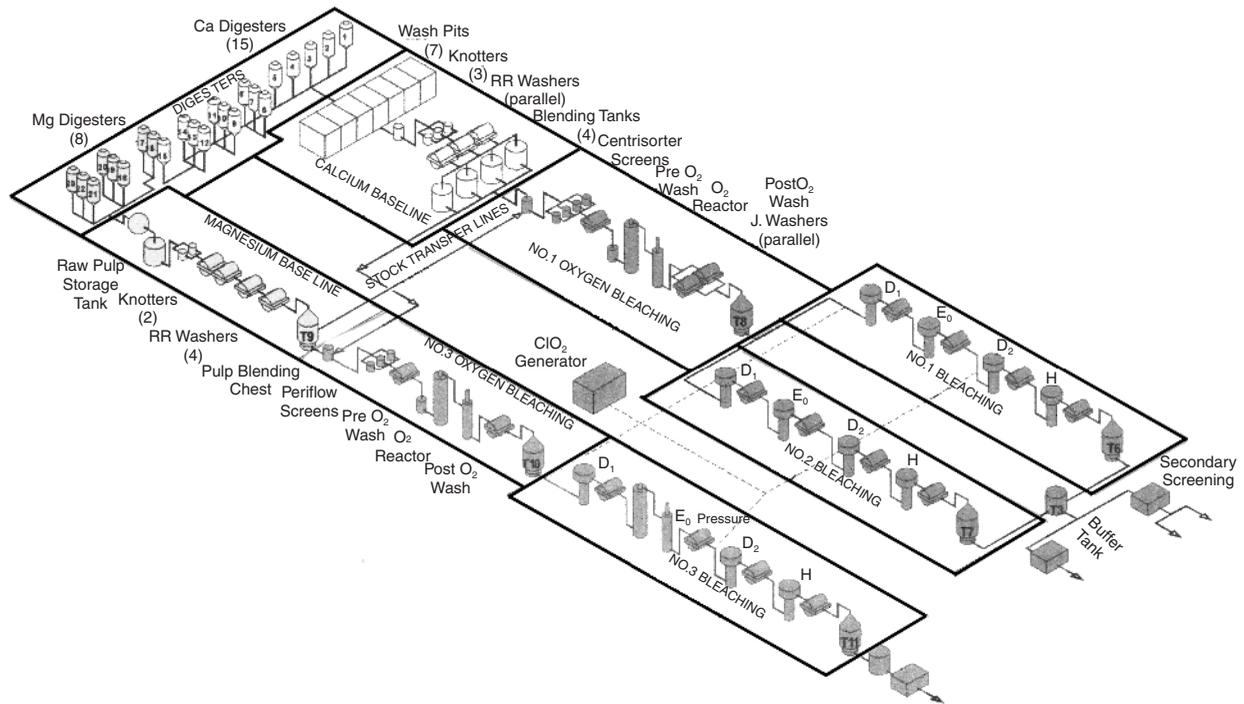
3.2 Typical sulphite pulping operation – overview.



3.3 Process overview.

the Kraft process must be preceded by a prehydrolysis acid treatment stage to remove the primary wall from the fibres in the wood.

Different pulps require different steeping conditions in order to achieve optimal viscose quality. This issue becomes particularly important when market pulps are used in blends in the viscose factory. Identifying the best compromise between optimum steeping conditions and effecting an intimate blend of the pulps is critical in achieving acceptable and stable viscose



3.4 Process overview.

quality. Such differences are largely associated with the different fibre dimensions of the pulp fibres derived from different wood sources, which result in different reaction rates in the viscose process. Hardwood (short fibre) and softwood (long fibre) blends are generally not recommended for this reason, although the introduction of a small percentage of softwood is often made to improve slurry drainage.

Many dissolving pulps which are to be used in the viscose process now contain a small amount of synthetic resin (surfactant) which is added prior to drying at the pulp mill. This material aids soda penetration at steeping and improves the swelling of the pulp.

Many pulp properties have a significant effect on the viscose process and subsequent fibre properties. These include the degree of polymerisation, the oxidation state of the cellulose, the level of lignin, the soda solubility and the residual level of pulp impurities like iron and silica.

3.2.2 Steeping

Historically, sheet steeping was the norm in the viscose industry, whereby sheets of dissolving pulp or cotton linters were placed in a rack and submerged in a tank of soda (steeping lye). Now, virtually all viscose production utilises slurry steeping, where the pulp is added to a vigorously agitated tank of soda. The process can be operated either continuously or batchwise. Because of viscosity effects, the slurry is relatively dilute, the consistency being typically less than 6% cellulose.

The objective of the steeping process is to convert the cellulose to its alkoxide derivative (alkcell) in as effective a manner as possible. However, the extent of conversion is hampered by the compact nature of the cellulose sheets, and by the accessibility of the soda into the discrete cellulose fibres. For effective xanthate formation later in the process, it is important that the cellulose is converted to its alkoxide form in both its amorphous and crystalline regions. A further objective is to remove the undesirable short-chain materials present in the pulp (hemicellulose and γ -cellulose), as these materials will otherwise consume CS_2 at xanthation and potentially deteriorate fibre quality.

Hence steeping conditions are optimised to ensure good formation of the alkoxide, and dissolving out of the hemi- and short-chain celluloses. Two main parameters are used to achieve optimum steeping, soda temperature and soda concentration.

A higher soda temperature dissolves out more of the short-chain material, but reduces the swelling of the pulp. Hence there is an optimum temperature, usually around 45–55°C. Some depolymerisation also takes place during steeping, and the extent of this will increase with increasing temperature.

For soda concentration, pulp swelling increases as the concentration is reduced, to a maximum at around 11%. A high degree of swelling is desirable because it opens up the pulp structure to enable short-chain material to be leached out, and to enable the soda to penetrate effectively into the fibre structure. However, higher concentrations are necessary to ensure that the conversion to the alkoxide derivative proceeds to an acceptable extent. In practice, around 17–19% soda is typical.

Typically, the residence time through steeping is around 5–10 min. After the steeping vessel (normally referred to as a pulper), the slurry is pumped into a retention tank to aid blending and ensure complete soda penetration. A typical residence time in the retention tank would be 10–20 min. The primary function of the retention tank is to provide a buffer volume to ensure a continuous supply of slurry to the presses.

3.2.3 Double steeping

Double steeping is a technique which was developed to reduce CS₂ consumption and by-product formation. Essentially, as the name suggests, there are two steeping stages:

- Stage 1: steep as normal in 17–19% soda, followed by relatively light pressing, and no shredding;
- Stage 2: steep in lower concentration soda, say 11–13%, followed by pressing and shredding as normal.

The first steep swells the pulp and converts the cellulose to the alkoxide derivative to the required extent. The second steep swells the pulp further still, allowing extra hemicellulose to be removed. Additionally, the excess soda remaining after pressing has a lower NaOH content than if the steep were performed with just normal concentration steep soda. Hence following the second steep the alkcell going to the churn has lower concentrations of hemi and NaOH than normal, resulting in lower CS₂ consumption.

Despite the theoretical advantages of this process, double steeping has found only limited commercial application. Attempts to achieve reductions in CS₂ using this technique have largely proved unsuccessful to date.

3.2.4 Pressing and soda recovery

The slurry presses remove excess soda from the alkcell slurry. The excess is returned to the steep soda circuit for re-use. Essentially the slurry is pumped between two nip rollers with a narrow gap of the order of 5–15 mm. The extent to which the soda is squeezed out will be determined by the roll speed (which essentially governs the residence time of the slurry between the rollers), and by the gap between the rollers. The roll material is sintered

metal, which allows the expressed soda to pass through and away for recovery. The recovered soda (press soda) is always of lower concentration than the steep soda because some of the NaOH combines with the cellulose. Hence strong soda is added to the steep soda circuit to maintain the concentration at target levels.

Other control parameters of importance at pressing are:

- slurry surge pressure, with high pressures giving high levels of pressing, but potentially excessive fibre levels in the press soda, and clumping of the cellulose fibres leading to uneven alkcell
- nip pressure, which increases as pressing becomes more difficult. High nip pressure reduces the press roll life.

Highly swelled pulp makes pressing difficult. Hence, as with the steeping stage of the process, there will be a trade-off required between achieving increased swelling to ensure good accessibility and hemi removal, and achieving acceptable press throughputs.

3.2.5 Hemi and low-molecular weight cellulose

The press soda contains a relatively high level of fines – usually fibres or pieces of fibre from the pulp. These are removed usually by Waco and plate and frame filters in series, which filter the fibres out from a sidestream off the soda system.

For normal staple fibre production, hemi levels in the steep soda circuit are allowed to reach a natural equilibrium. However, where fibre tensile properties are critical, it is often valuable and sometimes vital to reduce the hemicellulose at steeping down to 1.0–1.5%. This is usually achieved by employing a dialysis (or reverse osmosis) system, where the NaOH and hemi/low-molecular weight cellulose are separated using a membrane. This is usually performed on a sidestream from the steep soda circuit, with the flow through the dialysis plant being set to achieve the desired hemi level.

Following dialysis, the ‘clean’ soda is returned to the steep soda circuit. The ‘dirty’ or hemi-rich soda is used elsewhere, often in a less critical viscose process or for xanthate dissolving. The key here is that although the hemi that has been removed by dialysis may well be returned into the viscose at the mixing stage, it is absent during the critical xanthation stage.

3.2.6 Shredding

Following pressing, the alkcell composition is typically 30–36% cellulose and 13–17% soda. Although now present as a ‘crumb’, the alkcell is relatively dense. To assist the subsequent mercerising (pre-ageing) and

xanthation reactions, shredding is usually performed at this stage to open up the alkcell and facilitate the penetration of oxygen and CS_2 into the alkcell. Shredding reduces the alkcell density typically from 250–450 g l^{-1} down to 80–170 g l^{-1} .

Not all viscose operations utilise shredding but this is by far the normal approach.

3.2.7 Mercerising (pre-ageing)

As received, pulp typically has a DP of 750–850. For commercial viscose processes, this must be reduced to the point at which viscose dope of an acceptable viscosity will result, while maintaining the final fibre DP high enough to achieve acceptable fibre tensile properties.

For regular staple production, the DP of the alkcell going to xanthation needs to be around 270–350. The reduction in DP is achieved in all commercial viscose operations by oxidative depolymerisation, using time and temperature to control to the required DP. Some manufacturers employ catalysts (e.g. manganese) or enriched oxidation to speed up this process.

The alkcell is often stored in temperature and humidity controlled silos while the DP reduction takes place. Typical mercerising times range from 0.5–5 hours at temperatures of 40–60°C. A variety of devices are used to mix the alkcell including rotating horizontal drums and moving belts. In all cases, cellulose chain length is reduced by a combination of free radical and alkaline degradation. Alkaline degradation tends to occur either at the chain ends ('nibbling', which gives very little overall reduction in mean DP) or at reactive sites such as carbonyl groups on the chain backbone. Such sites arise naturally in cellulose, and also as a result of bleaching in the pulp process. Hence pulp with a high copper number (a measure of the number of carbonyl groups on cellulose) will mercerise faster than will pulp with a low copper number.

Free radical depolymerisation occurs randomly along the cellulose chain, although the dependence upon oxygen to initiate the sequence means that accessibility is an issue, with the crystalline areas potentially undergoing less degradation than the more accessible amorphous regions.

3.2.8 Irradiative depolymerisation

The reduction of pulp DP down to the levels required in alkcell at xanthation can be achieved by irradiative treatment, as opposed to the usual chemical mercerising. Electron beam and gamma irradiation both enable the required DP reductions to be achieved, and in addition these treatments have been found to 'activate' the pulp, making it more reactive in the

viscose process. Practically, this means that lower levels of CS_2 and NaOH are required to achieve a homogeneous viscose than is the case if regular non-irradiated pulp is used. Additionally, the irradiated pulp appears to give different rheological properties to the viscose dope, enabling much higher cellulose-in-viscose levels to be used whilst maintaining acceptable filtration and spinning performance.

The benefits associated with irradiation appear to stem from the ability of the electron or gamma beams to penetrate all regions of the pulp, crystalline and amorphous, equally, thereby giving a completely homogeneous depolymerisation. Additionally there is disruption of the crystalline lattices. These aspects facilitate much more even derivatisation, and therefore the resulting xanthate is more readily brought into solution than would otherwise be the case.

Electron (e-beam) processing is the treatment route that has found most favour. A number of industrial-scale trials have been performed and the results achieved have been very interesting. Further development work is required still to characterise the e-beam process fully, before any manufacturer would be in a position to commit to commercial operation using e-beam treated pulp. However, this is expected to occur by the end of 2002.

3.2.9 Alkcell transportation and cooling

Alkcell can be conveyed from the presses to mercerising and ultimately to xanthation by a mixture of platform conveyors, belts and/or airvey systems. All of these, but particularly the airvey system, allow the alkcell to cool from the steeping temperature to closer to the target xanthation temperature of 28–35°C. However, it is important to ensure that the alkcell, as it enters the xanthation vessel, has a minimal temperature difference relative to the xanthation vessel, to avoid condensation. Any alkcell which comes into contact with water will revert substantially to cellulose from its alkoxide form, and thereafter be unreactive at xanthation. Unreacted cellulose following xanthation will cause potentially extreme filtration problems, and may necessitate discarding of the viscose.

Some plants employ a forced cooling system for alkcell, in which a semi-fluidised bed of alkcell is passed continuously through a temperature and humidity controlled atmosphere. Other processes rely on the alkcell transportation to cool the alkcell.

Metal detectors are often employed to screen out extraneous metallic objects from the alkcell prior to addition to the churns. Metal items in the churn can cause spark formation which could in turn lead to an explosion when the churn is vented to atmosphere upon completion of the xanthation reaction.

3.2.10 Xanthation

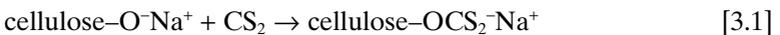
During xanthation, the mercerised alkcell reacts with CS₂ vapour to produce sodium cellulose xanthate. It is this derivative which is soluble in dilute caustic soda, and when so dissolved forms viscose dope. The reaction is performed under vacuum to ensure vaporisation of the CS₂ (CS₂ is a liquid at room temperature). Mass transfer rates are key to the xanthation reaction, as the reaction is heterogeneous. Commercially, three types of reaction vessel are used:

- 1 Wet churns, where the alkcell is slowly agitated as the CS₂ is added. Upon completion of the xanthation (seen as a vacuum 'regain' as the residual CS₂ vapour is consumed by the alkcell), the dissolving or mix soda is added directly to the churn. This is a batch process.
- 2 Dry churns, where the xanthate crumb is discharged into a separate dissolving vessel upon completion of the reaction. This is also a batch process.
- 3 Continuous belt xanthators, where the xanthate is conveyed through the reacting vessel, again under reduced pressure, as the CS₂ is added continuously. At the end of the conveyor, the formed xanthate drops into the mix soda and is pumped out to dissolving.

The time for complete xanthation depends on temperature and target CS₂ level, and typically lies between ½ and 1½ hours. Xanthation vessels are often jacketed to ensure constant temperature (typically 25–37°C).

During xanthation, CS₂ reacts principally with the C2 and C3 hydroxy substituents on the glucose rings in cellulose, as these positions are kinetically favoured over the C6 position. However, the availability of free NaOH and hemicelluloses/low molecular weight cellulose encourages a number of CS₂ – consuming side reactions to take place. Hence minimising the amount of these materials in the alkcell entering the churn is important in achieving low consumption of CS₂ and NaOH.

Sodium cellulose xanthate formation occurs as follows, Equation [3.1]:



By-product formation occurs by a much more complex series of reactions which may be summarised simply as follows, Equations [3.2] and [3.3]:



By-product formation is encouraged at higher temperatures, but dropping the xanthation temperature to achieve better CS₂ usage efficiency also

extends the xanthation time; hence a compromise is necessary between productivity and chemical usage.

3.2.11 Mixing (dissolving) of the xanthate

To form the viscose solution, xanthate must be dissolved in dilute sodium hydroxide solution of the required concentration to give the final target viscose composition in terms of percentage cellulose and soda in viscose. For a typical alkcell composition, the concentration of dissolving soda is normally 1.0–2.0% NaOH. Low temperatures are better, as the xanthate has greater solubility in NaOH at lower temperatures, and although most operations use 8–12°C, forced cooling of the dissolving soda down to 0–5°C will allow better dissolving and can enable CS₂ usage to be reduced somewhat. The xanthate is also more soluble in higher NaOH concentrations, and it is therefore doubly advantageous to press off as much soda as possible from the alkcell prior to the churns and use this to increase concentration of soda at mixing.

The mix soda is dosed into wet churns in two to three stages following the attainment of regain. In some operations the remaining churn vacuum is vented prior to addition, and for others venting occurs after addition. To minimise the risk of explosion at venting (as air mixes with the CS₂ vapour), nitrogen purging of the churns is sometimes used. Some operations employ a staged addition of mixing liquors of varying concentrations, emptying the churn between each addition to ensure a good degree of churn cleanliness for the next batch.

3.2.12 Viscose ageing

Viscose dope must be aged before spinning can take place to allow for the distribution of CS₂ evenly on the cellulose chains. Even distribution is vital if stable spinning and good fibre properties are to be achieved.

Sodium cellulose xanthate is an unstable compound. Although in the churn (or continuous belt xanthator), the xanthate substituted at C2 or C3 is kinetically favoured, this derivative is thermodynamically unstable when compared with the C6 derivative. Consequently, as time goes by the proportion of C6 derivative increases relative to the C2 and C3 substituents. The shift toward a greater proportion of C6 is due to a combination of ‘trans-xanthation’ (CS₂ coming off the C2 and C3 positions and re-xanthating at C6), and losses of CS₂ from the C2 and C3 positions to form more stable ‘by-products’ with hemi and soda. Clearly, for the trans-xanthation mechanism, CS₂ is also able to re-xanthate a previously unxanthated part of the chain, and this also helps to make the cellulose better solvated.

The degree of xanthation and the evenness of xanthation are measured by determining the concentration of salt solution required to precipitate the xanthate from viscose. The salt figure test uses sodium chloride solution, the Hottenroth test uses ammonium chloride.

3.2.13 Filtration

Regardless of how well the xanthate is brought into solution, there will always be particulate material in the viscose. This type of impurity needs to be substantially removed prior to spinning to prevent blockage of the holes in the spinning jet. Historically, cloth filters were employed in filter presses to remove particulates, with typically three stages of filtration, each stage consisting of a number of plate and frame (P&F) units in parallel. Once blinded by particulates, cloths would be removed manually and washed for re-use or discarded. It is believed to be important to establish a reasonable residence time for the viscose between each stage of filtration in order to achieve maximum particulate removal efficiencies.

The later generations of P&F filters employ a backwash facility, where cloths can be regenerated *in situ* by taking the filter off-line and backflushing with caustic soda. The backwash soda would then itself be filtered to concentrate the waste particulate material into a single stream for disposal, with the 'clean' backwash soda then being re-used elsewhere in the process (e.g. for mixing, washing, scrubbing, effluent neutralisation, etc.). A range of 'cloths' can be used for P&F filters based on cellulosic and/or synthetic materials.

Most modern viscose plants now favour the use of automatic mechanical filters. These essentially consist of sintered metal screens with hole sizes in the 10–20 μ m range. The filters backflush automatically on the basis of pressure build-up, with the reject material itself then being filtered, as with the P&F filters, to concentrate in a waste stream for disposal. In comparison to P&F units, this type of filter (e.g. Lenzing KKF, Brunswick) has a very low labour requirement, is compact, and is not prone to leaks. However, capital cost is higher than for P&Fs.

The two types of filter have very different performance characteristics. P&F filters will stop most particulates within the design specification limit of the filter medium until the filter 'blinds', at which point particulates will be pushed through the cloth and efficiency will start to fall. Additionally, P&F cloths are prone to releasing any deposited particulates if the system pressure or flow changes suddenly (this is referred to as 'shocking' the system). Mechanical filters can also allow certain materials to pass through, particularly fibres which in cross-section are smaller than the sinter hole size.

In addition to the 2 or 3 stages of viscose filtration in the 'cave', further filtration is sometimes effected at the spinning machines, either by central

filters on each spinning line, by candle filters on each spinning rounder arm and/or by filter cloths in each jet assembly.

3.2.14 Deaeration

To ensure continuity at spinning, the viscose must be deaerated to remove any dispersed air or other gases that might otherwise cause small bubbles to form as the viscose is extruded into filament form through the jet. Traditional deaeration techniques are employed (cone, film and tank deaerators) where a vacuum is applied while the viscose is passed over a surface to maximise its surface: volume ratio. Some CS_2 and water is lost from the viscose at deaeration.

3.2.15 Additives

Spinning aids, modifiers and pigments can be added to the viscose shortly before spinning. A range of surface active materials can be used to aid spinning performance. Largely these are fatty acid or fatty amine ethoxylates. Most only need a short residence time in viscose, and are added via a barrel mixer around 10–15 min before spinning. Titanium dioxide can also be added at this point to produce dull or matt fibres. The TiO_2 is usually either dispersed in dilute soda to form a fine slurry, or dispersed in viscose to produce an ‘injector viscose’ which itself is then metered into the main viscose.

3.3 Spinning

3.3.1 Jets and extrusion

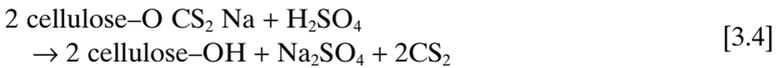
Most jets used to spin viscose fibres are fabricated from a platinum/gold alloy, the technologies used historically have, however, been very diverse. Two types of spinning jet are usually available, known as ‘full-face’ and ‘cluster’. With ‘full-face’ jets the holes are effectively punched directly in the jet cap. With cluster jets, which are becoming the norm, assemblies of discrete smaller spinnerets or thimbles are housed in a single larger plate. The gaps between the thimbles provide channels for spinbath liquor to access the forming filaments.

In cluster plates, the thimbles may be recessed to avoid damage. However, the recess has on occasion been implicated in poor spinning performance, as this region can suffer from poor acid access and flow vortex formation. Therefore some manufacturers have adopted spinning configurations where the thimbles are protruding. Typical cluster jets for spinning fine dtex fibre contain 30 000–50 000 holes. Each hole is typically 40–60 μm in diameter.

Each hole in the jet usually has an entry cone on its viscose feed side, typically at an angle of 20° to the hole axis. This is to allow for smooth, non-turbulent flow of the viscose through this region. The ratio hole length to diameter (L/D ratio) is normally 1.20–1.80, with the larger ratios (longer capillaries) in theory giving better spinning performance by virtue of reduced turbulence and increased shear.

3.3.2 Spinning chemistry and filament regeneration

The sequence of physical and chemical transformations taking place at spinning is extremely complex and still not fully characterised. The main reaction is clearly reformation of cellulose from sodium cellulose xanthate by the action of sulphuric acid, Equation [3.4]:



However, this follows the transient formation of the more stable zinc cellulose xanthate in certain regions, with additional more complex species also being formed if viscose modifiers are used. Zinc sulphate is soluble up to around pH 8.5, so this material penetrates into the forming filaments ahead of neutralisation (reaction 3.4 above). However, after the initial formation of zinc cellulose xanthate (followed rapidly by regeneration to cellulose) in the outer regions of the filaments, further penetration is believed to be impeded by the formation of other zinc species such as Zn(OH)_2 and ZnS . Hence the formation of a transient region of zinc cellulose xanthate is 'overtaken' by the penetration of acid.

The region in which zinc cellulose xanthate has formed is believed to be responsible for the skin effect which can be seen in rayon fibre cross-sections. The skin region retains dye because of a greater degree of crystal structure relative to the core. The transient zinc complex is believed to aid the formation of greater crystallinity by delaying regeneration relative to sodium cellulose xanthate (the zinc variant is more stable), and possibly also by cross-linking between neighbouring cellulose chains, allowing greater orientation to be achieved.

Because of the effect of zinc on crystallinity, which ultimately translates to improved tensile strength, the production of high strength rayon usually involves high levels of zinc in the spinbath. Most plants use between 0.5 and 1.5% zinc sulphate in the spinbath for regular staple production. Below 0.5%, a significant deterioration in fibre tensiles results which can to some extent be recovered by raising sodium sulphate concentration and reducing the acid concentration. At very low levels of zinc in the spinbath, the filament cross-section becomes very irregular, with only a small amount of skin being apparent.

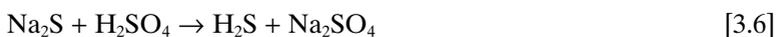
Sodium sulphate in the spinbath causes the filament to shrink and precipitate by a 'salting out' mechanism, with the high concentration salt drawing out the water from the viscose filament (85% of viscose is water).

Temperature and immersion depth affect the extent of regeneration, the latter only to a small degree owing to the amount of spinbath liquor usually carried forward with the tow.

3.3.3 Hydrogen sulphide formation at spinning

The by-products formed between CS_2 and NaOH degrade to CS_2 , H_2S and Na_2SO_4 at spinning. The percentage of CS_2 used at xanthation which is converted to H_2S is referred to as the A-factor, and is dependent principally on the age of the viscose. For low CS_2 viscoses, there is a requirement to spin at a low age in order to maintain the spinning viscose salt figure at an acceptably high level. Hence low CS_2 viscose gives a low level of conversion of CS_2 to H_2S by virtue of the necessarily lower age.

The by-product formation reactions shown earlier support this empirical observation, with the sodium trithiocarbonate which is formed initially reacting with further NaOH to produce sodium sulphide. At regeneration, sodium sulphide forms H_2S and Na_2SO_4 . Sodium trithiocarbonate, on the other hand, releases both CS_2 and H_2S , Equations [3.5] and [3.6]:



Hence as more trithiocarbonate is converted to sulphide as the viscose ages, the greater will be the amount of H_2S formed at spinning.

3.3.4 Modifiers

Retarding the rate of regeneration helps to achieve improved fibre tensile properties because it allows extra orientating stretch to be applied. As explained earlier, zinc helps to achieve this by forming a more stable intermediate species. Certain surface active materials, particularly amines and polyglycols can further retard regeneration. A number of mechanisms have been proposed to explain how these materials function.

For primary and secondary amines formation of a more stable intermediate complex with free CS_2 , zinc, and cellulose xanthate is thought to be the main effect. The complex may additionally act as a semi-permeable membrane, retarding penetration of acid into the filament, or may allow the zinc to penetrate further into the filament by being soluble at higher pHs. For tertiary amines, which include most commercial modifiers, the

materials possibly undergo xanthation, and then act in the same way as the primary and secondary amines in slowing regeneration.

On the other hand polyglycol materials can become protonated upon contact with the spinbath liquor, thereby forming a positively charged barrier to impede further acid penetration into the filament. Additionally, they can complex with zinc to give a more stable zinc cellulose xanthate and/or a less pH-sensitive zinc species.

Modifiers have also found application in the production of certain speciality modified cross-section fibres where their use is essential if a symmetrical and resilient fibre cross-section with clearly defined limbs is to be achieved.

3.3.5 Stretching

To achieve acceptable tensile properties particularly for textile end-uses, the fibre must be stretched during or very soon after extrusion. Cellulose is not thermoplastic like polyester, and therefore cannot be heat stretched at a later stage in the process. However, at the very early stages in regeneration the structure is not fixed within the filaments, and therefore the cellulose chains which will ultimately constitute the fibre can be aligned by stretching.

The stretch may be applied in a number of ways. The filaments may be run over godet rollers at a slower speed than the final traction units. Some stretch may also be applied in the spinbath where a significant speed differential exists between extrusion velocity and take-up speed at the godet. More commonly two stages of stretch are applied: pin stretching immediately after the spinbath, followed immediately by roll stretching (akin to godet stretching) of the whole tow. Although pin stretching has limited flexibility in terms of making changes to the degree of stretch applied relative to godets, the process is considerably simpler and enables the majority of stretch to be applied as early as possible.

Some plants employ hot stretch systems where the secondary stretch occurs in hot dilute sulphuric acid. This enables the final fixing of the fibre structure to take place while the fibre is held under tension in its state of maximum orientation.

3.3.6 Effects of process variables on fibre properties

This is a complex area where only a cursory treatment is possible.

3.3.6.1 *Viscose dope viscosity*

Higher dope viscosities ('ballfalls') generally result in more stable extrusion, and consequently lower trash figures. Low ballfalls, particularly less

than 30 ballfall seconds (as measured at 18°C), can give rise to dead viscose (DV) and stuck filament (SF) trash* problems.

3.3.6.2 *Salt figure*

High salt figure viscose requires more time for complete regeneration than is the case with lower salt figure. Consequently, this can enable increased stretch to be applied, with correspondingly higher tenacity and extension. However, stuck filament trash can be formed as a result of neighbouring poorly regenerated filaments sticking together just after extrusion.

3.3.6.3 *Spinbath acid*

Reduced acid levels allow more stretch to be applied and greater tenacity/extension to be realised. However, high DV and SF trash can result from low acid spinning. Low acid will result in greater crimp formation and potentially higher fibre cohesion.

3.3.6.4 *Spinbath zinc*

Reduced levels of zinc will adversely affect tenacity, significantly so below 0.5%.

3.3.6.5 *Sodium sulphate*

High levels of sulphate should in principle help tenacity, although with normal levels of zinc in the spinbath and at normal acid levels the effect is likely to be small.

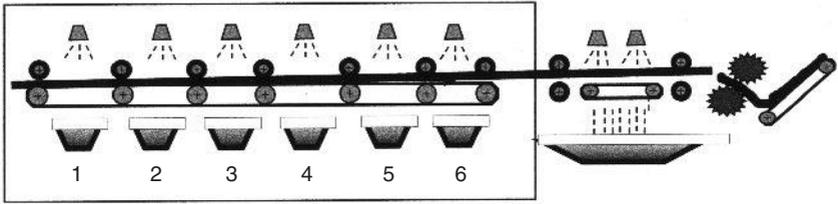
3.3.6.6 *Cutting and washing*

Many companies now employ some form of tow washing prior to cutting. Most systems enable a relatively high degree of washing to be achieved using a relatively small volume of wash liquor, and this means that the recovery of chemicals from this wash liquor becomes more economically viable.

Maurer cutters are the industry norm. These provide a relatively clean cut end, but with bigger tows they can result in poor fibre openness, with

*Dead viscose and stuck filaments are respectively lumps and sticks of hard cellulose that will disrupt web and yarn making processes. Together they are known as trash.

The washing stage



1. Acid water wash
2. $\text{Na}_2\text{S}/\text{NaOH}$ wash, desulphurisation
3. Water wash
4. Bleaching (Peroxide or NaClO)
5. Acid water wash
6. Water wash

3.5 The washing stage.

high levels of compressed fibre ‘chips’ being carried down to the wash conveyor.

Washing is an essential component of the viscose fibre production process (see Fig. 3.5). After regeneration the fibre is contaminated principally with sulphuric acid, zinc sulphate, sodium sulphate, hydrogen sulphide and carbon sulphide as well as various by products from the spinning reaction including sulphur and polysulphides. To remove these contaminants the fibre must be thoroughly washed. Washing of viscose fibre requires an interchange of liquor and is not determined by residence time. Washing is usually accomplished by having a multistage countercurrent wash machine. This may be enclosed and of a moving rail, flat bed or tank immersion type. Fibre is usually washed as staple but may be kept as tow for all or part of the washing cycle. The flowrate of wash liquor has to be about 10 times the fibre rate to ensure good displacement. The presentation of the fibre blanket has to be good enough to ensure effective and consistent penetration of liquor into the fibre.

The first washing stage may actually be the stretching zone following spinning if this stretching is carried out in hot water or hot dilute acid. Although the primary purpose of this step is to align the molecules, some washing and further regeneration occurs. The next stage is usually termed the hot water wash. It is carried out at around 90°C and its purpose is to complete the regeneration reaction and to vaporise the H_2S and CS_2 . In addition it has the secondary objective of washing away all the soluble contaminants, by countercurrent washing. This can be efficiently achieved on modern lines, however, some of the sulphur contaminants are insoluble and remain in the fibre. The effluent from this section is sent for heat recovery and in most cases for zinc recovery.

The next stage is the desulphurisation stage, which is carried out in a recirculating liquor stream of NaOH/NaSH at around 60°C and pH 11–12. The intention here is to dissolve any sulphur or residual polysulphides, so that they can be washed in the next stage. Also any acid is neutralised and any zinc is converted to a less soluble form. The fibre at this stage will swell and washing becomes harder.

Following this the sulphide wash is performed. This is a simple hot water countercurrent washing stage performed at around 70°C which will remove the alkaline soluble contaminants. The highly alkaline effluent from this section is usually sent for heat recovery and then to effluent treatment.

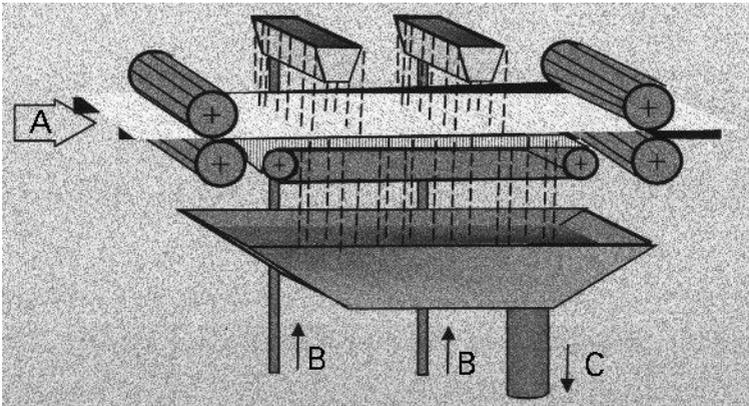
After the sulphide wash most fibres are bleached using either hydrogen peroxide or ozone for ‘totally chlorine-free’ products or sodium hypochlorite for ‘elementally chlorine-free’ products. Bleaching usually consists of a recirculating bath containing the aqueous bleaching agent. However, bleach can also be applied with the finish. Bleaching gives the fibre a bright appearance and is also an important purifying stage. After bleaching, residual bleach is removed usually by a single-stage post-bleach section with clean ambient-temperature water. The effluent from this stage may be used to feed a single prebleach section.

After post-bleach washing, the fibre is exposed to a final fresh water wash at around 50°C. This should remove all the contaminants to leave a pure product. Half way through this section a small amount of acid may be added to the wash liquor. This will correct the fibre pH and convert any residual zinc to a soluble form. At this stage the fibre is ready for finishing with a processing lubricant.

3.3.6.7 *Finishing*

In almost all commercial cases viscose fibres are finished with a processing lubricant prior to drying and baling. The choice of the lubricant depends on the end-use requirements for the fibre but in fact finishing is also necessary for subsequent smooth processing through the baling stage.

Lubrication during down stream processing must be provided because the virgin surfaces of the fibres give such high frictional forces that moving contact with another surface will abrade the fibre and ultimately break the filaments. An antistat may also be added to control static generation during processing which can make the fibres difficult to handle. Modern processing equipment is putting increasing demands on the performance of fibre lubricants and these chemicals are now engineered to work effectively at very high speeds and temperatures. Finishes must also be capable of being handled easily and applied consistently, usually in aqueous systems. Lubricant chemicals must also have very high levels of safety and environmental approval. This is particularly true for sensitive medical and hygiene



3.6 The finishing stage. (A) Fibre blanket from wash machine; (B) Soft finish inlet; (C) Soft finish regulation to make-up.

applications where a wide range of regulatory criteria must be met. In the case of viscose, lubricant materials are usually chosen to have the minimum impact on the hydrophilicity, softness and lustre of the fibre. However, hydrophobic treatments for viscose are available.

The most commonly used lubricants on viscose fibres are mixtures of fatty acids, salts of fatty acids and ethoxylated fatty acids and ethers. The antistatic agents of choice are either quaternary salts of fatty acids or phosphates. These finish mixtures once selected may be applied to the fibre by a variety of methods including full or part bath immersion, from a 'dripbar' or as a fine spray and via a kiss roller or padding device. Full bath immersion usually leads to the most consistent application but this also depends on the method of drying, the fibre moisture, the contact time between bath and finish and the length of storage time in the bale (Fig. 3.6).

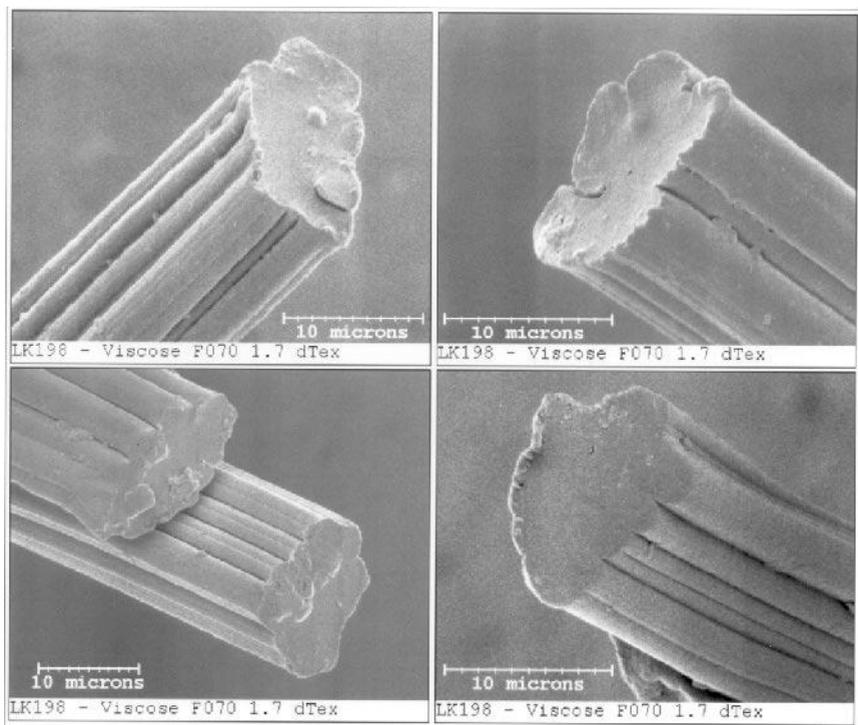
In terms of finish level analysis on viscose fibre, wet chemical test methods are being replaced by advanced spectroscopic methods including IR, near-IR and NMR. These techniques are beginning to be used on-line with good success.

Figure 3.7 shows viscose SEMs.

3.4 Chemical recovery and environmental control

3.4.1 Viscose process chemicals

As outlined earlier, the soda pressed out of the alkcell slurry is returned to the main steep soda circuit. There are off-takes from this circuit for other



3.7 Viscose fibre scanning electron microscope (SEM) micrographs.

process areas which require soda (filter backwash, xanthate dissolving, H_2S scrubbing, fibre washing, effluent neutralisation being examples), but otherwise the system is operated largely as a closed cycle. The exception is the soda in viscose, which at spinning is neutralised to Na_2SO_4 and must be removed from the spinbath system in order to maintain an acceptable equilibrium level (see later).

Viscose waste arising at the filters is concentrated by further filtration, and then either fed to the waste water treatment plant (WWTP) or incinerated. Alkcell waste is either landfilled, incinerated or fed to the WWTP. In emergency situations, volumes of viscose or steeping soda will be discharged to drain, to be dealt with by the WWTP.

3.4.2 Degassing

Following spinning, the spinbath liquor contains appreciable amounts of dissolved CS_2 and H_2S . These components need to be removed by degassing prior to evaporation, not just to facilitate their recovery, but also because

the presence of appreciable quantities of CS_2 and H_2S will foul the evaporators and present safety problems. Some operations use vacuum degassers, where others rely on the high level of liquor turbulence in the spent tank system plus air sparges to effect removal of CS_2 and H_2S . Some plants have no degassers on the main liquor system, but do degas the evaporator feed in a packed tower with air.

3.4.3 Evaporation

A side-stream of spent spinbath acid is taken for evaporation, the volume flow being set to achieve the desired level of water removal and (following crystallisation) the required Na_2SO_4 concentration. Evaporation is effected by passing the recovered spinbath liquor through bundles of tubes which are heated on the outside by steam. Multistage evaporators are used to maximise heat efficiency, whereby the hot vapours from later stages will be used to heat the early stages or to preheat the incoming process liquor.

3.4.4 Crystallisation and anhydrous sodium sulphate production

As with evaporation, crystallisation is effectively a heat transfer process where the hot saturated spinbath liquor is cooled in heat exchange with chilled water. Many crystallisers are available including plastic films, where the chilled water flows down one side of a plastic sheet, and the acid down the other. The precipitated crystals of hydrated Na_2SO_4 (Glauber salt) may then be removed by rotary vacuum filters. Vacuum crystallisers are also available, with separation of the Glauber salt usually done by centrifuge.

Historically, Glauber salt was disposed of via the process effluent. However, most viscose plants now heat the Glauber salt to convert it into saleable anhydrous sodium sulphate (ASS) for use, for example, in detergent manufacture.

3.4.5 Spinbath clarification

Various particulate materials accumulate in the spinbath circuit over time. The extruded viscose contains particulate material, often dirt from the pulp or other process chemicals, but also potentially resins from the pulp, silica, and so on. At spinning, a range of insoluble by-products are formed, particularly sulphur, polysulphides and zinc sulphide, and these materials can form deposits on process pipework, and more critically on the spinning jets.

To avoid this type of deposition, surface-active additives are often added to the liquor at parts per million (ppm) levels, and these materials effectively disperse the particulates in the spinbath. Although the dispersion of such materials in the spinbath does not cause any problems with spinning or fibre quality, particulates can cause problems at evaporation (tube fouling and loss of efficiency) and in ASS production (product contamination). Hence there is a need to remove particulates.

Removal can be effected by filtration, sand filters being the norm, or by flocculation followed by froth flotation for example. As with evaporation, clarification/filtration is performed on a degassed sidestream from the main spinbath circuit.

3.4.6 Recovery of acid and zinc

The majority of acid and zinc employed during spinning remains in the spinbath circuit. However, a significant quantity is carried forward by the advancing tow to later process stages. For both environmental and cost reasons it is important to recover as much as possible from these later process stages. However, the later stages of the washing process result in more and more dilute waste streams, and these become increasingly costly to evaporate in order to re-use the acid/zinc concentrate in the spinbath circuit. Consequently, recovery of the chemicals from the wash liquors is usually only economically feasible for the initial wash stages.

3.4.7 Effluent treatment

As outlined in the previous section, there are some effluent streams at most factories for which chemical recovery is impractical: this is particularly true of the later wash stages. Where evaporation capacity is limited, there will be a corresponding limit on the amount of acid that can be recovered for re-use; beyond this limit, the process liquors must be discharged as effluent. Additionally, there are sometimes circumstances where a bulk discharge of material must be made in an emergency. For example, a 'bad batch' of viscose which is likely to cause the immediate blockage of filtration and loss of spinning, will need to be discharged to effluent.

The viscose plants employ a range of effluent treatment facilities, ranging from just buffering and pH correction through to chemical treatment and biological aerobic digestion. Some viscose manufacturers use a biological treatment plant to reduce the effluent COD (chemical oxygen demand) to acceptable levels. The waste sludge arising from the biological processes is usually separated by filtration, dried, then either landfilled or incinerated.

3.4.8 CS₂ and H₂S recovery

Increasingly stringent environmental legislation has forced the viscose industry to employ more and more effective systems for recovering CS₂ and H₂S. However, certainly for CS₂ there is clearly a cost benefit to the process in re-using this expensive raw material.

As with evaporating spinning liquors for acid recovery, the key to achieving an efficient level of recovery is to establish as high a concentration of CS₂ in the waste air stream as possible. CS₂ is a highly flammable material, however, with a wide explosive range (10–50%), and hence any streams falling in this range must be made inert by replacing air with steam or nitrogen as the ventilation gas.

Condensation is the most widely used means of recovering CS₂ from the more concentrated process exhaust gases. Adsorption is commonly employed for the lower concentration streams, but absorption is also used. Condensation is insensitive to the presence of H₂S, but H₂S must be removed prior to adsorption to prevent fouling of the activated carbon. H₂S is commonly scrubbed using either NaOH (to give NaSH and/or Na₂S), or by a redox-based catalytic oxidation process such as the Ferrox process (based on ferric hydroxide scrubbers).

For some plants, it is attractive to take the combined foul air stream and catalytically convert the CS₂ and H₂S to sulphuric acid. The acid thus produced can then be re-used in spinbath liquor make-up.

Biological scrubbing of CS₂ is a new technique which has found favour in some quarters. However, this approach generates large volumes of dilute sulphuric acid which, given existing limits on evaporative capacity for spinbath liquor recovery, could only be neutralised and disposed of as effluent.